

Division of Polymer Chemistry (POLY)

Graphical Abstracts



Submitted for the 256th ACS National Meeting & Exposition

Boston, MA | August 19-23, 2018

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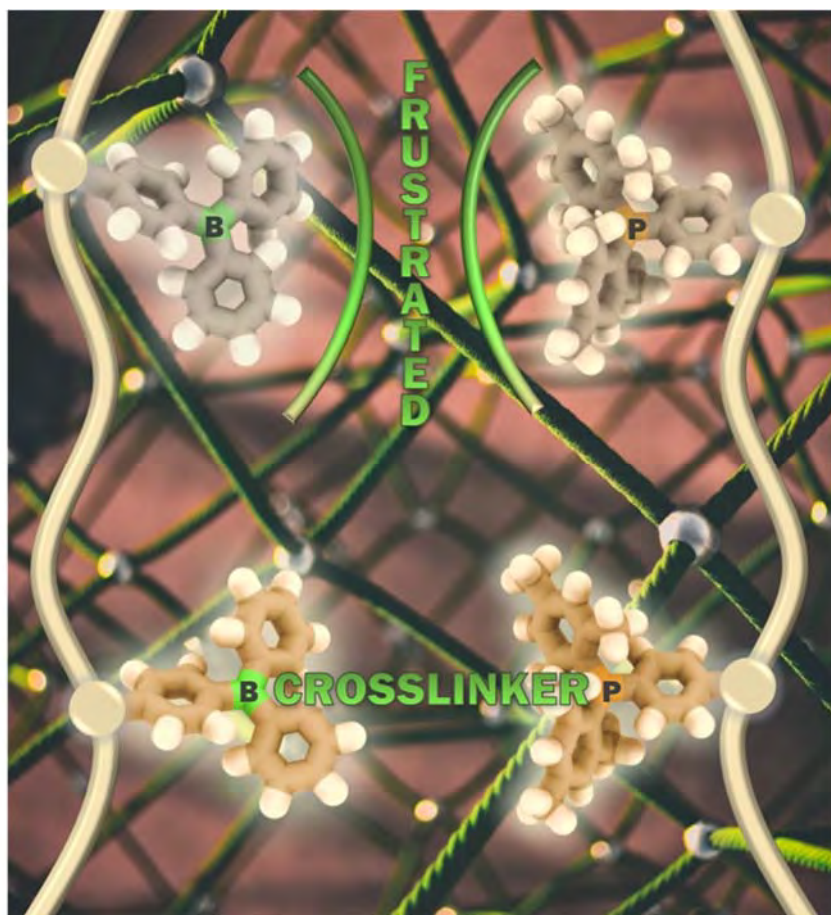
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POLY 1: Polymeric frustrated Lewis pairs

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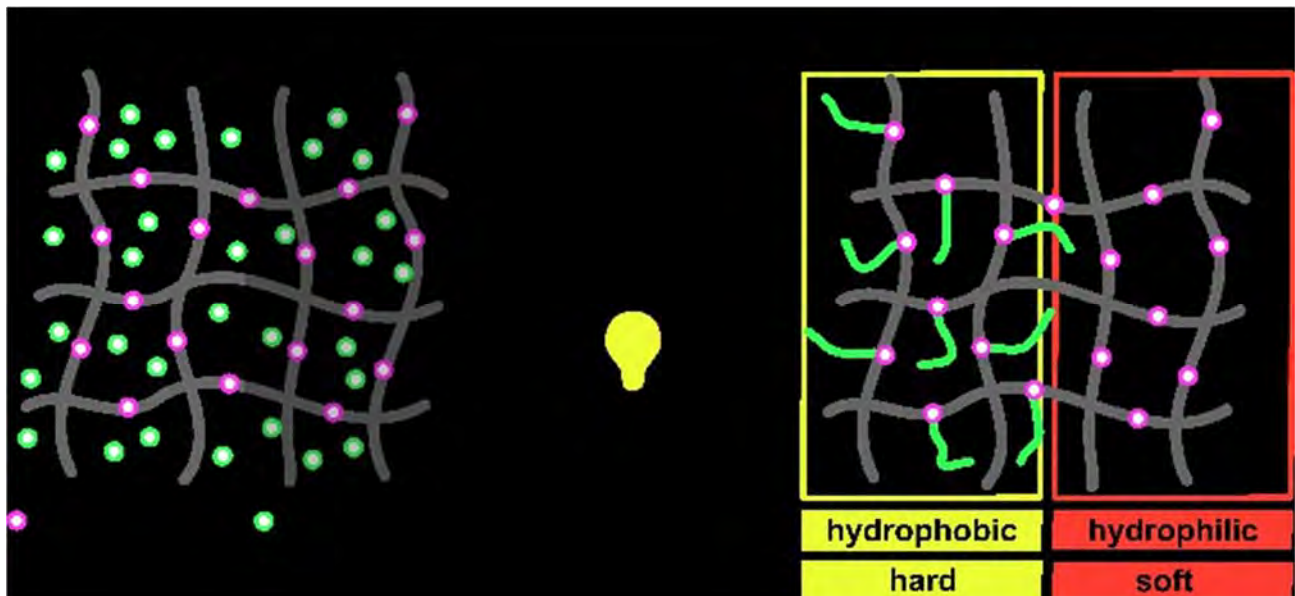
Steric bulk prevents the formation of strong bonds between Lewis acids and bases in frustrated Lewis pairs (FLPs), masking a reactivity that has led to metal-free hydrogenation catalysts and extensive small molecule activation chemistry. We recently extended the concept of FLPs to polymeric systems. Our fully macromolecular FLPs, built from linear copolymers that containing either a sterically encumbered Lewis base or Lewis acid as a pendant functional group, are formed by a controlled radical copolymerization of styrenes and acrylates with designer boron or phosphorus containing monomers. Mixtures of the B- and P-functionalized polystyrenes do not react, with the steric bulk of the functional monomers preventing the favorable Lewis acid base interaction. Addition of a small molecule (diethyl azodicarboxylate) promotes rapid network formation, crosslinking the reactive polymer chains with covalent LAB bonds. The resulting gel is dynamic, can self-heal, is heat responsive, and can be reshaped post-gelation.



POLY 2: Structurally tailored and engineered macromolecular (STEM) gels

Krzysztof Matyjaszewski, km3b@andrew.cmu.edu. CMU, Pittsburgh, Pennsylvania, United States

Structurally Tailored and Engineered Macromolecular (STEM) gels are polymer networks containing latent initiator sites available for post-synthesis modification. STEM gels were synthesized by controlled radical polymerization (CRP). First, reversible addition-fragmentation chain transfer (RAFT) polymerization was used to copolymerize (meth)acrylate monomer, di(meth)acrylate crosslinker and inimer for the subsequent atom transfer radical polymerization (ATRP) grafting-from process. The resulting STEM gels were infiltrated with a second monomer, which formed side chains grafted from the inimer sites by photo-activated ATRP. This approach permits significant spatial and temporal control over the structure of the resulting material. This technique was used to transform primary STEM gels into single-piece amphiphilic and hard/soft materials.



POLY 3: Unconventional chemistries for vitrimers

Jacob S. Ishibashi, *ishibashi@northwestern.edu*, Julia A. Kalow. Chemistry, Northwestern University, Evanston, Illinois, United States

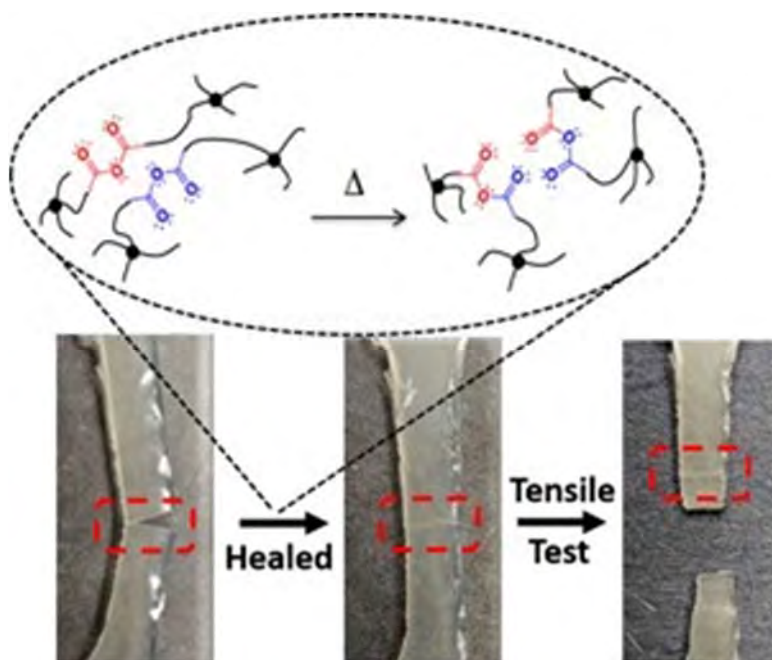
The covalent crosslinks present in elastomers and thermosets impart superior mechanical properties, but the permanence of these linkages also inhibits recycling. Existing associative exchange chemistries (i.e., ester or urethane exchange) require high temperatures and/or catalysts to operate. These high temperatures can cause thermal degradation of the material after prolonged exposure, and catalysts always have the potential to leach and deactivate. We are pursuing two strategies toward recyclable polymers through nontraditional and reversible crosslinking chemistry. First, we are investigating photoinduced nucleophilic aromatic substitution (S_NAr^*) as a way to exchange alkoxy groups of electron-deficient aryl ethers. These aryl chromophores will act as crosslinkers, rendering the polymer networks recyclable by irradiation with ultraviolet light. The second strategy exploits a fast and reversible thiol-Michael click reaction, enabling the synthesis of vitrimeric siloxane elastomers. Broken pieces of these siloxane rubbers can be compression remolded at 150 °C within minutes. These rubbers show no deterioration in rubbery plateau storage modulus (E') or Young's modulus after reprocessing, and the crosslinks remain dynamic as evidenced by fast stress relaxation at elevated temperature (120–150 °C) even after recycling ten times.



POLY 4: Self-healing polyanhydrides through dynamic covalent exchange

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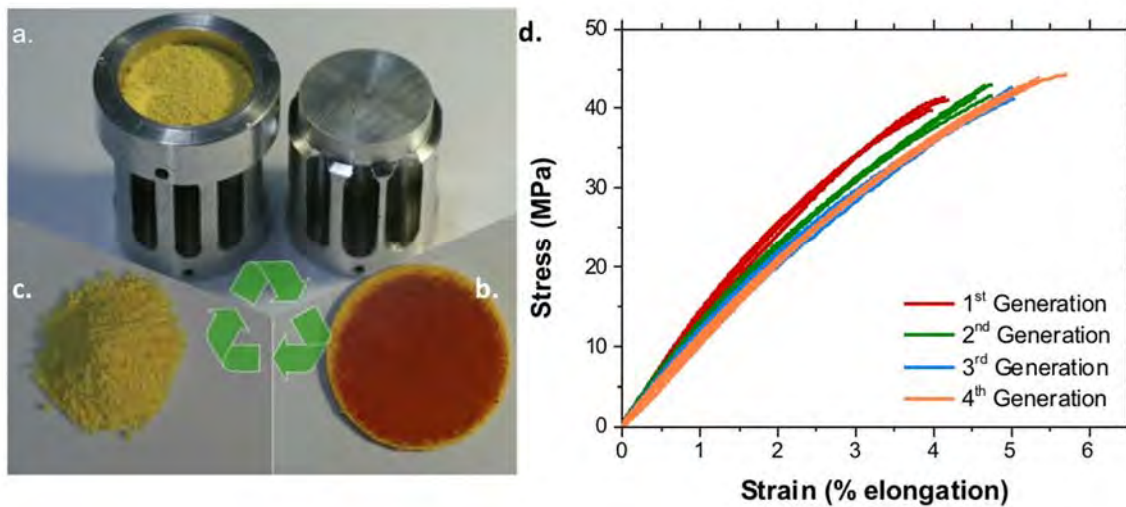
Polyanhydrides have become an intriguing option as a degradable polymer in various fields due to the development of new synthetic routes such as thiol-ene click polymerizations. Our group has studied polyanhydrides made by this technique, varying in compositions ranging from elastomeric to semi-crystalline. We have published their use as controlled drug release systems, patternable molds, and functionalized particles. More recently, a polyanhydride-poly(ϵ -caprolactone) composite being studied as a shape memory elastomeric composite (SMEC) led to a discovery that polyanhydrides can undergo a dynamic covalent exchange between the anhydride moieties. Through thermomechanical analysis, gel permeation chromatography and gas chromatography-mass spectroscopy, we have proven that dynamic covalent exchange occurs and determined that it is dependent on temperature and the chemical structure. The goal of our research is to take advantage of the anhydride dynamic covalent exchange and synthesize an all-polyanhydride network that can undergo self-healing and determine what affect this process has on the material properties and degradation profiles.



POLY 5: Novel malleable covalent network polymers and their applications in developing rehealable and fully recyclable functional composite materials

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Polymeric materials have been divided into two categories: linear polymers and cross-linked or network polymers. Linear polymers typically have melting points and can be reprocessed and recycled, but are not durable enough for many applications. Crosslinked polymers, commonly called thermosets, are mechanically tough, but are not able to be recycled. Malleable crosslinked polymers are a new class of materials, wherein reversible covalent bonds are employed. These materials can exhibit mechanical properties of typical thermosets under ambient conditions, yet at elevated temperatures or under other stimuli they can be reprocessed and recycled through a cross-link exchange and rearrangement process, usually with the aid of catalysts. This presentation will focus on the development of an imine-linked catalyst-free network polymer, which becomes malleable by application of either heat or water, thus enabling its unique processability and full recyclability while retaining tough mechanical properties. The application of such malleable polyimine thermoset in functional composites fabrication, e.g., solid-state electrolyte membrane, carbon fiber reinforced composites, and electronic skin, will also be discussed.

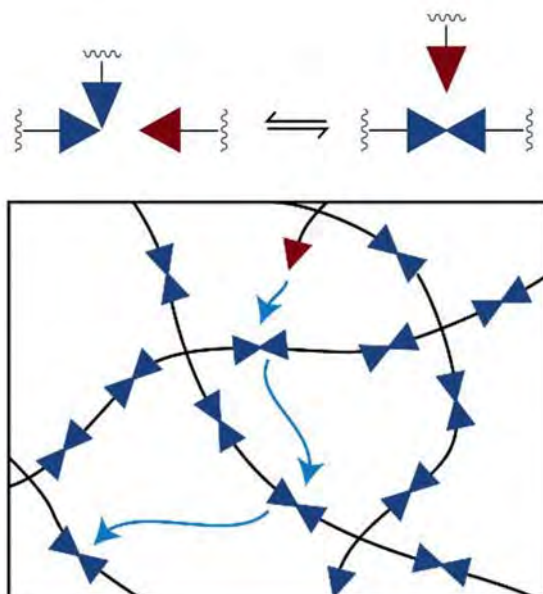


POLY 6: Click-based covalent adaptable networks

Christopher J. Kloxin^{1,2}, cjk@udel.edu. (1) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (2) Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States

Covalent adaptable networks are a unique class of chemically crosslinked polymers that possess dynamic network connectivity. Through either reversible addition or exchange reactions, the material is able to undergo strand rearrangement-based relaxation, leading to new processing properties that otherwise would not be possible in a chemical gel. Many of the recent literature examples of exchange-based networks employ transesterification bond rearrangement (i.e., vitrimers), where the networks are typically formed by reaction between carboxylic acid and epoxy monomers, producing an ester crosslink and a free hydroxyl functional group. At elevated temperatures and in the presence of a catalyst, the alcohol of an adjacent chain is able to undergo an exchange reaction with the ester.

Here, we use the orthogonal nature of click crosslinking reactions that are separate from the exchange reaction, thereby allowing independent control over the network connectivity and the presentation of reversible exchange functional groups. Specifically, we create a triazole-based network using multifunctional azide and alkyne monomers possessing pendant alcohol and ester functional groups. Network formation is light-triggered using photo-mediated copper(I) catalyzed azide-alkyne cycloaddition polymerization. The resultant material combines the unique toughness and shape memory properties associated with triazole-based networks at low-to-moderate temperatures with the dynamics and processing characteristics associated with covalent adaptable networks at elevated temperatures. These new materials represent dynamic yet robust macromolecular architectures with complex behaviors that are readily applied to a wide range of new applications.



POLY 7: Star hyperbranched polymers as precursors to vitrimers or dynamic covalent networks

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End functional stars based on hyperbranched cores have been prepared as precursors to vitrimers or dynamic covalent networks. Several strategies have been applied.

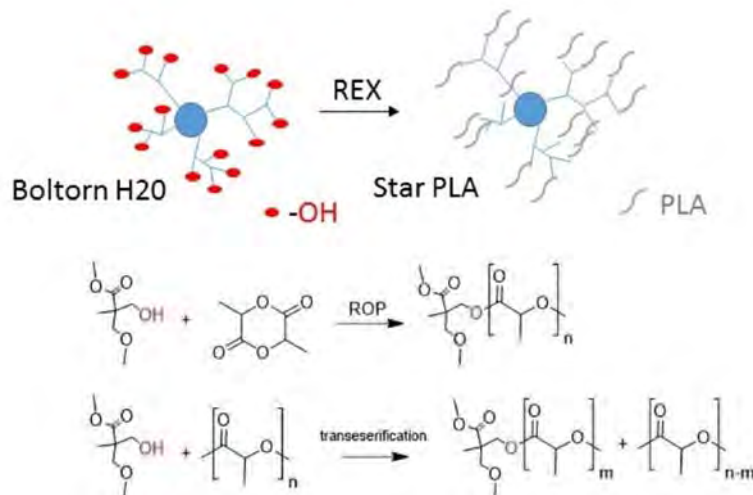
(a) A hyperbranched polymer has been prepared by RAFT crosslinking polymerization, arms and end functionality were then appended by further RAFT polymerization to provide the star.

(b) A star polymers has been prepared by arm-first RAFT polymerization mediated by an end-functional macro RAFT agent.

(c) A commercial hyperbranched polyester (Boltorn) has been transformed into a star polymer by transesterification with a linear polyester during extrusion then end functionalised.

(d) A commercial hyperbranched polyester (Boltorn) has been used as an initiator for ring opening polymerization to provide a star that was then end-functionalised.

The utility, advantages and limitations of these processes will be compared.

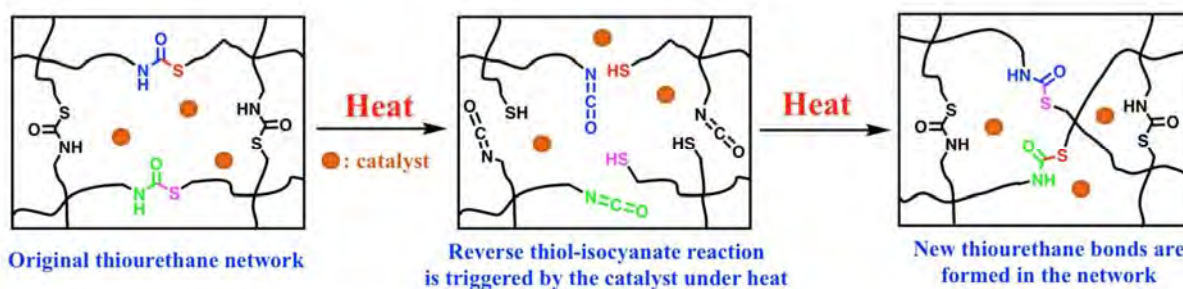


POLY 8: Development of a new covalent adaptable network through dynamic thiourethane bond

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Covalent adaptable networks (CANs) incorporate dynamic covalent bonds that undergo rearrangement in response to the application of a particular stimuli. These dynamic systems enable the CAN materials to possess novel properties such as recycling, self-healing, and stress relaxation. In recent decades, various types of CAN materials have been developed based on different dynamic bond rearrangements, such as metal-catalyzed transesterification, Diels-Alder reactions, imine exchange, and addition-fragmentation. Herein, we reported a new type of CAN materials which is cross-linked and dynamically exchanged through thiourethane bonds under heat and with the assistance of catalysts. Because of the well-known optical and mechanical advantages, thiourethane polymers gain much more attentions recently. However, to our best knowledge, it is the first case to describe the dynamic thiourethane bonds in CAN materials.

The thiourethane networks were constructed through thiol-isocyanate click reaction with ethoxilated-trimethylolpropan tri(3-mercaptopropionate) (ETTMP, $M_n = 1300$), hexamethylene diisocyanate (HMDI), and thiourethane bond exchange catalysts. Various catalysts were screened based on the stress-relaxation experiments of the corresponding networks on dynamic mechanical analysis instrument. 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) was attested to be the most efficient catalyst, which enables 100% relaxation of the thiourethane networks in 40 min at 90 °C with 1 mmol% loading. The exchange mechanism was also decently explored through small molecule model reaction and real-time IR monitoring. Moreover, this thiourethane network showed that its stress-relaxation efficiency is well maintained after at least three cycles of stress-relaxation experiments on the same film.



Scheme 1. Dynamic exchange of thiourethane covalent adaptable network.

POLY 9: Synthesis of brush polypeptides

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We will report the integration of ring-opening metathesis polymerization (ROMP) and ring-opening polymerization of the amino acid *N*-carboxyanhydride (NCA) to allow facile synthesis of brush-like polymers containing polypeptide brush. ROMP of *N*-trimethylsilyl norbornenes renders the preparation of poly(norbornene)s bearing pendant *N*-TMS groups. With no need to purify the resulting polymers, such macromolecular initiators can subsequently initiate controlled NCA polymerizations. Brush-like poly(norbornene)s with grafted polypeptides are readily obtained with controlled molecular weights and narrow molecular weight distributions. We find that the polymerization can finish with very fast kinetics and very high yield. Polypeptide brushes with up to 1000 degree of polymerization can be obtained with low polydispersity. Because many ROMP and NCA monomers are widely available, this novel polymerization technique will allow easy access to numerous brush-like hybrid macromolecules with unprecedented properties and broad applications.

POLY 10: Protein engineered biopolymers as biomaterials

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Through centuries of evolution, nature has developed biopolymers capable of folding and assembling into discrete structures with a functional consequence. Inspired by this, our lab focuses on engineering “intelligent” protein materials with entirely new properties and function. In particular, our lab has fabricated protein-derived nanomaterials: coiled-coil nanofibers, helix-elastin nanoparticles, and protein-lipid complexes or lipoproteoplexes. We investigate the fundamental self-assembly and molecular recognition capabilities of these systems. More importantly, we are able to harness these structures to interface with small molecule therapeutics, genes and deliver them for biomedicine.



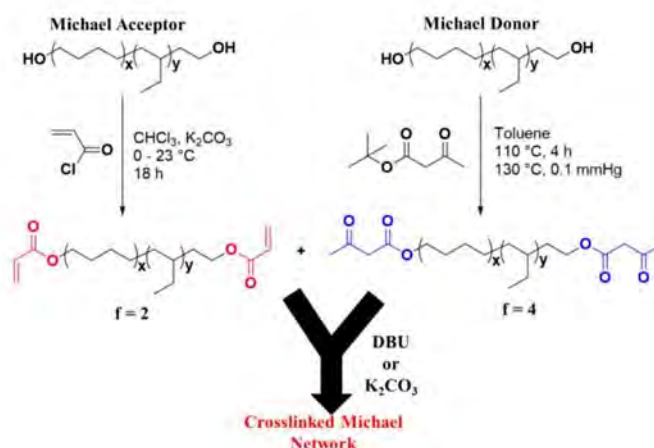
POLY 11: Advances in crosslinking enabling lots of new everyday things: From solvent-free adhesives and elastomers for construction to 3D printing automobile parts

Timothy E. Long¹, *telong@vt.edu*, Katherine A. Heifferon², Nicholas G. Moon³, Mingtao Chen⁴, Xi Chen². (1) Macromolecules Innovation Institute (MII), Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Roanoke, Virginia, United States (3) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (4) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Michael additions comprise a versatile set of reactions that are suitable for many emerging technologies. The efficiency of these reactions at room temperature provide not only an ease of synthesis for organic small molecules but also a viable pathway to next generation crosslinked networks. The reactions are categorized by the absence of a volatile by-product, quantitative yields, diversity of base selection, and rapid room temperature kinetics. Our research group demonstrated a unique approach to development of a novel two component crosslinking process that occurs in the absence of solvent for construction applications. A one-step synthetic method synthesized the novel oligomer-based bisacetoacetate (bisAcAc) and diacrylate (DA) with a hydrocarbon backbone, and a wide range of structures were utilized to tune thermomechanical properties, hydrophobicity, and morphology. This novel Michael donor-acceptor system provided a solvent-free method of producing a crosslinked adhesive with tunable kinetics through adjustment of the catalyst loading. These networks found use in roof-top adhesives although their tunability affords consideration in a wide range of other applications. This lecture will highlight adhesives used in construction and the continuing need to remove solvent from polymer products and processes.

Michael reactions also enable the design of next generation hydrogels for brachytherapy in cancer treatment. Base catalyzed thiol Michael addition of multifunctional thiols to multifunctional acrylates enabled the preparation of hydrogels that were amenable to two-part delivery in the presence of sodium bicarbonate catalyst. The gels exhibited sufficient modulus to displace and protect healthy tissue, while not interfering with imaging techniques during clinical practice.

Recent efforts in 3D printing will demonstrate how additive manufacturing will change everyday things. This lecture will conclude with the demonstration of new polymer compositions for printing a range of polymers from polyimides for aerospace to water soluble polymers for drug delivery.

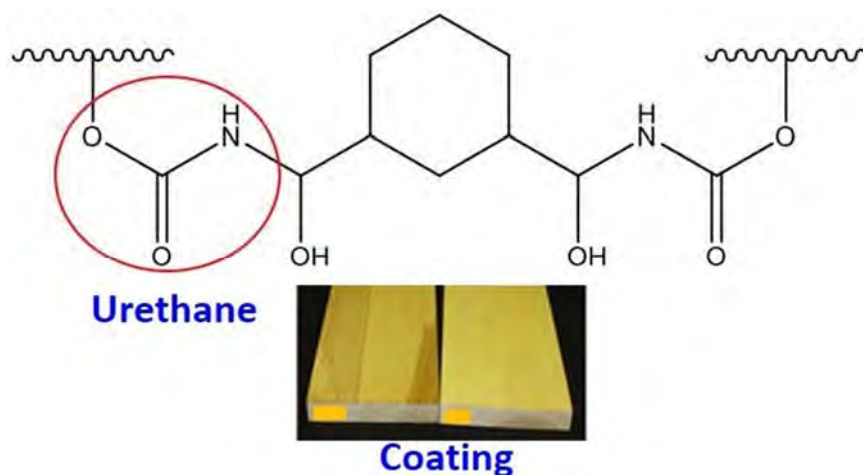


POLY 12: Isocyanate free coating and PET foaming: Polymer chemistry promoted by analytical sciences

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Less toxicity and less environmental footprint are two of the major driving forces for industrial product development. Two examples that impact people's everyday life is isocyanate free coating technology and foaming process with recycled poly(ethylene terephthalate) (PET). Isocyanates have been widely used to make urethane linkages by reaction with polyols, with applications in coatings, foaming, adhesives, et al. However, there is a growing concern about exposure to isocyanates. An alternative route to urethane linkages has been developed by the Dow Chemical Company and is based on the reaction of polycarbamates with polyaldehydes. Also, in the last several years, the production of PET foamed items attracted rising interests, with attention paid to recycled PET as compared to the commonly used thermoplastic resins.

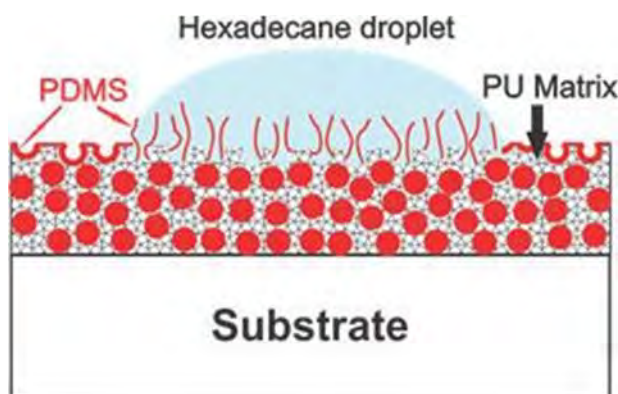
During the product development, analytical sciences played critical role in understanding the crosslinking mechanism, reaction kinetics, copolymer structure, as well as unexpected reactions, which even led to the discovery of new chemistry and potential applications.



POLY 13: Waterborne PDMS-containing polyurethane formulation for anti-smudge coatings and superhydrophobic textiles

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Durable and transparent anti-smudge coatings that repel both water- and oil-borne contaminants have many potential applications. Perfluorinated moieties were commonly used in the past to prepare water- and oil-repellant coatings. These species are expensive and of environmental concern. Further, organic solvents have been traditionally used to formulate such coatings. Solvent-based coating formulations contribute to emission of volatile organic compounds and are of safety hazard. We report in this presentation the development of transparent and durable water-borne anti-smudge polyurethane coatings. These coatings are obtained by casting micellar solutions of a blocked polyisocyanate dispersed in water using a graft copolymer polyol-*g*-PDMS, where the polyol backbone is water soluble and PDMS denotes poly(dimethyl siloxane). On these coatings, small 5- μ L droplets of various liquids such as cooking and engine oils have no problem to glide cleanly off at substrate tilting angles $< 5^\circ$. Artificial fingerprint liquids, inks, and paints readily shrink into tiny droplets after application on them and the residuals of these composite liquids after solvent evaporation are readily wiped off with a tissue. We will further show that this coating formulation can also be used to coat textile fibers. After coating textile fibers using a water-based approach, the resultant textile becomes superhydrophobic. We will discuss the challenges associated with switching from a solvent-based to a water-based formulation for the targeted coatings. The greenness of the coating formation process should be of practical value.

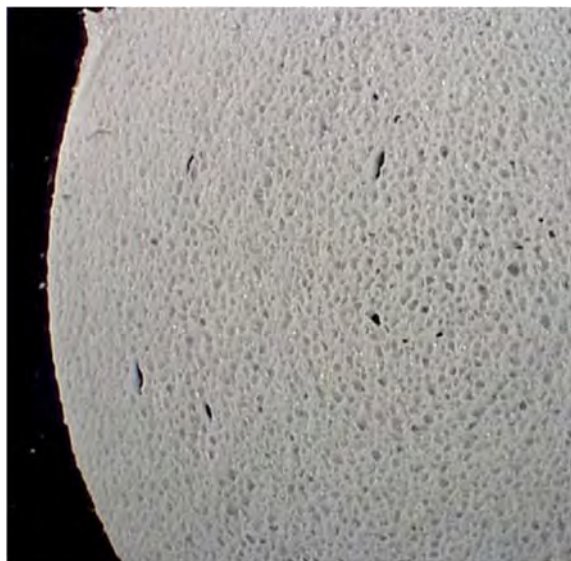


Schematic cross-sectional view of a NP-GLIDE PU coating containing PDMS as the de-wetting enabler

POLY 14: New methacrylate composition for ultrahigh molecular weight poly(vinyl chloride) foam process aid

Michael Petr², mp3d@alum.mit.edu, *Michelle Kubik*¹, *Sam LaRosa*¹, *Wen-Shiue Young*³. (1) *Plastics Additives, Dow Chemical, Collegeville, Pennsylvania, United States* (2) *Formulation Science, Dow Chemical, Collegeville, Pennsylvania, United States* (3) *Analytical Science, Dow Chemical, Collegeville, Pennsylvania, United States*

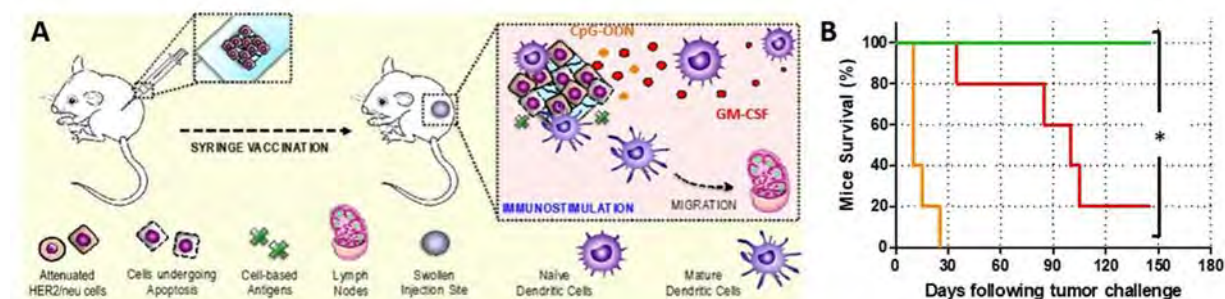
In the building and construction industry, poly(vinyl chloride) (PVC) is often used as a foam because it is more rigid, lighter and cheaper. As such, it can function as a wood replacement that is strong, resistant to the environment, and low maintenance. The foam is produced by formulation with a chemical blowing agent and a high molecular weight (meth)acrylic process aid, which is added to increase the melt viscosity and provide entanglements to reduce the PVC melt relaxation as well as to provide extra die swell and further foam expansion. Standard foam process aids are (meth)acrylate based copolymers with extremely high molecular weight, usually 1-20 Mg/mol, made with emulsion polymerization, which pushes the limit of what can be synthesized both in the lab and commercially. However, an alternative (meth)acrylate composition has been identified, which produces a new foam process aid with ~50% greater molecular weight and ~15% greater foam expansion. Furthermore, this new composition leads to a reduction in the residual monomer concentration, resulting in a more environmentally friendly product.



POLY 15: Injectable cryogel-based vaccine for breast cancer immunotherapy

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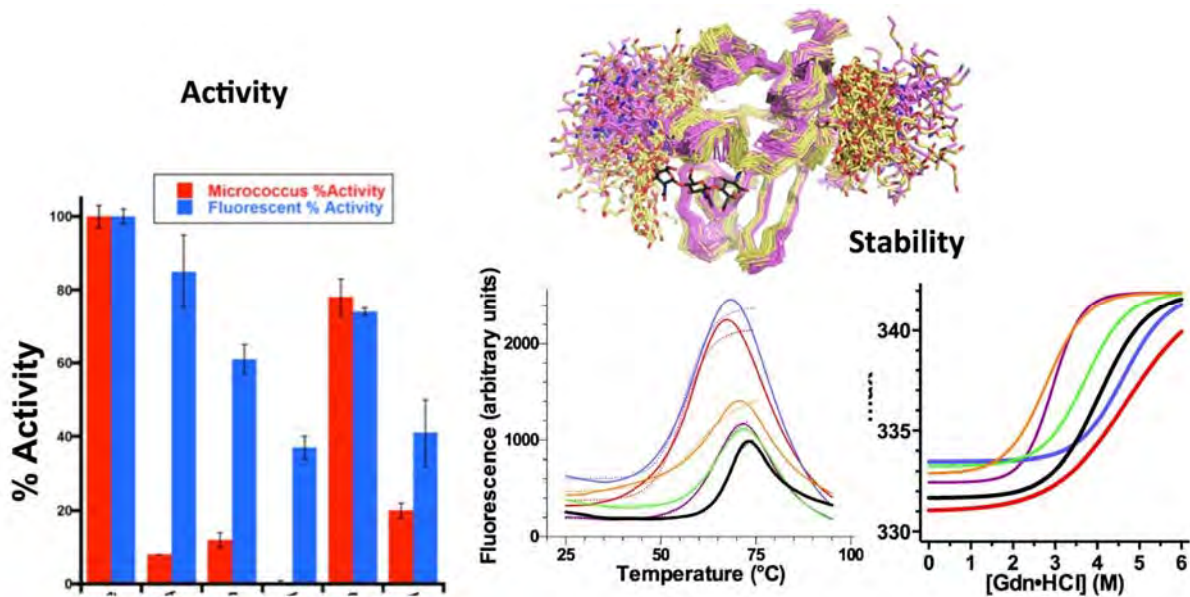
Passive immunotherapy using monoclonal antibodies has become a promising adjunct for the treatment of HER2/neu positive breast cancer. However, late-stage patients are often unlikely to respond to this therapy due to an acute cancer-driven immunosuppression, motivating the need to develop new strategies. One approach is to use polymeric biomaterials to manipulate immune cells in vivo, providing an additional route to engineer the most effective immune responses. Our team has recently developed injectable preformed macroporous scaffolds, namely cryogels, as a platform to both deliver immunomodulatory factors and tumor-associated antigens (TAA) while providing a macroporous physical space to control immune cell trafficking and activation within the body. This cryogel system acts as a whole-cell scaffold-based cancer vaccine. It contains live attenuated HER2/neu-overexpressing breast tumor cells as source of TAA and provides a sustained release of both GM-CSF to recruit and host dendritic cells (DCs) and a TLR9 ligand, CpG-ODN, to activate resident DCs (Fig. 1A). Subcutaneous injection of cryogel vaccines through a small-bore needle led to a strong and long-lasting cellular and humoral antigen-specific immune responses. Compared to bolus injection of attenuated GM-CSF-secreting HER2/neu breast tumor cells (GVAX, a whole-cell cancer vaccine standard), cryogel vaccines induced a 5-fold increase in HER2/neu-specific antibodies production as well as a high level of specific cytotoxic T lymphocytes. Strikingly, 100% survival was achieved in cryogel-vaccinated mice demonstrating a potent anticancer immunostimulation (Fig. 1B). Cryogel vaccines represent a promising tool for the development of active immunotherapeutic approaches to treat cancer patients and has the potential to be combined with other clinically promising immunotherapies (e.g. immune checkpoint inhibitors) to synergistically boost anticancer effects.



POLY 16: Polymer-bioconjugation as post-translational modification for protein structure and function

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Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

Conjugation of a synthetic polymer to a protein can be thought of as a post translational modification. Bioconjugates have a range of interesting properties industrial biocatalysis and biomedicine. However, protein's poor tolerance to thermal and chemical challenges can limit the performance of the biomaterials. In nature post-translational modifications modulate a proteins function and stability. This abstract will discuss the impact of polymer modification, as a post translational modification, on protein structure and function for a range of enzymatic proteins. Through the use of reversible deactivation radical polymerization, synthetic polymers of various functionalities can be synthesized including ones that have distinct ionic character (cationic vs anionic) as well as those with different hydrogen bonding capability. The impact of polymer structure on bioconjugate performance will be discussed as well as distinct assays for the bioconjugate properties.

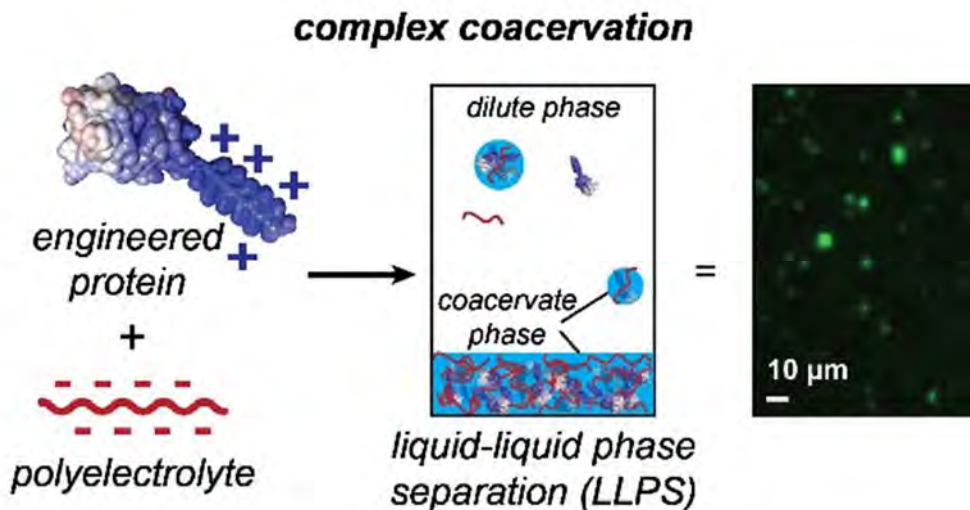


POLY 17: Phase behavior of engineered protein sequences with polyelectrolytes

Allie Obermeyer, aco2134@columbia.edu, **Chad Cummings**, **Rachel Kapelner**, **Nicholas Zervoudis**. *Chemical Engineering, Columbia University, New York, New York, United States*

Oppositely charged polyelectrolytes are known to undergo a liquid-liquid phase separation, termed complex coacervation, under the appropriate solution conditions. Protein polyelectrolytes have also been shown to phase separate with polyelectrolytes. However, protein polymers differ significantly from synthetic polyelectrolytes. Proteins are zwitterionic, have low charge density, and typically adopt a globular folded structure. These differences impact the complex coacervation of proteins and polyelectrolytes. These differences also make protein polymers interesting to study in this context; the charge, charge density, and charge orientation on proteins can be precisely controlled through genetic engineering.

We have synthesized a panel of engineered proteins with varying net charge and charge distribution. Phase separation of the engineered proteins with strong and weak polyelectrolytes has been investigated by light scattering and optical microscopy. Key differences in the phase behavior were observed based on the spatial distribution of charges on the protein. Finally, design rules for complex coacervation of globular proteins have been established and should enable future applications of these materials.



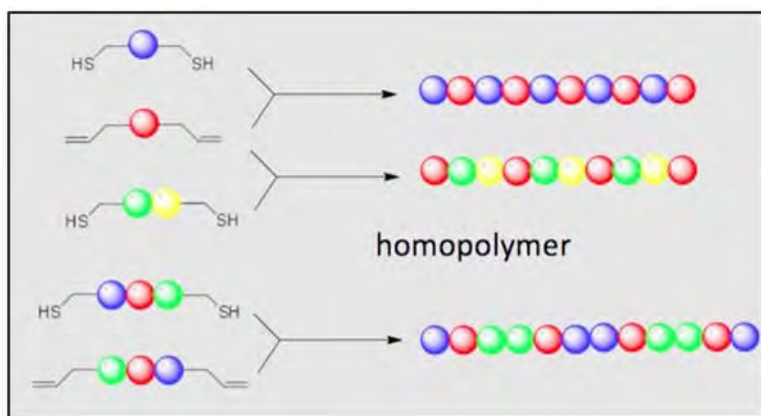
POLY 18: Nucleic acid analogs via thiol-click reactions

Christopher Bowman, *christopher.bowman@colorado.edu*. Department of Chemical and Biological Engineering, Materials Science and Engineering Program, University of Colorado, Boulder, Colorado, United States

Nucleic acids, DNA and RNA, are most widely recognized for their genetic role. Recent research has identified additional roles in biology, medicine and directed assembly of materials. To mitigate the challenges of native nucleic acids, analogues with non-natural backbones have been designed though each suffers from similar synthetic challenges to native nucleic acids.

By utilizing thiol-click reactions, particularly the radical thiol-ene addition, we have developed nucleic acid analogues, designated CNAs for “Click Nucleic Acid,” with sulfur-containing backbone polymers, that bind with complementary sequences of single stranded DNA with high specificity. These uncharged backbones permit hybridization without charge shielding and the oligomers are not susceptible to degradation via the same physiological mechanisms as native nucleic acids. Furthermore, in contrast to the solid phase synthesis of nucleic acids and their analogues, which may require as much as one hour per residue, CNAs can be synthesized from monomers in less than one minute. Additionally, solution phase synthesis allows for easily scalable synthesis that is not subject to the surface area constraints of heterogenous solid phase-supported reactions.

Such CNAs can be grafted to or grafted on synthetic and natural polymers to create a variety of block copolymer architectures which can subsequently assemble into higher order structures. Taking advantage of the intermolecular interactions of nucleobases, this approach has allowed us to generate drug-loaded block copolymer nanoparticles and physically crosslinked gels that assemble via sequence specific CNA-DNA interaction. Copolymers of CNAs are also capable of rapid cell uptake, portending applications in the delivery of tethered payloads. In summary, in addition to addressing the challenges of alternative nucleic acid and nucleic acid analog syntheses and application, employment of thiol-click reactions for the synthesis of CNAs generates new potential for custom macromolecular and materials design.

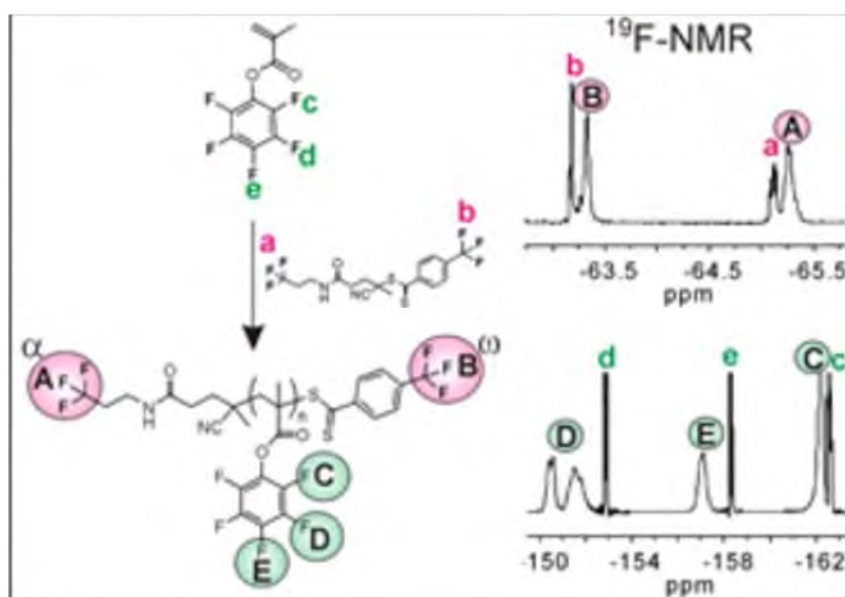


Mechanism for forming sequence controlled polymers from defined oligomers in combination with thiol-ene polymerizations

POLY 19: Trace element and isotope labels to study uptake and intracellular trafficking of polymer conjugates

Harm A. Klok, *harm-anton.klok@epfl.ch*. STI-IMX-LP, EPFL, Lausanne, Switzerland

Fluorescent labeled polymers are extensively used to monitor internalization and intracellular trafficking of polymers and polymer nanoparticles. There are, however, also some drawbacks and limitations related to the use of fluorescent dyes. Exposure of polymer-dye conjugates to the degradative intracellular environment, for example, can result in release of the dye. Furthermore, there is the risk for pH- and concentration-dependent quenching or photobleaching. Last but not least, fluorescent labels may alter the uptake or intracellular trafficking behavior of the polymer. Over the past years, an increasing number of techniques has become available that do not require the use of fluorescently-labeled polymers. This includes Raman spectroscopy as well as nanoscale secondary ion mass spectrometry (NanoSIMS) and synchrotron X-ray fluorescence imaging. As a consequence, there is a need for simple and efficient protocols to synthesize polymers that are labeled with isotopes and trace elements. This presentation will report the preparation of fluorine-chain-end-labeled side chain reactive polymers via RAFT polymerization of pentafluorophenyl methacrylate (PFMA) mediated by two new fluorinated chain transfer agents (CTAs), which contained either one (R) or two (R,Z) fluorine labels. While the α -label, which derives from the R-group, is introduced for bioimaging purposes, the ω -label that is due to the Z-group allows to monitor end-group fidelity of the PPFMA polymers produced via this process using ^{19}F -NMR spectroscopy. The PPFMA polymers are attractive since they serve as a platform for post-polymerization modification and can be converted to generate α -fluorine, ω -Rhodamine red end-labeled poly(N-(2-hydroxypropyl)methacrylamide) (PHPMA), which serves as a proof-of-concept since this polymer has been widely used for the preparation of polymer-drug conjugates. Uptake and intracellular trafficking of this PHPMA polymer was studied with confocal microscopy and NanoSIMS.

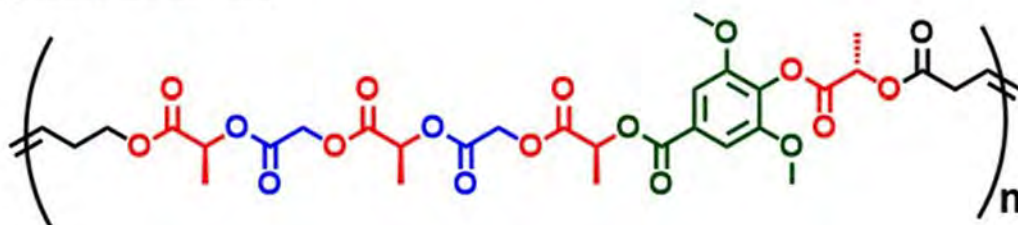


POLY 20: Effect of minor sequence errors on the degradation behavior and properties of biodegradable periodic poly(α -hydroxy acid)s

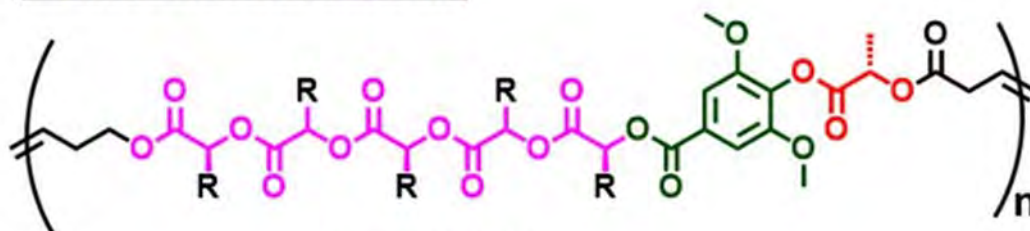
Jamie A. Nowalk¹, **Tara Y. Meyer**^{1,2}, tmeyer@pitt.edu. (1) Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States (2) McGowan Center for Regenerative Medicine, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

We have previously found that the degradation and properties of poly(α -hydroxy acid)s, which are commonly used in bioengineering applications such as drug delivery and scaffolding, depends on sequence. Periodic copolymers have been found to exhibit markedly different behaviors when compared with each other and with fully random analogues. To more precisely probe the effects of sequence fidelity/errors in these materials, we have prepared a precisely sequenced cyclic macromonomer, **Cyc-SyLMLGLGL** (Cyc = cyclic; Sy = syringic acid; L = L-lactic acid; G = glycolic acid; M = olefin-containing linker), as well as a controlled random macrocycle containing the same "linker" sequence (SyLM) but with a random sequence pentamer of the same L:G composition. These macromonomers were polymerized to identical molecular weight and cast as films from solution. The films were subjected to *in vitro* hydrolysis conditions (pH = 7.4, 37 °C). Molecular weight decrease, mass loss, thermal characteristics, photographs of whole samples, and SEM images were acquired over a period of 10 weeks.

Sequenced



Controlled Random

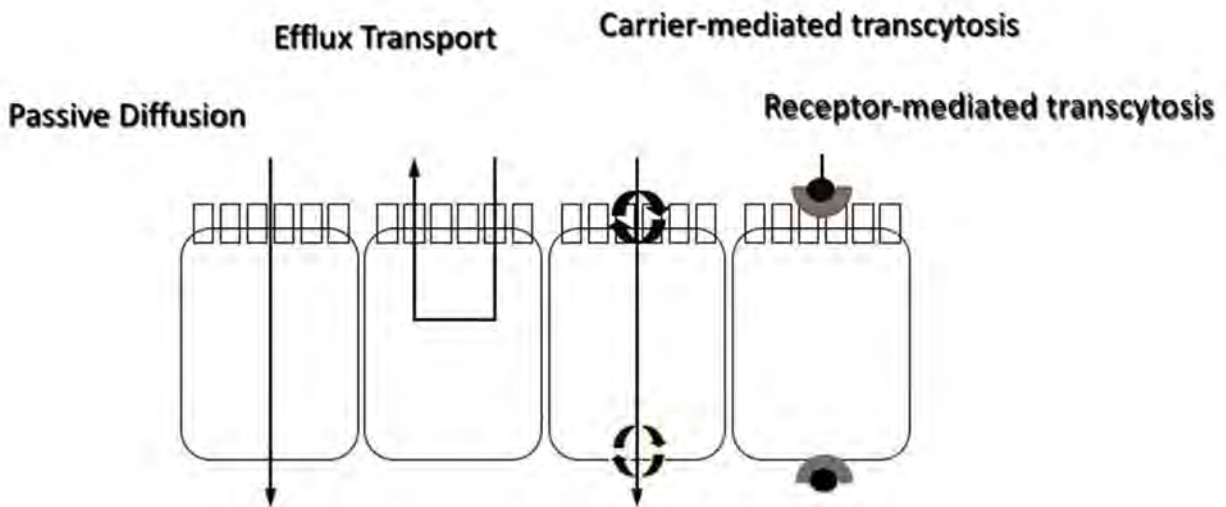


R = 3:2 Me:H

POLY 21: Intelligent nanoscale polymer networks on epithelial cells: Surface and difusional effects

Nicholas Peppas, peppas@che.utexas.edu, Julia Vela Ramirez, David Spencer. Dept of Chemical Engineering, University of Texas Dept Chem Eng, Austin, Texas, United States

We have started designing advanced hybrid systems that can provide recognition of the causes of various diseases. These systems are based on smart biomaterials that can recognize various undesirable analytes and inform the medical practitioner of the early stages of a disease. This revolutionary method of detection is based on engineering principles, good materials properties and interaction in “real” systems. Recent developments in protein delivery have been directed towards the preparation of targeted formulations for protein delivery to specific sites, use of environmentally-responsive polymers to achieve pH- or temperature-triggered delivery, usually in modulated mode, and improvement of the behavior of their mucoadhesive behavior and cell recognition. We address design and synthesis characteristics of novel biomaterials capable of protein release as well as artificial molecular structures capable of specific molecular recognition of biological molecules. With such systems we can prepare biomimetic materials for intelligent drug delivery, drug targeting, and tissue engineering.



Mechanisms of nanoparticle transport in contact with epithelial cells

POLY 22: Bottom-up assembly of stimuli responsive functional polymeric systems

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Polymersomes are bilayer vesicles, self-assembled from amphiphilic block copolymers. They are versatile nanocapsules since many of their properties, such as flexibility, permeability, size, and functionality, are adjustable. The control over the shape and function however has proven difficult so far, despite its relevance for many applications. Herein we report our recent developments regarding the control of both shape and function of self-assembled structures. I will show how we can precisely control the polymersome shape via out-of-equilibrium self-assembly by selecting a specific osmotic pressure and permeability (Figure 1). The second part of the talk will focus on the emergent functions of these structures with emphasis on autonomous movement. Functionalization and entrapment of coupled with catalytic components such as inorganic nanoparticles or enzymes allow the assembly of functional locomotive systems able to move directional and sense their environment. Attachment of stimuli responsive units on their surface allow for further control in the movement of these particles and their use for biomedical applications.

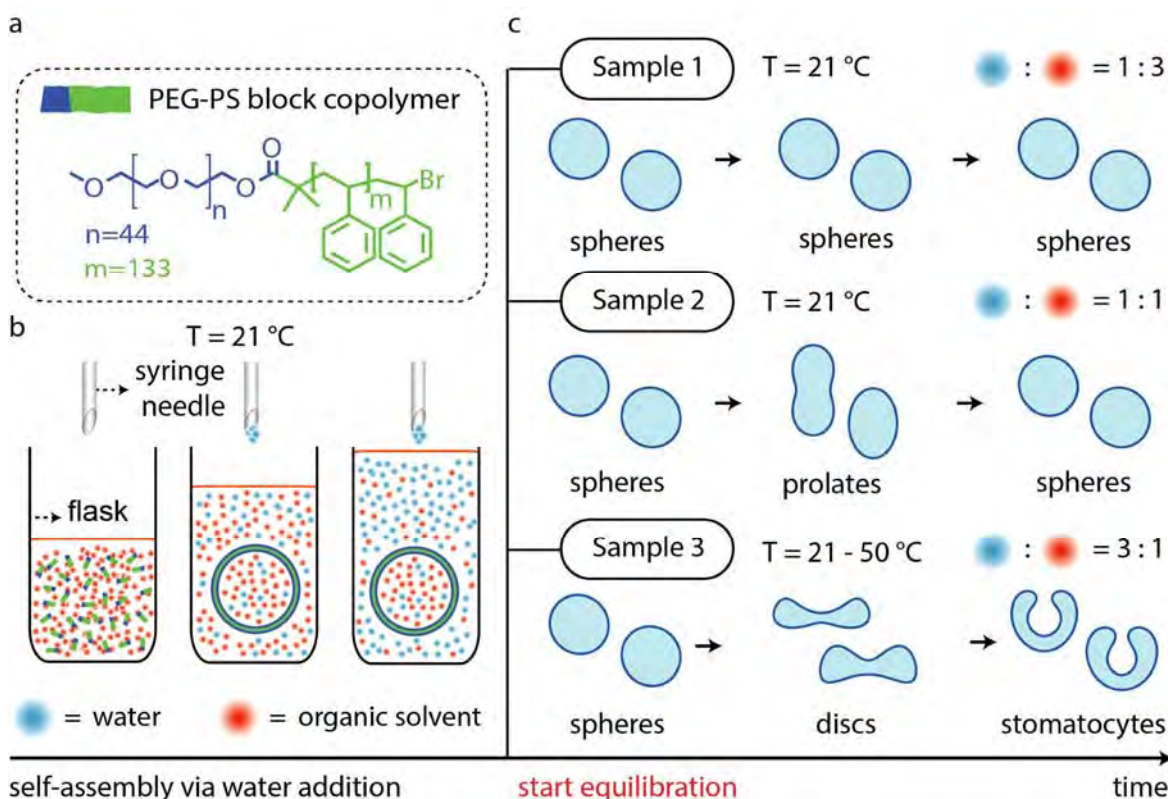
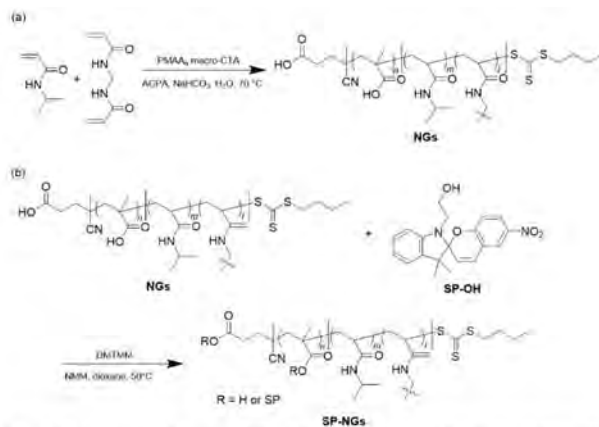


Figure 1. Shape control of polymersomes.

POLY 23: Preparation of multi-stimuli-responsive active colloids via RAFT polymerization-induced thermal self-assembly

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Collective motions observed in living organism, such as flock of birds, schools of fish, self-organization of bacterial colonies, formation of tissues from cells, *etc.* serve important biological functions. Over the last decades, synthetic materials that mimic those collective motions powered by external stimuli, so called “active matter”, have attracted increasing attention for biomedical applications including directed molecular delivery. However, many of the reported active matters so far consist of hard condensed materials within which guest molecules are hard to be encapsulated. Thus, it is of great importance to prepare the active matter from stimuli-responsive soft materials as potential delivery vehicles. Herein, we report the preparation of active colloids consisting of nanogels (NGs) which vary their physical properties in response to external stimuli, *e.g.* pH, temperature, and UV light irradiation. The NGs were synthesized via RAFT polymerization-induced thermal self-assembly (PITSA) of *N*-isopropylacrylamide (NIPAM) with a small amount of *N,N'*-methylenebis(acrylamide) (MBAM) as a cross-linker mediated by hydrophilic macromolecular chain transfer agent (macro-CTA) of poly(methacrylic acid) (PMAA) and 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as a radical initiator in water at 70 °C, a temperature higher than the lower critical solution temperature (LCST) of the PNIPAM, followed by post-polymerization functionalization of the NGs with a photo-responsive spiropyran (SP) derivative. The hydrodynamic radii (R_h) of the NGs vary with phase transition of the PNIPAM moiety by heating/cooling around their cloud point temperatures (T_{cp}). The T_{cp} and thermo-responsive property of the NGs vary by adjusting pH below/above pK_a of MAA ($pK_{aMAA} = 4.36$). Photoisomerization of the SP moiety on the surface of the NGs from nonionic SP form to highly polarized zwitterionic merocyanine (MC) form induced self-propelled collective motion of the colloids toward UV light source.



Scheme 1. (a) Synthesis of the nanogels (NGs) via RAFT polymerization-induced thermal self-assembly (PITSA) and (b) post-polymerization functionalization of the NGs with SP-OH via esterification.

POLY 24: Design of reducing environment-responsive gel capsules via miniemulsion periphery RAFT polymerization as drug delivery carrier

Akifumi Kawamura, *akifumi@kansai-u.ac.jp*, Hiroshi Nakaura, Takashi Miyata. Kansai Univ, Suita, Osaka, Japan

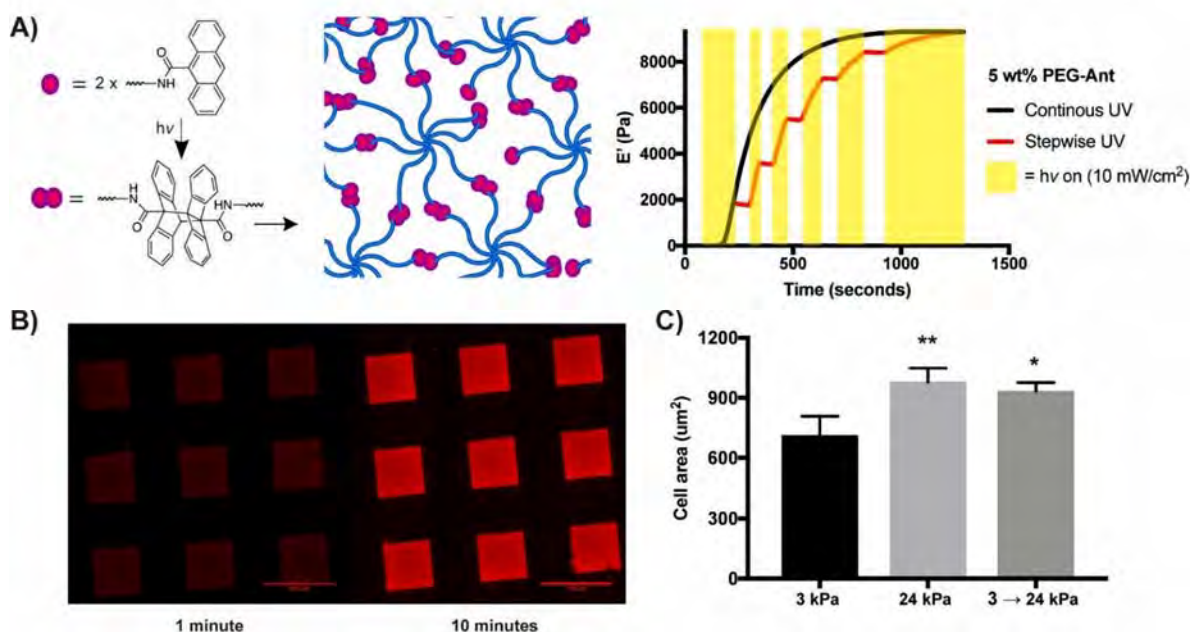
Nano and micro-sized capsules having an inner water phase, such as liposomes and polymersomes, have been extensively studied as drug carriers because they can load water-soluble protein drugs. However, they have a few disadvantages of low mechanical strength and low loading efficiency of drugs. Therefore, the preparation of stable capsules having an inner water phase is required for constructing carriers for water-soluble protein drugs. In this study, the gel capsules consisting of a hydrophilic capsule membrane and an inner water phase were strategically prepared via miniemulsion periphery reversible addition fragmentation chain transfer (RAFT) polymerization. A water-soluble block copolymer composed of a hydrophilic 2-methacryloyloxyethyl phosphorylcholine (MPC) block and an amphiphilic oligo(ethylene glycol) methacrylate (OEGMA) block was synthesized by RAFT polymerization. The resulting block copolymer (PMPC-*b*-POEGMA) had a narrow molecular weight distribution. Water-in-oil (W/O) emulsions were formed using chloroform as an oil phase in the presence of water-soluble PMPC-*b*-POEGMA. Then, gel layer was prepared by the subsequent polymerization of poly(ethylene glycol) methacrylate (PEGMA) as an amphiphilic monomer and bis(2-methacryloyl)oxyethyl disulfide (BMOD) as a reducing environment-responsive crosslinker from the PMPC-*b*-POEGMA macro RAFT agent that stabilized the W/O emulsions. Furthermore, we investigated drug release behavior from gel capsules containing fluorescein-conjugated dextran (FITC-Dex) as a model drug. The FITC-Dex release from the gel capsules in the phosphate buffer solution (pH 7.4, 20 mM) with DTT was faster than that without DTT. The reducing environment-responsive FITC-Dex release is attributed to the dissociation of disulfide bonds that act as crosslinks of the gel layer. Thus, the gel capsules that exhibit stimuli-responsive drug release are promising as water-soluble drug delivery carriers.



POLY 25: On demand stiffening poly(ethylene glycol) (PEG) hydrogels via [4+4] photocycloaddition of anthracenes

Kemal A. Günay, *Kemal.Gunay@colorado.edu*, **Kristi S. Anseth**, *Department of Chemical and Biological Engineering and the BioFrontiers Institute, University of Colorado at Boulder, Boulder, Colorado, United States*

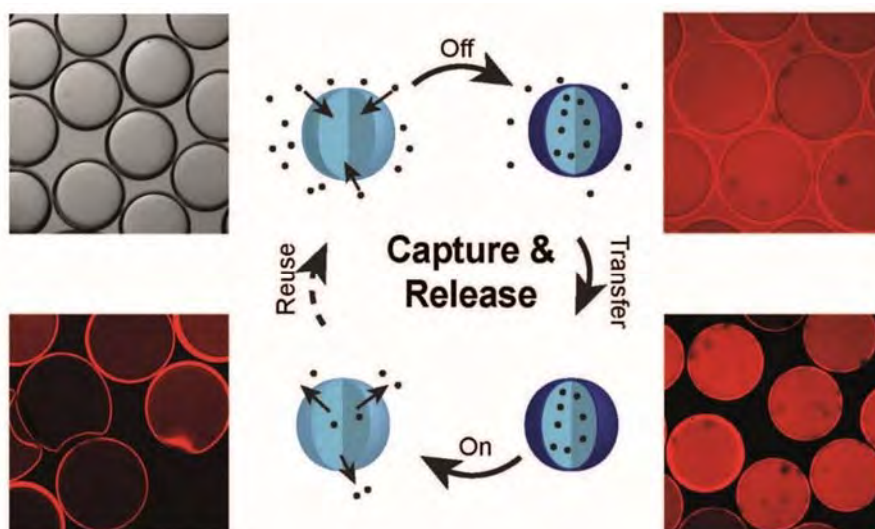
Stimuli-responsive hydrogels with adaptable mechanical properties are attractive for a wide variety of applications, including self-healing materials, drug delivery reservoirs, and for mechanobiology studies. In this work, anthracene (Ant)-functionalized PEG hydrogels are prepared as an on-demand stiffening material. Hydrogel formation is achieved via 365 nm light-mediated intermolecular [4+4] photocycloaddition between anthracene end-groups on 8-arm 20 kDa PEG-Ant chains. Gel evolution was controlled either in one or multiple steps by shuttering the light source on and off (**A**). The reaction is compatible with cell culture media and does not require a radical initiator that can elicit cellular toxicity. For PEG-Ant solutions in PBS at pH 7.4, photodimerization proceeds with a rate constant between 0.72-0.93 L·mol⁻¹·sec⁻¹ at 10 mW/cm² irradiation, which is comparable to typical click reactions. Furthermore, when the macromolecular precursors are only partially reacted, unreacted Ant groups can be subsequently photopatterned to stiffen the gel or incorporate biological signals to permit localized presentation of cues to cells. As a proof of concept, a hydrogel with 35 mol% of unreacted Ant groups was photopatterned with a heterobifunctional Ant-PEG₃₄₀₀-rhodamine linker (1-10 min, 10 mW/cm²) (**B**). To demonstrate its feasibility as a scaffold to study mechanobiology, C2C12 myoblast cell lines were cultured on static and stiffening hydrogels (2 mM Ant-GRGDS, E' = 3-24 kPa). C2C12 cells were observed to increase their cell area upon *in situ* stiffening (**C**). In summary, PEG-Ant hydrogels offer a simple but robust platform to produce multifunctional gels can be used for diverse biomaterial applications.



POLY 26: Dynamic microcapsules with reversibly trigger-responsive membranes

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Microcapsules are widely employed to protect and release sensitive cargo at a predetermined trigger-event and rate, yet their functionality is commonly one-dimensional. Release mechanisms involve degradation or destruction of the shell membrane, rendering microcapsules single-use, one-way encapsulants. Due to the destructive mechanism, stopping of the release is impossible once initiated. Microcapsules that reversibly respond to external stimuli could turn release off repeatedly upon reversal of the trigger. The encapsulating shell in such systems would purely act as an active gate-keeper, regulating diffusion in and out of the aqueous core compartment in response to changes in its environment. The aqueous core of such dynamic capsule systems could be loaded numerous times with cargo substances making reuse and recycling of microcapsules over multiple cycles possible. The challenge to fabricate aqueous microcapsules with shells whose permeability can be reversibly altered without sacrificial templates has hampered the development of such dynamic microcapsule systems. Here we describe the development of a number of polymer chemistries that allow for the synthesis of trigger-responsive hydrogel shells in complex emulsion drops for dynamically responsive microcapsules. We employ microfluidic fabrication of double emulsion drops with hydrophobic monomers as shells to synthesize trigger-responsive hydrogel membranes directly around water drops. The permeability and molecular weight cut-off for molecules that are able to diffuse through the shell is dynamically and actively tunable with external triggers. We demonstrate that the release from these dynamic microcapsule systems can be controllably activated and deactivated, enabling self-adjusting on-off release profiles. Furthermore, the capsules can be repeatedly cycled between their permeable and impermeable state, enabling capture, trap, and release of substances from the capsule environment with molecular selectivity.



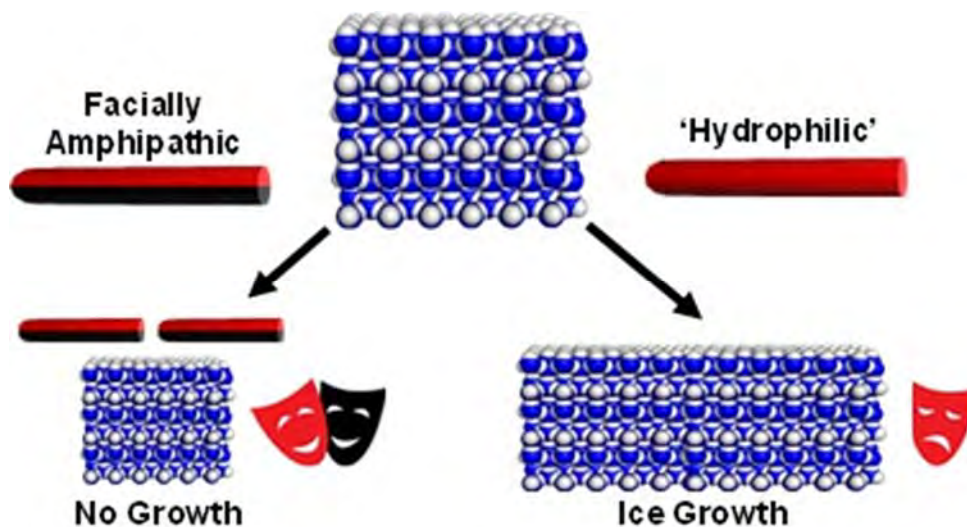
POLY 27: Facially amphipathic glycopolymers to mimic the 3-D structure of antifreeze glycoproteins

Ben Graham¹, *B.Graham.1@warwick.ac.uk*, **Matthew I. Gibson**². (1) University of Warwick, Coventry, United Kingdom (2) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom

Antifreeze (glyco)proteins, AF(G)Ps, from polar fish, represent a remarkable group of biomacromolecules which allow extremophiles to survive in freezing temperatures. AF(G)Ps are however unsuited to biomedical translation, and synthetic analogues are needed to mimic their ice recrystallisation inhibitory properties, which may find use in cryopreservation.

Despite the lack of an X-Ray crystal structure of AF(G)P, its adoption of an amphipathic polyproline II like helix is believed to be responsible for its activity. A variety of species which have been found to be IRI active (such as Nisin A) have also been shown to possess these distinct amphipathic regions. We are therefore interested in developing new IRI active biomimetics of AF(G)Ps based on synthetic macromolecular scaffolds, by drawing upon the observations of structural amphipathy in the natural products. We are engaged in the rational design and synthesis of new biomimetic species featuring amphipathic character, followed by IRI activity screening.

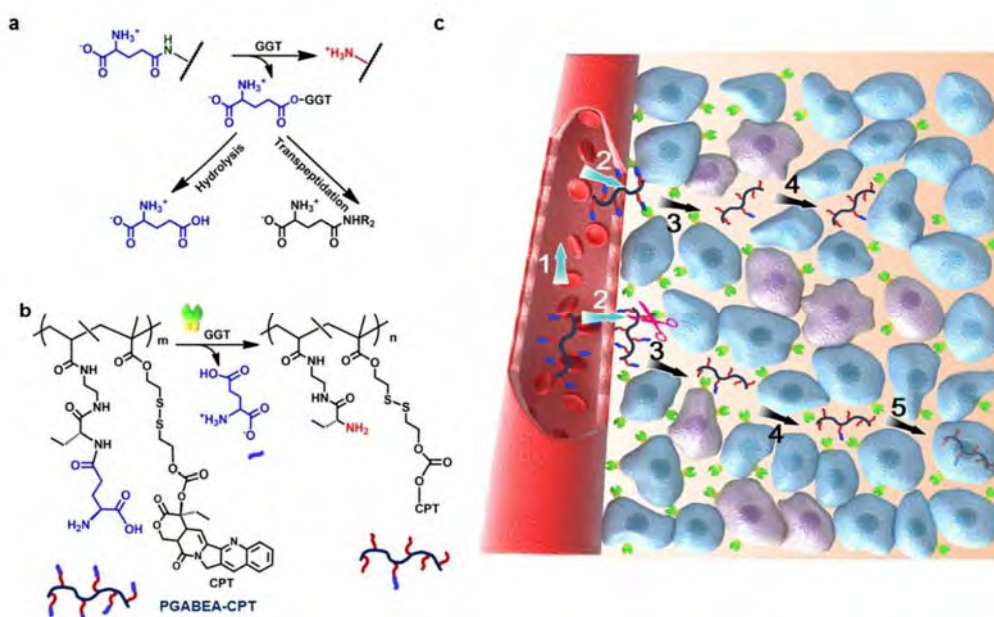
Here I will showcase our 2nd generation IRI-active glycopolymers which have been designed to mimic AF(G)Ps. In particular, I will demonstrate how we can use the local hydrophobic/philic balance of the polymers, rather than designed ice-binding motifs, as a universal route to introduce IRI activity. A series of amphipathic monomers polymerised by Ring-opening Metathesis Polymerisation (ROMP) yielded a highly potent panel of IRI active macromolecules. As confirmed by small-angle neutron scattering (SANS), the intrinsic structural rigidity provided for by ROMP (which is unobtainable through classical radical polymerisation methods, and gives rigid-rod like structures), supports a mechanism of activity driven by amphipathy, highlighting the importance of spatial domain segregation in rational IRI design.



POLY 28: Enzyme-responsive charge-reversal polymer for enhanced anticancer drug delivery

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For effective anticancer drug delivery, neutral stealthy nanocarriers are essential to turn into positively charged once accumulated in the tumor site for facilitated tumor penetration, cellular uptake and even nuclear localization. Such a neutral/negative-to-positive charge-reversal is typically realized by acid-catalyzed hydrolysis of *b*-carboxylic acid amides into amines triggered by the acidity of the tumor microenvironment or the intracellular compartments. However, the clinical relevance of this acid-triggered charge-reversal is limited by the low occurrence of the acidic tumor regions in small human tumors and the inaccessibility of nanocarriers to these weakly acidic regions that are far away from tumor blood vessel network. To this end, we here demonstrate an enzyme-triggered charge-reversal strategy, taking advantage of the more general enzyme overexpression in tumors. γ -Glutamyl transpeptidase (GGT) is highly expressed on the surface of metabolically active tumor cells in aggressive edges and blood vessel periphery of tumors. A γ -glutamylamide-based zwitterionic polymer is long circulating in blood compartment. In GGT-positive tumors, the overexpressed GGT cleaves off the γ -glutamyl moieties to expose primary amine groups, making the polymer positively charged and highly efficient in tumor accumulation, penetration and cell uptake. As a result, its conjugate with camptothecin shows much more potent antitumor activity than non GGT-sensitive ones, leading to complete eradication of small solid tumors ($\sim 100 \text{ mm}^3$) and dramatic regression of large established tumors with the clinically relevant size ($\sim 500 \text{ mm}^3$). Furthermore, this conjugate also significantly extends the survival of mice bearing orthotopic pancreatic tumors compared to the first-line drug gemcitabine. Thus, this work demonstrates the first example of enzymatic charge-reversal for design of highly effect cancer nanomedicine.



POLY 29: Sequence-defined polymer architectures: Need for multi-functionality and absolute precision

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Polymer chemists have made great progress in the preparation of highly functionalized and complex polymer architectures with defined structure-property relationships in the last decades, yet these structures do not reach the same potential as their natural counterparts (DNA, RNA & proteins). Thus, in the last decade, efforts have increased to achieve control over the primary structure of macromolecules to create stronger correlations between properties and structure/function.

In our research, multifunctional and monodisperse sequence-defined oligomers were obtained on solid support from a protecting-group-free two-step iterative protocol, based on the inherent functionalization features of a thiolactone unit. While a very wide variety of functionalities has been installed on those structures, the reaction conditions were closely monitored in order to fine-tune the applied strategy as well as facilitate the translation to an automated protocol, executed in a peptide synthesizer.

The importance of the versatile monomer alphabet, the monodispersity of the obtained structures and the fact that many chemical functionalities can be combined in one single structure will be exemplified by writing/reading a sentence and a QR-code.



POLY 30: Facile synthesis of polystyrene-polyphenylsiloxane Janus nanoparticles and their use as intermediate for the synthesis of tailored plasmonic materials

Pascal Buskens^{1,2}, pascal.buskens@tno.nl, Daniel Mann^{3,2}, Helmut Keul⁴, Martin Moller⁵, Marcel Verheijen⁶, Stefanie Voogt³. (1) The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, Netherlands (2) Hasselt University, Hasselt, Belgium (3) DWI/RWTH Aachen University, Aachen, Germany (4) RWTH, Aachen, Germany (5) Dwi An Der RWTH E V, Aachen, Germany (6) Philips Innovation Labs, Eindhoven, Netherlands

Janus particles are of great research interest because of their reduced symmetry, which provides them with unique physical and chemical properties. Here, we present a facile route for the synthesis of such particles through colloidal assembly of glucose-functionalized polystyrene spheres and an emulsion of phenyltrimethoxysilane (Ph-TMS) in aqueous ammonia, followed by interfacial polycondensation of Ph-TMS to form a polyphenylsiloxane patch (Fig. 1) [1]. The selectivity in the formation of these Janus nanoparticles is unexpectedly high, and we demonstrate that both the size of the polystyrene sphere and the polyphenylsiloxane patch can be adapted independently from each other [2]. Furthermore, we report insights into the details of the mechanism of formation of the Janus particles, and apply those to adapt the synthesis conditions in a way that polystyrene spheres decorated with multiple polyphenylsiloxane patches are formed (Fig. 1) [1]. The Janus particles are used as an intermediate in the formation of specific plasmonic materials, so called Au semishells [2]. The particles are coated with Au in a seeding-plating sequence, and subsequently the polyphenylsiloxane patch decorated with Au is removed through dissolution in toluene, yielding a polystyrene sphere which is partially covered with a Au semishell (Fig. 2). These materials are optically characterized, and of interest for their plasmonic properties, e.g. for application in optical and optoelectronic devices [2].



Fig. 1: Formation of polystyrene-polyphenylsiloxane Janus particles, and polystyrene particles with multiple polyphenylsiloxane patches.

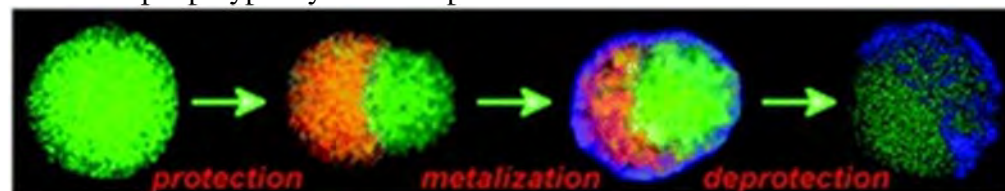
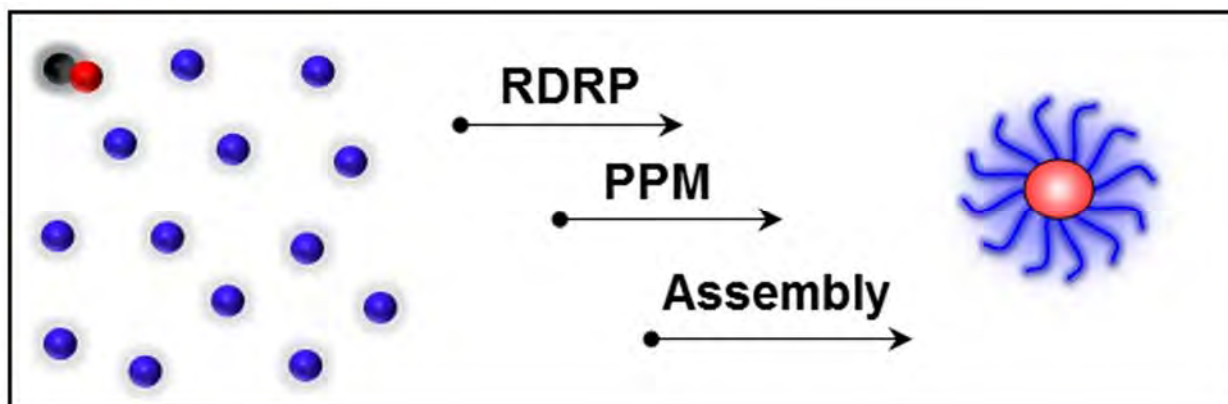


Fig. 2: (S)TEM-EDX images of Au semishells and intermediate products.

POLY 31: Towards functional materials *via* macromolecular design using cross-coupling and alkylboranes

Andrew J. Magenau, *amagenau@coe.drexel.edu*. Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States

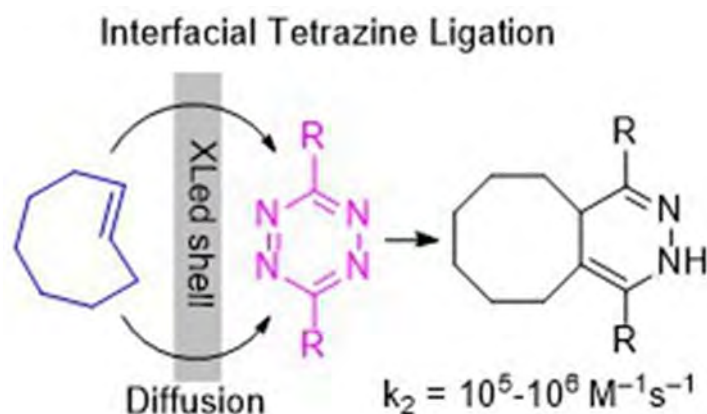
Synthetic strategies enabling the design of precision macromolecules are a central element of developing advanced soft-materials with strategic properties. Two powerful approaches to macromolecular design are highly-efficient post-polymerization modifications (PPM) and robust reversible deactivation radical polymerizations (RDRP). Pd-catalyzed Suzuki-Miyaura cross-coupling is explored as a versatile PPM for installing structurally diverse functionalities, tailoring polymer properties, and synthesizing complex architectures. Alkylborane initiated RAFT is also explored as an alternative RDRP initiation platform for synthesizing well-defined polymers under convenient conditions at room-temperature and in oxygen.



POLY 32: Interfacial tetrazine ligation for the fabrication of cell-instructive matrices

Kevin T. Dicker, Jiyeon Song, Joseph M. Fox, **Xinqiao Jia**, xjia@udel.edu. University of Delaware, Newark, Delaware, United States

The cycloaddition of s-tetrazine (Tz) with trans-cyclooctene (TCO) derivatives is particularly attractive for the synthesis of cell-instructive hydrogel matrices. This reaction is high yielding, does not require catalysis, does not produce any toxic side products, and is more than three orders of magnitude faster than pre-existing methods for bioorthogonal ligation. Using tetrazine-modified hyaluronic acid (HA-Tz, >200 kDa) and polyethylene glycol flanked with TCO (bisTCO, <2 kDa), we demonstrated the formation of hydrogel spheres via a diffusion-controlled process at the gel-liquid interface. Syringe delivery of HA-Tz to a bath of bisTCO resulted in the instantaneous formation of a crosslinked shell, through which bis-TCO diffused inwards to complete the crosslinking. The interfacial diffusion-controlled process has permitted the creation of hydrogel spheres with pre-determined spatial distribution of TCO-tagged biomolecules. Through temporally controlled introduction of TCO conjugates during the crosslinking process, the enzymatic degradability, cell adhesivity, and mechanical properties of the synthetic microenvironment can be tuned with spatial precision. Alternatively, when an aqueous solution of bis-TCO is added to a reservoir of HA-Tz, a crosslinked channel wall forms instantaneously. As the reaction proceeds, the smaller bis-TCO molecule diffuses outwards across the crosslinked wall to react with HA-Tz at the interface, thereby growing the channel wall outward until bisTCO is fully exhausted. By alternating cell laden HA-Tz reservoirs during the channel formation, cells can be spatially patterned into the channel wall in a physiologically relevant spatial order. In conclusion, interfacial tetrazine ligation has enabled facile fabrication of cell-laden matrices for tissue engineering applications.



Diffusion-controlled interfacial bioorthogonal crosslinking for the preparation of functional biomaterials

POLY 33: New polymerization methodology of amino acids

Youhua Tao, youhua.tao@ciac.ac.cn. Changchun Institute of Applied Chemistry, Changchun, Jilin, China

Poly(amino acid) is an important biomimetic materials due to their unique biocompatibility, and potential application in gene transfection, drug delivery, and prevention of viral infections.¹⁻² For example, ϵ -Poly-lysine (ϵ -PL) is an uncommon cationic homopolymer produced by the fermentation process. Due to its significant antimicrobial activity and nontoxicity to humans, ϵ -PL is now industrially produced as an additive, e.g. for food and cosmetics. However, due to the lack of appropriate polymerization method, ϵ -PL is now produced mainly by a fermentation process. Here, we report a new chemical strategy, based on ring-opening polymerization (ROP) of lactam, to obtain ϵ -PL with diverse molecular weight from renewable lysine monomer. Compared with ROP of lysine *via* the *N*-carboxyanhydride (NCA) intermediate, this new strategy for ϵ -PL, through ROP and without phosgene, allows for new opportunities in biomaterials applications.³⁻⁴

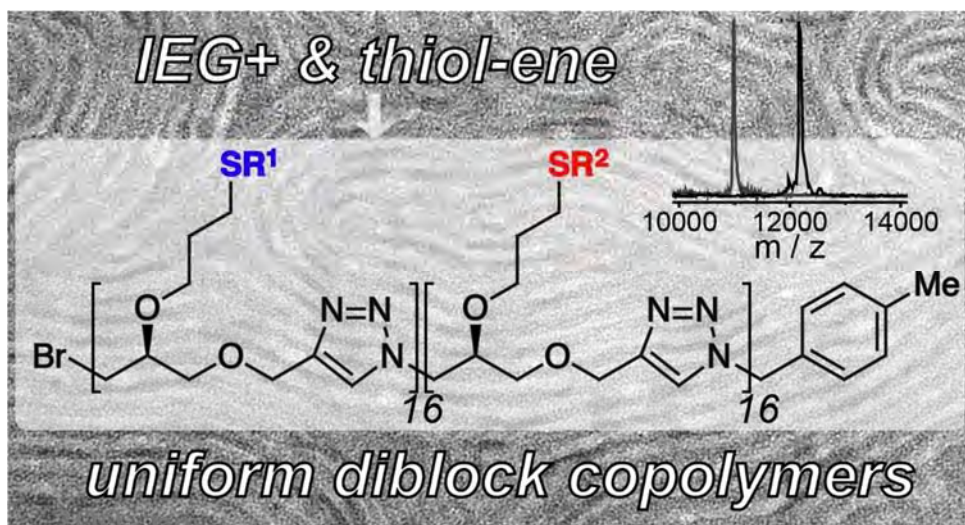


Figure 1. Ring-opening polymerization of lactam monomer for the synthesis of poly(amino acid).

POLY 34: Iterative exponential growth of stereo- and sequence-controlled polymers

Yivan Jiang¹, yivan@mit.edu, Matthew Golder², Paul Teichen³, Hung V. Nguyen², Wencong Wang¹, Nicole Milos¹, Jonathan C. Barnes^{1,4}, Deborah Ehrlich¹, Jeremiah A. Johnson¹. (1) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Chemistry, Massachusetts Institute of Technology, Somerville, Massachusetts, United States (4) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

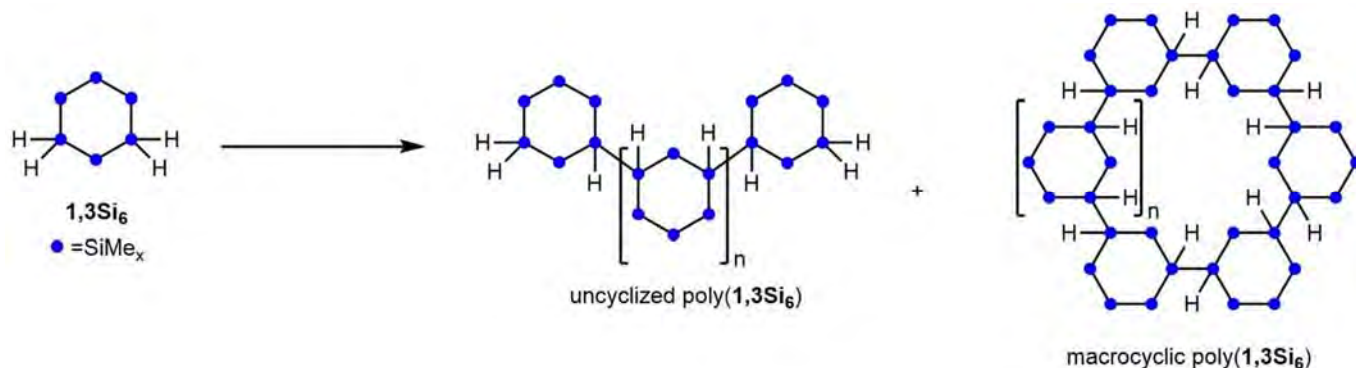
Polymer chemists have long tried to replicate Nature's remarkable ability to make macromolecules of defined length, sequence, and chirality. Many new synthetic approaches have attempted to access precisely defined and diversely functionalized uniform macromolecules in useful quantities. We are advancing a promising alternative synthetic strategy called Iterative Exponential Growth (IEG) wherein doubly protected molecules of length L undergo cycles of orthogonal activations and couplings to yield macromolecules with length $L \times (2^n)$ cycles. Though IEG is limited to repetitive or palindromic sequences, we have used it to make unimolecular, fully sequence-controlled and stereocontrolled polymers on multigram scales. Through synthetic modification of our base monomers, we can install a variety of functionalities such as alcohols, electron donating and accepting aromatics, free amines, and primary alkenes. We have only just started exploring the vast sequences and topologies that can be made using our system. For instance, using sequential thiol-ene click chemistry, we have synthesized unimolecular block copolymers (BCPs) of up to 12.1 kDa on a gram scale in under a week. BCPs of decane-based side chains and either triethyleneglycol- or thioglycerol-based side chains phase-segregate into hexagonal cylinder morphologies. It is our hope that by using our IEG system, we will elucidate the structure-property relationships that will guide the design of next-generation polymeric materials.



POLY 35: Directional building blocks provide curvature in poly(cyclohexasilane)

Eric Marro¹, emarro1@jhu.edu, **Eric Press**¹, **Rebekka S. Klausen**². (1) John's Hopkins University, Baltimore, Maryland, United States (2) JHU/Chemistry Dept., Baltimore, Maryland, United States

Nanoscale silicon materials possess properties with great promise for energy and optoelectronic applications. The discovery of new silicon-based building blocks will expand the silicon chemist's synthetic toolbox. We report the synthesis of a "meta"-like cyclohexasilane building block. Dehydrocoupling polymerization of this cyclohexasilane yields a mixture of macrocycles and linear oligomers. ¹H and ²⁹Si NMR spectroscopy provide evidence for a high symmetry macromolecule. Comparison to calculated and experimental infrared spectra of model systems support the structural assignment.



POLY 36: Scaling up and down with metal-free ring-opening metathesis polymerization

Andrew J. Boydston, *boydston@chem.washington.edu*, **Laura M. Pascual**, **Victoria Kensy**, **John Goldstone**. *Chemistry, University of Washington, Seattle, Washington, United States*

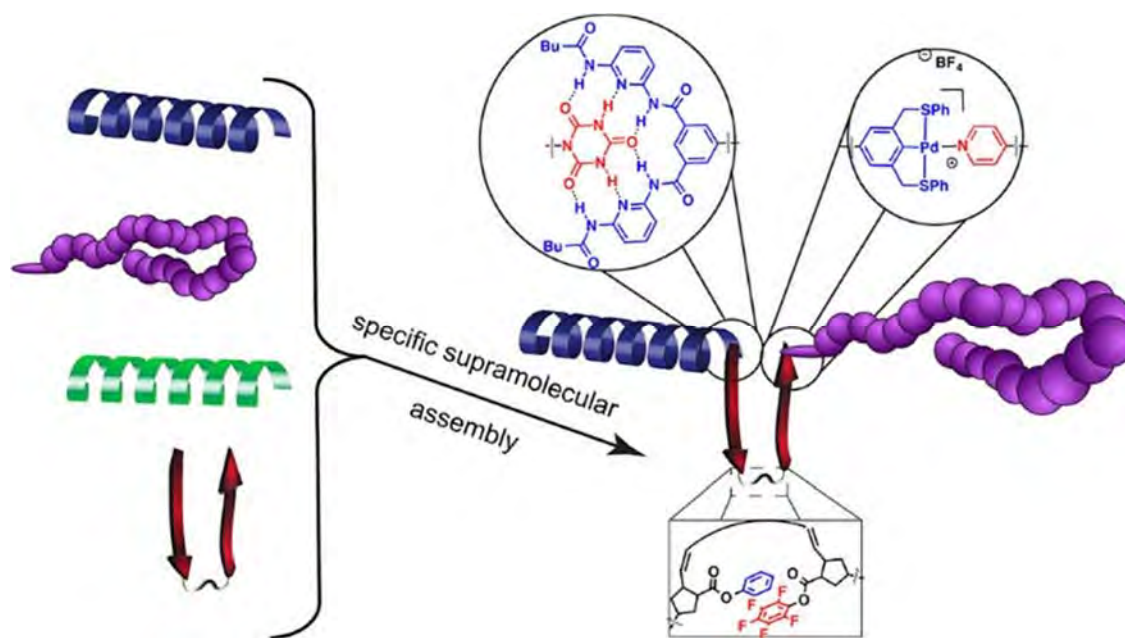
We have investigated the use of continuous flow reactors to produce large-scale quantities of oligomers and polymers via photoredox-mediated metal-free ring-opening metathesis polymerization. Optimizations have led to multi-gram and kilogram level production of homo- and copolymers. Additionally, we specifically targeted methods for achieving controlled low molecular weight species (oligomers). Adjustment of monomer to initiator ratios revealed several challenges, whereas introduction of chain transfer agents enabled efficient production of the target materials.



POLY 37: Functionalized helical poly(isocyanide)s and their use in covalent and supramolecular block copolymers

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This contribution describes the synthesis of a pyridine-functionalized palladium(II) initiator via a simple two-step process and its use in the polymerization of a menthol-based isocyanide monomer, which results in a monotelechelic, static helical poly(isocyanide). The helical poly(isocyanide) was supramolecularly assembled with telechelic blocks of different secondary structures to form di- and multiblock copolymers. In addition, the facile syntheses of sheet-coil-helix and coil-sheet-helix covalent triblock copolymers will be presented. We show that the individual blocks contained within these supramolecular and covalent systems retain their secondary structures throughout the synthesis and assembly events. Future work will focus on the formation of triblock copolymers that include heterotelechelic helical middle blocks, as well as the incorporation of side chain functionalized helical blocks into supramolecular copolymers to further increase the complexity of our systems.



"Plug-and-play" assembly strategy for the synthesis of supramolecular multiblock copolymers

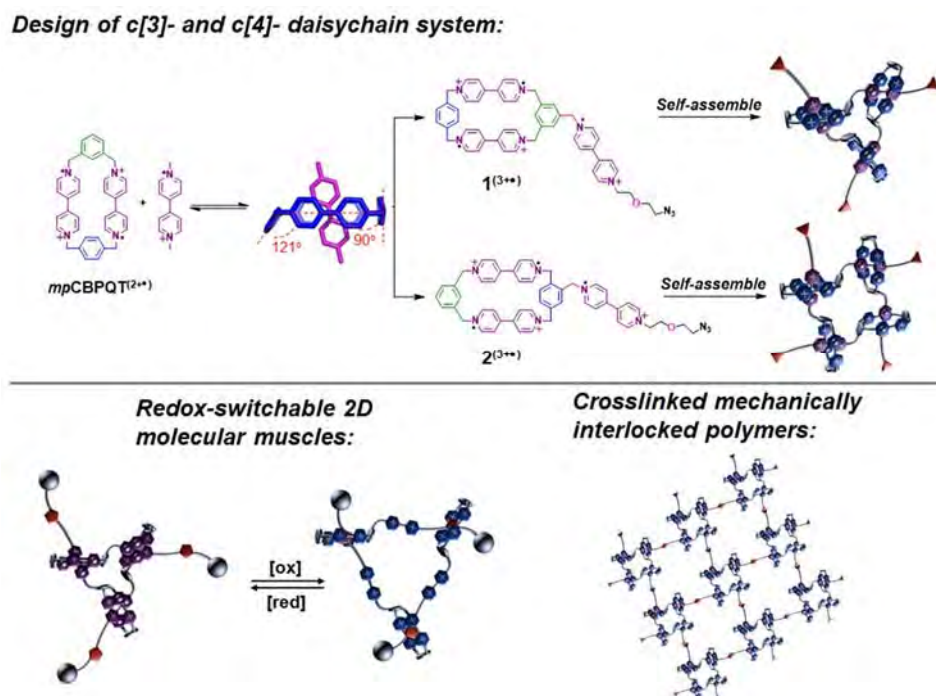
POLY 38: Cyclic[n]daisychains for mechanically-interlocked polymers and frameworks

Kang Cai¹, kang.cai.811@gmail.com, James F. Stoddart². (1) Chemistry, Northwestern University, Beijing, China (2) Department of Chemistry, Northwestern University, Evanston, Illinois, United States

Cyclic molecular daisy-chains (c[n]DCs, where n is the number of repeating units) have long been attractive synthetic targets for supramolecular chemists due to its unique interlock structure and potential muscle-like motions. However, there is still very few examples of multidimensional artificial molecular muscles based on c[3]- and c[4]-DC due to synthetic difficulties.

Herein we designed a new c[n]DC system based on radical host-guest pairing interaction between 4,4-bipyridinium radicals and cyclobis(paraquat-*p*-phenylene) radicals. By carefully modulating the linker between 4,4-bipyridinium units and cyclobis(paraquat-*p*-phenylene) units, c[3]- and c[4]-DCs were successfully obtained with high selectivity, which were characterized by UV-Vis-NIR, EPR, HR-MS, electrochemistry and single-crystal X-ray diffraction. These c[n]DC molecules showed interesting reversible expansion-contraction motions under redox-control.

More interestingly, the c[3]- and c[4]- daisychain motifs can served as A3-type and A4-type monomers for synthesizing novel mechanically interlocked crosslinked polymers or framework materials with redox-responsive properties.

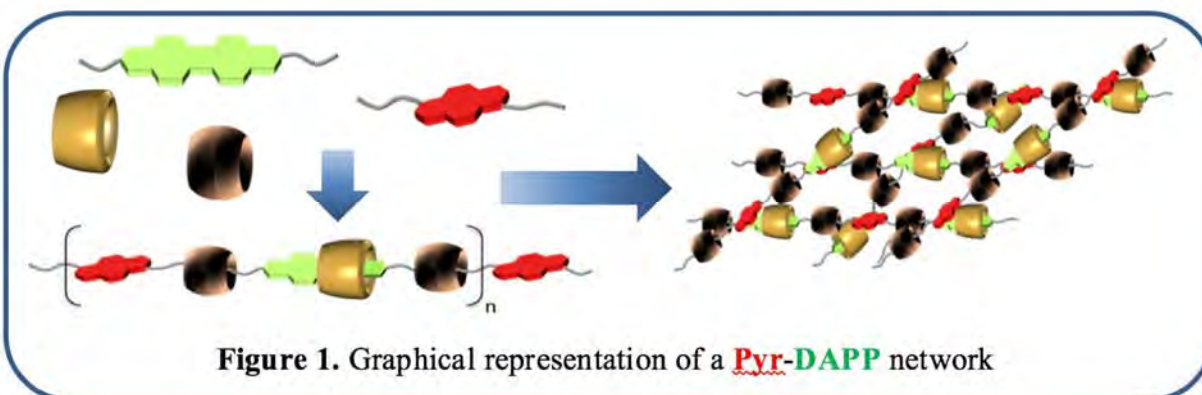
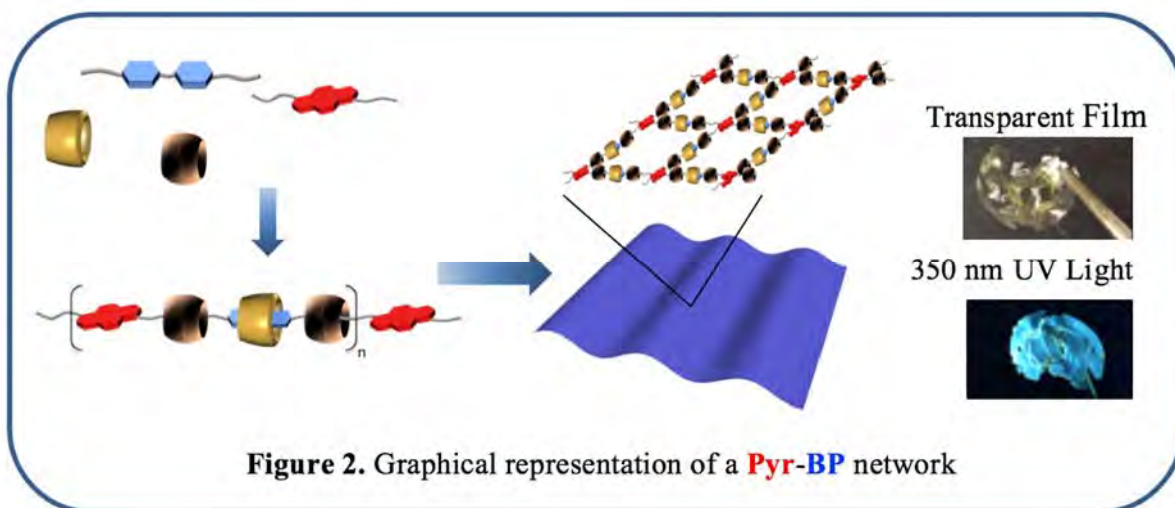


Scheme 1. The design of c[3]- and c[4]- daisychain systems and their applications

POLY 39: Construction of covalent and supramolecular organic framework

Yi Shi, *yi.shi1@northwestern.edu*, chemistry, Northwestern University, Evanston, Illinois, United States

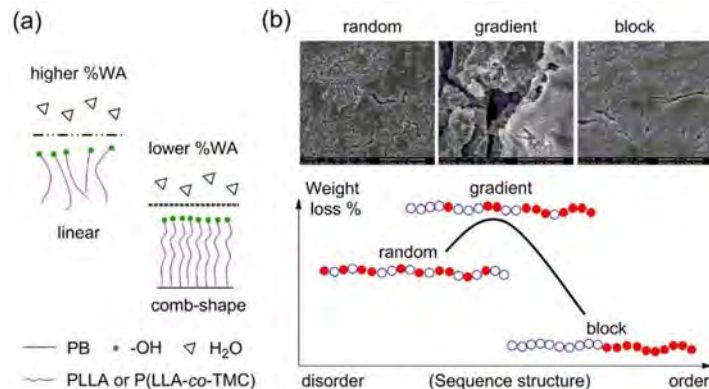
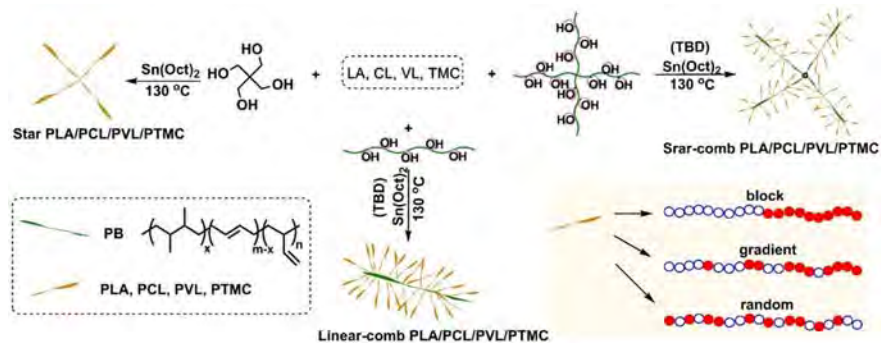
Here, we report a covalent and supramolecular hybrid organic framework with interlocked poly[n]rotaxane residues, which enables the fabrication of layered thin sheets. The dumbbell of the pseudo-polyrotaxane was connected covalently via an efficient cooperative CB-AAC reaction, and connected supramolecularly in the second dimension upon self-assembly by the dint of donor-acceptor (Figure 1, **Pyr-DAPP**) or p-p (Figure 2, **Pyr-BP**) interactions. The secondary structure of this material has been characterized by NMR spectroscopy, SEM, TEM, high-resolution TEM, AFM and PXRD technologies. This unique structure (covalent and supramolecular hybrid connection, interlocked poly[n]rotaxane residues) opens up the way for designing novel frameworks with emergent properties.



POLY 40: Synthesis of star-comb and linear-comb copolymers: Effect of chain topology on crystallization and degradation behaviors

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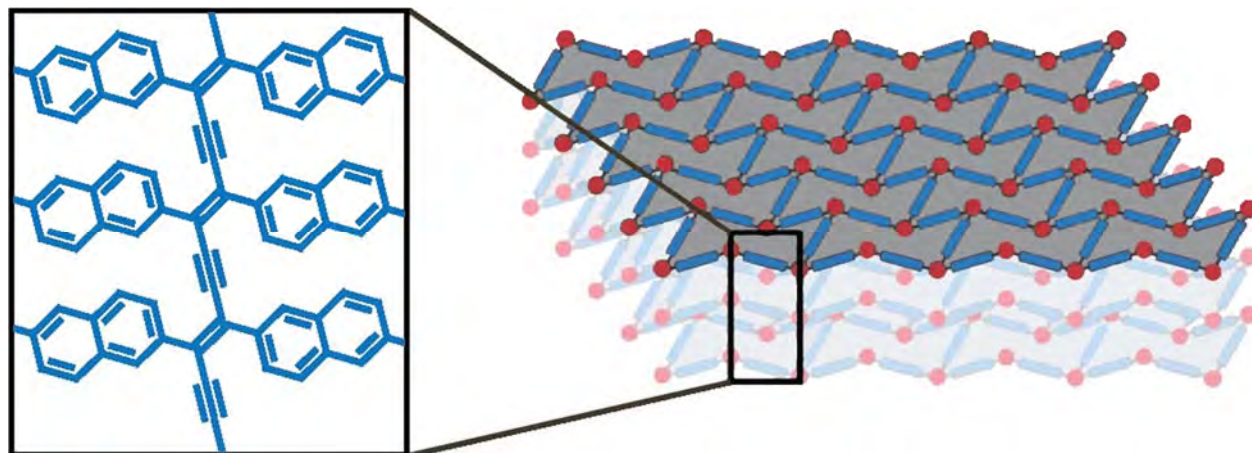
A series of highly branched star-comb poly(ϵ -caprolactone)-*block*-poly(L-lactide) (scPCL-*b*-PLLA) and linear-comb poly(trimethylene carbonate)-*block*-poly(L-lactide) (lcPTMC-*b*-PLLA) were successfully achieved using star-shaped/linear-shaped hydroxylated polybutadiene (HPB) as macroinitiator by a simple “grafting from” strategy. The ration of each segment could be controlled by the feed ratio of comonomer. These star-comb double crystalline PCL-*b*-PLLA were first synthesized and expected to illustrate the influences of the polymer chain topology by comparing with their counterparts in linear-shaped, star-shaped and linear-comb shape. The crystallization behaviors of scPCL-*b*-PLLA copolymers and the degradation of lcPTMC-*b*-PLLA) were investigated systematically. For PCL-*b*-PLLA, it is shown that the comb branched architectures promote the crystallization behavior of each constituent significantly. Both crystallinity and melting temperature greatly raised from linear to comb-shaped copolymers. Compared to linear-comb topology, the star-comb shape presents some steric hindrance of the graft points, which decreased the crystallinity of scPCL-*b*-PLLA. For PTMC-*b*-PLLA, it was found that the properties of the copolymers depended not only on the comonomer content but also on their topologies. Compared with block structure, the gradient and random structure of side chain could yield unordinary properties and degradation behavior. Effects of chain topology and copolymer composition on the crystallization and degradation behaviors were studied and discussed.



POLY 41: Topochemical polymerizations of a novel covalent organic framework

Evan S. O'Brien, evanoe@gmail.com. Chemistry, Columbia University, New York, New York, United States

COFs have emerged as a new class of structurally and functionally diverse crystalline materials whose applications range from molecular catalysis to energy storage and everything between. While the design principles for growing these compounds are well established and diverse, few reports demonstrate significant post-synthetic structural transformation. Here we describe a novel structure whose unusual structural topology enables post-synthetic topochemical polymerization of the framework linker fragments along the COF's vertical axis. The polymerization of the bisaryl-1,3-butadiyne into a polydiacetylene backbone covalently crosslinks the material without compromising its original crystallinity and while affecting a significant color change from white to blue. We perform the polymerization thermally and can unambiguously confirm the transformation using both raman and NMR spectroscopies. This work not only enables the preparation of more structurally resilient COFs, but also diversifies the design space for this emerging class of materials.

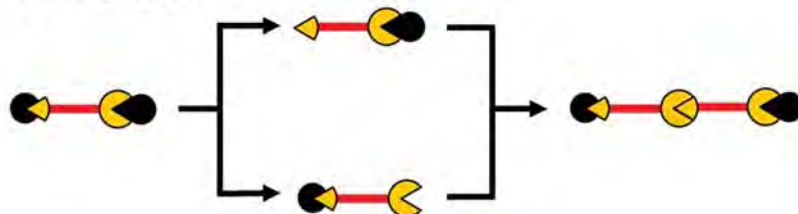


POLY 42: Diversifying the backbone structures of IEG polymers

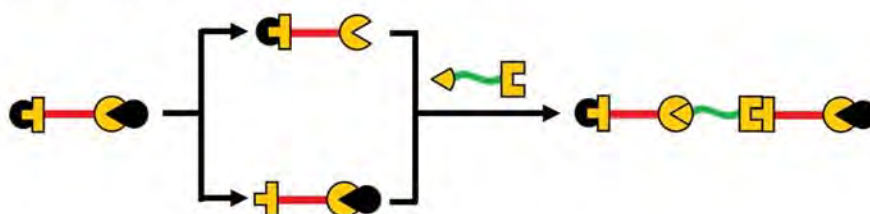
Ke Qin¹, peterqin315@gmail.com, Bo Qiao¹, Yivan Jiang², Jeremiah A. Johnson³. (1) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Chemistry, Massachusetts Institute of Tehcnology, Cambridge, Massachusetts, United States (3) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Synthesis of sequence-defined polymers has great potential for applications in fields such as polymer physics, self-assembly and the fabrication of organic photonic and electronic devices. Previous approaches, most based on iterative addition of monomers to a polymer chain, prove to be time-consuming and difficult to scale. A more efficient approach is iterative exponential growth (IEG), in which two chains are selectively deprotected and coupled, thus doubling the molecular weight in each iteration. Herein we seek to diversify the backbone structure of polymers synthesized via IEG by utilizing novel coupling chemistries, such as Sulfur(VI) Fluoride Exchange (SuFEx).

Previous IEG:



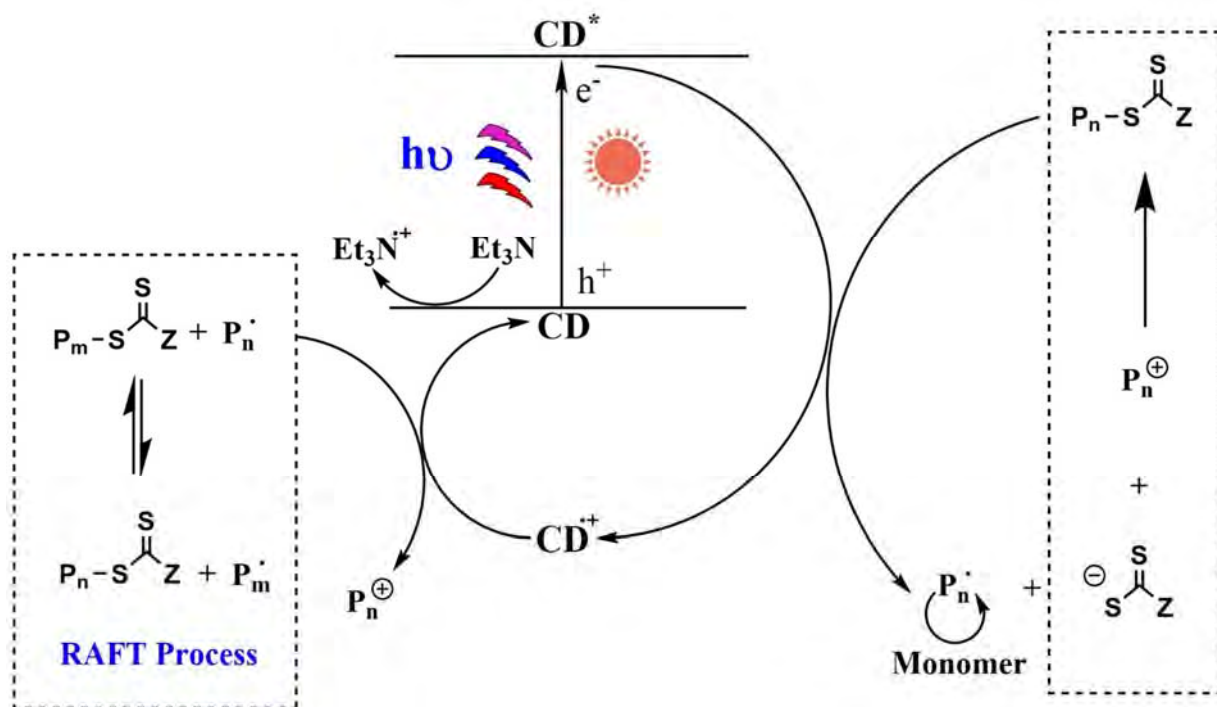
This work:



POLY 43: Study on a robust PET-RAFT polymerization catalyzed by carbon quantum dots (CDs)

Jingjie Jiang, *jjkuaile@aliyun.com*, Zhe Wang, Gang Ye, Xiaomei Huo, Jing Chen.
Tsinghua University, Beijing, China

Photo-induced electron transfer reversible addition-fragmentation chain transfer polymerization (PET-RAFT) represents one of the advanced living radical polymerization technologies for controlled synthesis of polymers with predetermined molecular weight (MW) and narrow distribution. In this study, a series of carbon quantum dots (CDs) were synthesized and used as organophotocatalysts for the PET-RAFT polymerization of methyl methacrylate (MMA) under mild visible lights. The influences of the CD composition, light wavelength, and the addition of electron donor agent were investigated. Catalyzed by one of sulfur-doped CDs, PMMA products with the degree of polymerization (DP) >300, high chain-end fidelity, and a minimum polydispersity index (PDI) of 1.05 were obtained under a blue light ($\lambda_{\max}=465$ nm). The PET-RAFT polymerization exhibited the typical pseudo-first-order kinetics, and might be explained according to an oxidation quenching mechanism (Scheme 1). Besides, the successful PET-RAFT polymerization of MMA was also achieved under natural sunlight with a narrow distribution (PDI ~ 1.14) of the product.



POLY 44: Scandium-catalyzed olefin polymerizations: Polar comonomer enchainment and nuclearity effects

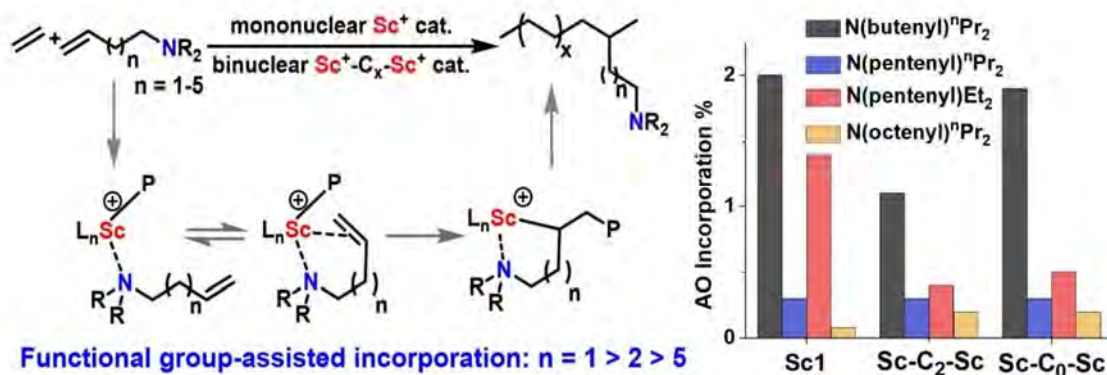
Jiazhen Chen, jiazhenchenpku@gmail.com, Tracy Lohr, Tobin J. Marks. Northwestern Univ, Evanston, Illinois, United States

Polyolefins represent more than half of the polymers produced. Introducing functionality into polyolefin can dramatically improve macromolecular properties. Direct copolymerization of ethylene with functionalized comonomers is highly desirable and is a “holy grail” challenge. However, the high Lewis basicity of functional groups poisons catalysts and depresses activity. Finding effective alternatives, with respect to the heavily studied group 4 and late transition metal catalysts, would represent an entirely new approach. Scandium, with +3 oxidation state and larger ionic radius than Ti^{4+} , may exhibit great functional group tolerance than its group 4 congener. Sc also exhibits unusual bonding character and may enable unusual reactivity.

We report that mono- and binuclear organoscandium complexes are active catalysts for the copolymerization of ethylene with amino-olefins (AOs, $H_2C=CH(CH_2)_nNR_2$) in the absence of sacrificial masking reagents. The activity (up to 4.2×10^2 kg/mol-h-atm) and comonomer incorporation (up to 12 %) are both appreciable. Chain length (n) dependent AO enchainment (butenyl > pentenyl > octenyl) and other mechanistic probes support an unusual functional group-assisted AO incorporation mechanism. Furthermore, binuclear catalysts exhibit enhanced AO tolerance and n -dependent selectivity, suggesting a cooperative enchainment mechanism may be operative. Contact angle measurements of the product ethylene/AO copolymers indicate that AO incorporation modifies the surface properties significantly.

Polyisoprene/polybutadiene are among the most significant rubbers. We report that varying both catalyst and cocatalyst nuclearity has significant effects on polymer microstructures in isoprene polymerization and ethylene/isoprene copolymerization. Binuclear catalysts regulate the isometric unit selectivity and favor 3,4~3,4~3,4~3,4 blocks. The percentage of *trans*-1,4- units increased ~5x when using binuclear cocatalyst versus mononuclear control.

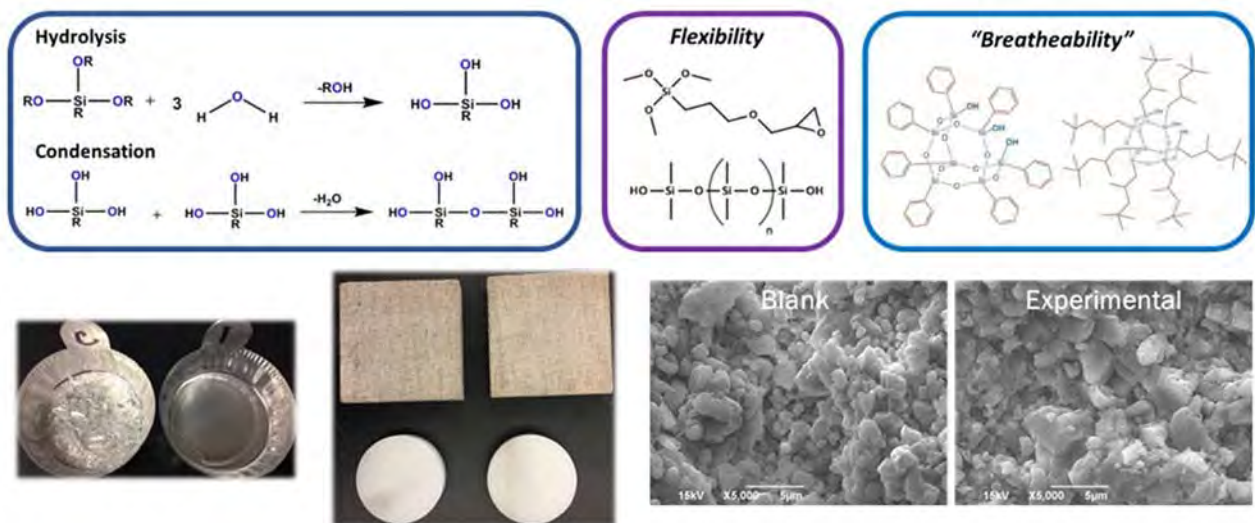
In summary, our research demonstrates that new polyolefin structures with functional groups can be accessed through Sc catalysis, highlights the importance of the nuclearity of catalyst and cocatalyst, and suggests that this influence can be tuned to access specific polymeric microstructures.



POLY 45: Alkoxysilane sol-gel consolidants for calcareous stone

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Ancient stone artifacts and architecture deteriorate over time due to environmental factors such as air pollution, salt efflorescence, and biodeterioration. As a result, effective stone consolidants are necessary for the conservation and protection of stone materials, specifically calcareous stones. Alkoxysilanes are effective stone consolidants, undergoing hydrolysis and condensation to produce a sol-gel capable of penetrating the stones internal porous structure. However, demands for improvements in commercial formulations have led to research efforts focused on increasing flexibility, “breathability” and durability. In order to allow water vapor evaporation out of the stones internal pores post-consolidation, a “breathable” component within the formulation is required to permit the transport of water molecules. Polyhedral oligomeric silsesquioxane (POSS) structurally contains a nano-meter sized cage, allowing for water permeability in addition to mechanical integrity. Polydimethylsiloxane (PDMS) was utilized for increasing flexibility and hydrophobicity. Consolidant formulations incorporating both POSS, PDMS, and additional compounds were sprayed on Indiana Limestone and Royal Danby Marble. The experimental formulations were optimized using Design Expert and analyzed by weight loss profile, percent solids, contact angle, film appearance, mechanical testing and accelerated weathering.



POLY 46: Synthetic polymers used as adhesives for glass conservation

Stephen P. Koob, koobsp@cmog.org. *Conservation, Corning Museum of Glass, Corning, New York, United States*

Glass has always been a challenge to repair, both because of the way it breaks, and the early lack of suitable adhesives. Natural resins and the early synthetic adhesives did not bond well to glass and were sensitive to heat and/or moisture, and often yellowed, sometimes within a few years.

Fortunately, newer and more stable synthetic resins have provided better options. The choice of an adhesive for glass conservation can be narrowed to very few materials, using the following the requirements or guidelines:

The material should not damage the glass during application, curing or ageing

It should bond well

It should be removable or “reversible” without risk of damage

It should be ‘water’ clear

It should be easy to use, with consistent results.

It should remain stable within the parameters of a Class A resin (100 years)

Two very different synthetic polymers can be recommended as adhesives for repairing glass, and these are Paraloid B-72, an acrylic copolymer of ethyl methacrylate and methyl acrylate, and epoxy resins. B-72 is a solvent-based adhesive and the epoxies are two-part resin/hardener liquids that are thermosetting adhesives. Both adhesives have advantages and disadvantages for use on glass. The advantages of B-72 over previous adhesives are numerous and include its stability, reversibility, moderate strength and non-yellowing. It also can easily be softened, using low heat, to adjust or correct misaligned joints.

No adhesive is easy to use when repairing glass and significant experience is required. Glass repairs that involve dozens or hundreds of fragments require careful and precise alignment, usually requiring low-power magnification under a binocular microscope.

Both B-72 and epoxies are suitable for various assembly techniques, including piece-by-piece assembly (or “additive” assembly), and injection, or infiltration by capillary action. Both adhesives can also be tinted or colored to achieve an almost invisible match with colored glass.

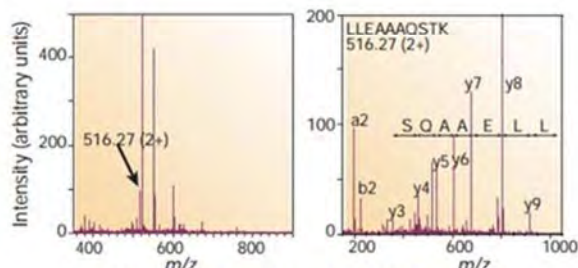
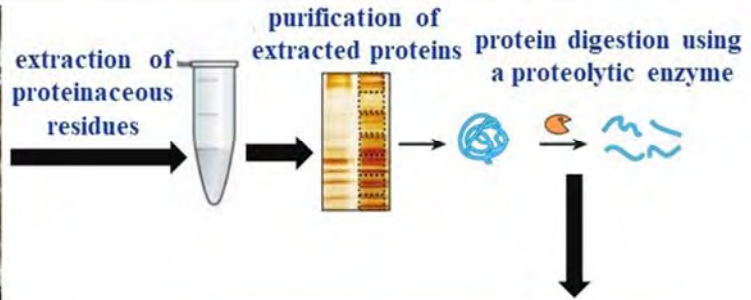


Broken glass, before assembly

POLY 47: Accurate identification of degraded residues of proteinaceous adhesives in historic mural paintings in Kizil Grottos, Sinkiang, China by HPLC-MS/MS

Zhanyun Zhu, 31560595@acs.org. Northwestern Polytechnical University, Xi'an, China

Most proteinaceous adhesives used in historic mural paintings are extremely degraded, thus in extra low content, even no visible vestige can be observed, which leads to great difficulty in sampling and scientific identification. To combat this, we propose an accurate identification methodology for ancient proteinaceous adhesives. This approach is composed of five main steps, i.e. extraction of proteinaceous residues, purification of extracted proteins, protein digestion using a proteolytic enzyme, analysis of digested peptides by nano (High Performance Liquid Chromatography) HPLC – (Electronic Spray Ionization) ESI – Tandem Mass Spectroscopy (MS/MS), and protein identification by bioinformatics using protein database. The analytical methodology was optimized with fresh binders before applying on historic residues. This approach allowed the identification of proteins in a sample from paintings in a World Heritage Site - Kizil Grotto, Sinkiang, China. The findings will contribute significantly to understanding the craftsmanship of invaluable cultural heritage and designing preventive conservation measures for them.



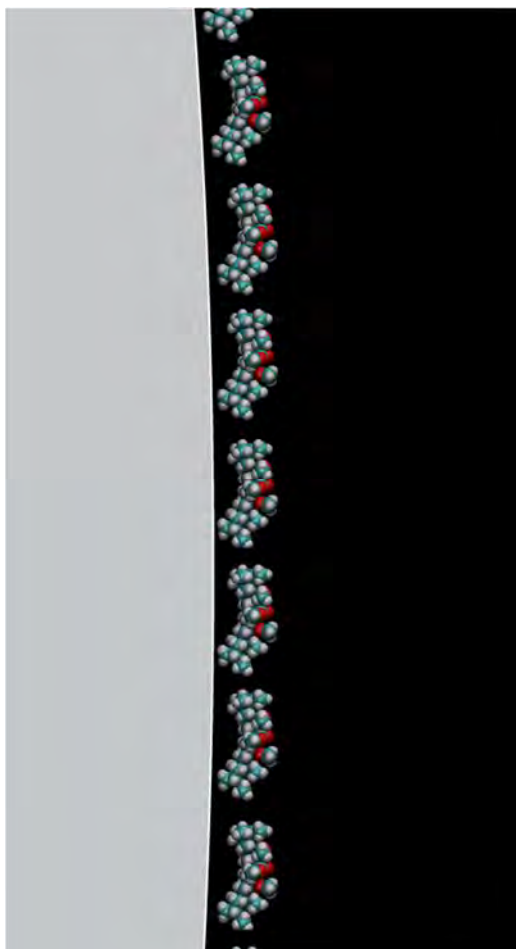
protein identification by bioinformatics using protein databases

nano (High Performance Liquid Chromatography) HPLC – (Electronic Spray Ionization) ESI – Tandem Mass Spectroscopy (MS/MS) 11

POLY 48: How pigment/binder interactions affect single-sided NMR measurements of acrylic paints

Tyler K. Meldrum, tkmeldrum@wm.edu, Mary T. Rooney. Chemistry Department, The College of William and Mary, Williamsburg, Virginia, United States

Acrylic emulsion paint is one of the most common media employed by 20th century painters. Since early acrylic paintings have begun to require the attention of conservators, scientists are working to characterize the properties of these paints to facilitate conservation efforts. In this study, we report an investigation of the physical and chemical properties of acrylic emulsion paints using single-sided NMR in conjunction with gloss measurements and scanning electron microscopy coupled with energy dispersive spectrometry. Combining the data from these techniques gives insight into pigment-binder interactions and the acrylic curing process, showing that as pigment concentration is increased in paints, the amount of binder adsorbed to pigment particles increases, resulting in films with differing relaxation times. Furthermore, pigments with a larger surface area or smaller particle size will have a greater effect on physical properties as concentration increases. This research emphasizes the efficacy of NMR relaxometry in studying cultural heritage objects, and may prompt further study into the effects of pigment concentration on the curing and conservation of acrylic paint films.

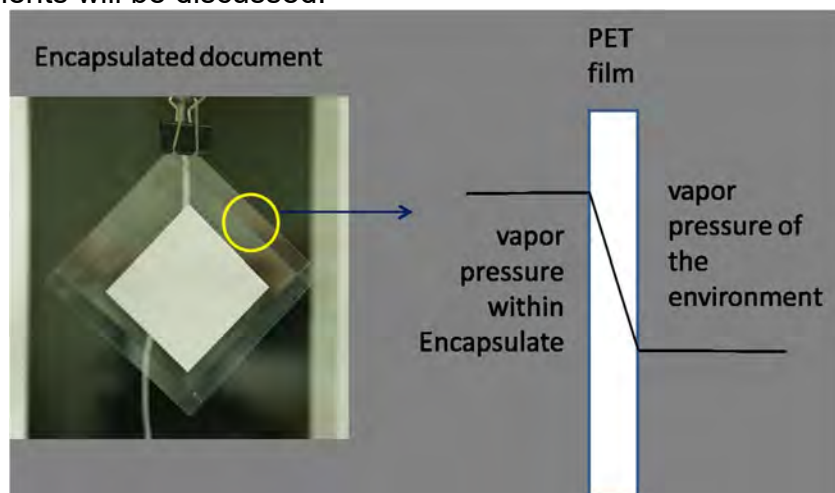


POLY 49: Permeability of PET by water, acetic acid, and formic acid: A study of the microenvironment of encapsulated documents

Patricia M. McGuiggan¹, patricia.mcguiggan@jhu.edu, **Andrea K. Half**, **Molly McGath**³.
(1) *Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States* (2) *Conservation & Preservation, The Sheridan Libraries & Museums, Johns Hopkins University, Baltimore, Maryland, United States* (3) *Conservation and Preservation, Johns Hopkins University, Baltimore, Maryland, United States*

Historic documents are frequently protected by placing them in a sealed polyethylene-terephthalate (PET) envelope. Although the paper is mechanically stabilized, the PET film retards transmission of moisture or acidic degradation by-products of the paper. This creates a microenvironment for the encapsulated document. The permeation of water, acetic acid, and formic acid vapor through the PET film was measured to understand the microenvironment within an encapsulated enclosure. The vapor mass flux through 3 mil, 4 mil, and 5 mil PET film was measured. Water vapor was found to flow into or out of the PET film depending on the sample and environmental conditions. As expected, the measured rate of vapor flux through the PET film increases with decreasing PET thickness. We find that the rate of mass loss from a 3 mil PET enclosure is approximately 38% greater than from a 4 mil enclosure. The rate of mass loss from a 5 mil enclosure is approximately 20% smaller than from a 4 mil enclosure. The PET encapsulation provides a microenvironment that will buffer the encapsulated object from large swings in humidity. This attenuated fluctuation in humidity is expected to protect the paper since humidity fluctuations may expose the paper to unwanted stresses.

The permeation of formic acid and acetic acid, two by-products of cellulose degradation, was also measured. Formic acid permeated through the PET, but at a much slower rate than water vapor. Acetic acid either did not diffuse through the PET, or it diffused at such a slow rate as to not be measured. The difference in the rate of permeation is due to the size difference between the vapor molecules. The impact of these results on historic documents will be discussed.

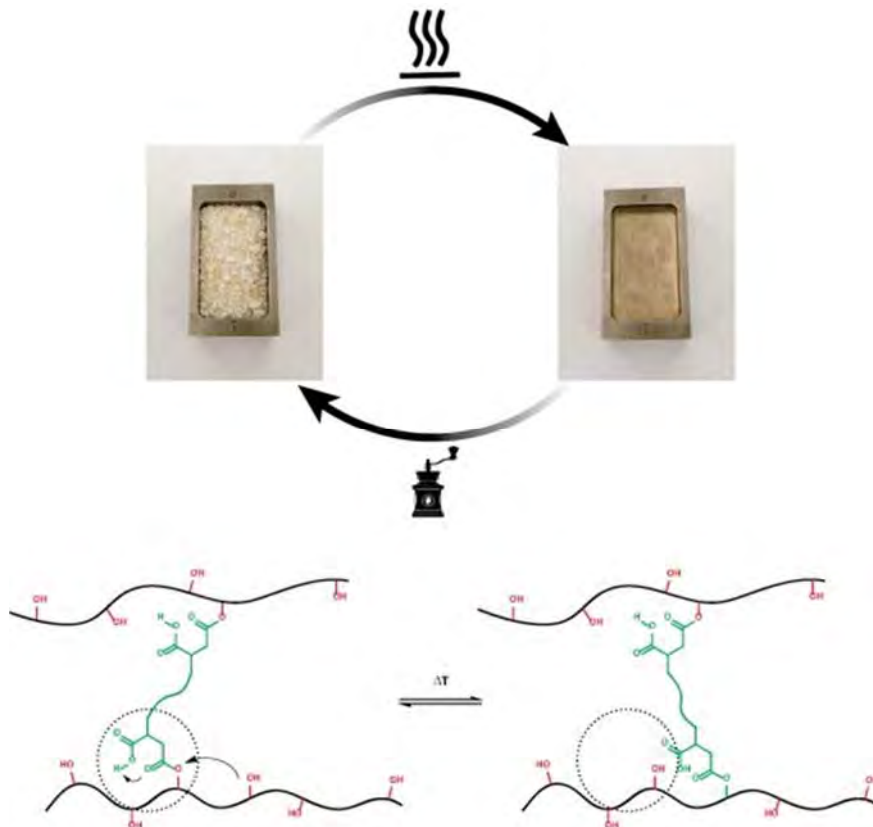


Vapor Permeation through PET

POLY 50: Internally catalysed covalent adaptable networks

Filip E. Du Prez, *filip.duprez@ugent.be*, Maarten Delahaye. Ghent Univ Poly Chem Div, Gent, Belgium

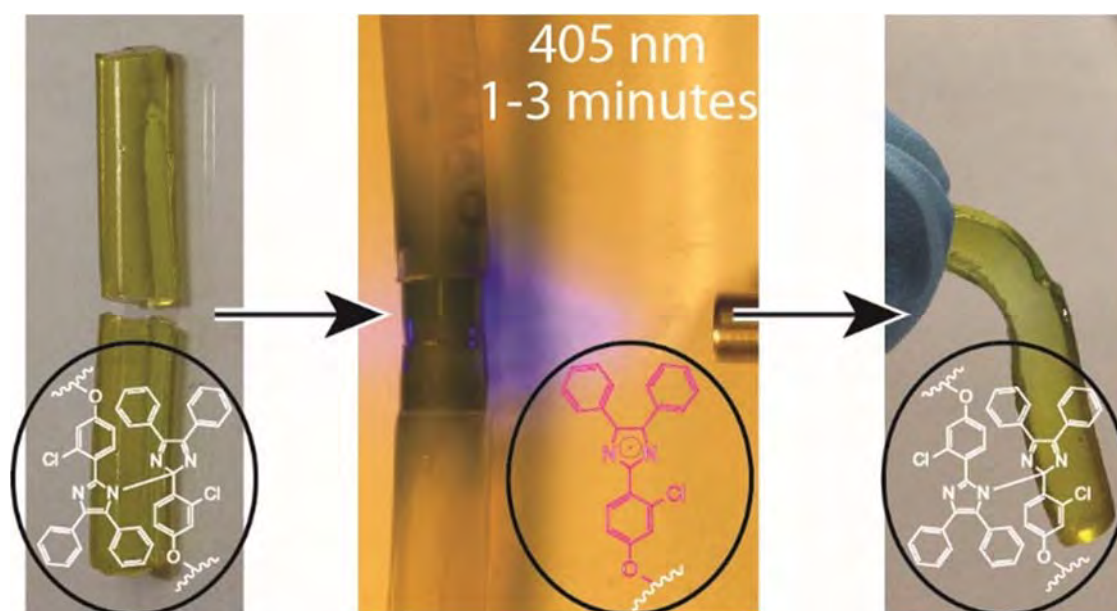
An attractive chemical strategy to achieve the combination of plastic and thermosetting properties in a synthetic material is offered by the introduction of exchangeable chemical bonds into a polymer network, leading to dynamic cross-links. Polymer networks containing such exchangeable bonds are also known as covalent adaptable networks (CANs). These established systems sometimes suffer from important drawbacks. To achieve a swift exchange reaction, rapid enough to allow macroscopic flow at useful temperatures, usually a catalyst needs to be included as a material additive, resulting in problems with catalyst ageing or leaching, and often also a change in material properties, such as a drop in glass transition temperature (T_g). A solution of this problem could be the use of internal catalysis or neighbouring group participation (NGP), where the presence of proximal groups results in a reaction rate-enhancing effect. In this presentation, the effect of neighbouring carboxylic acids in the transesterification reaction will be demonstrated. The results of a model study are transferred on a material level to obtain CANs without the use of an external catalyst. Besides, some recent results on our vitrimer research efforts will be highlighted.



POLY 51: Latent, long-lived reactive species in covalently cross-linked networks

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Although free radicals are typically extremely reactive species with negligible recombination activation energies, resulting in diffusion-controlled termination rates, several examples of relatively stable radical species exist. For example, trityl (i.e., triphenylmethyl) radicals in solution exist in equilibrium with their quinoid dimer form owing to the radical stability afforded by resonance and steric stabilization. One particularly interesting class of radical-generating compounds consists of hexaarylbiimidazoles (HABIs) which have been the focus of significant research activity owing to their photochromic, piezochromic, and thermochromic nature for more than five decades and have found industrial utility as radical polymerization initiators. First synthesized by Hayashi and Maeda in 1960, they have since been investigated for use in photographic films as leuco dye photooxidants, color proofing systems, and as radical polymerization photoinitiators. The photochromism exhibited by HABIs is attributable to their homolytic cleavage upon irradiation to yield two strongly colored lophyl (i.e., triphenylimidazolyl) radicals that are relatively stable in oxygen-saturated surroundings and show slow recombination rates; thus, analogous to the influence of temperature on the trityl radical/quinoid dimer equilibrium, light can be employed to shift the lophyl radical/HABI dimer equilibrium. Here, we will describe the incorporation of HABI-based functional groups into the backbone of cross-linked polymer networks, and examine the hypothesis that, upon irradiation, a high fraction of network strands would be transiently broken, temporarily decreasing the cross-link density and enabling rapid, photo-mediated polymer healing.



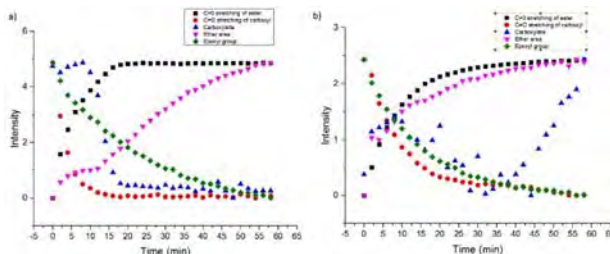
POLY 52: Tuning of the glass transition temperature of dicarboxylic acid-epoxy vitrimers by off-stoichiometric acid content

Quentin-Arthur A. Poutrel^{1,2}, quentin.a.poutrel@gmail.com, Francois Tournilhac³, Jonny J. Blaker⁴, Constantinos Soutis², Matthieu Gresil^{1,2}. (1) *i-Composites Lab, School of Materials, The University of Manchester, Manchester, United Kingdom* (2) *Aerospace Research Institute, The University of Manchester, Manchester, United Kingdom* (3) *ESPCI - ParisTech, Paris, France* (4) *Bio-active Materials Group, School of Materials, The University of Manchester, Manchester, United Kingdom*

Epoxy-based vitrimer networks were first developed by the group of Leibler in 2011, and they showed the possibility to tune the T_g of vitrimers from room temperature up to 90°C by using different hardeners. So far, the increase in T_g and mechanical properties has been achieved by changing the hardener, for example with the use of anhydrides instead of acid hardeners, or stronger acid structures. However, all of this research has focused on a 1:1 stoichiometry of the equivalent molar mass between epoxy and hardener.

The present study focuses on a sebacic acid-epoxy network with 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst, and aims to demonstrate that vitrimers properties - such as T_g and tensile Young's modulus - can be tuned by manufacturing off-stoichiometric acid-epoxy ratio vitrimers without losing their attractive qualities. Several epoxy-to-sebacic acid ratios were produced: 1:1; 1:0.75; 1:0.5; 1:0.3, and for each ratio, the content of TBD was varied to 5% to 10% of the epoxide groups. Swelling tests were performed at 135°C in trichlorobenzene to demonstrate cross-linking of the network, and creep experiments were completed to calculate the activation energy of the system. Tensile tests and differential scanning calorimetry (DSC) measurements were made to study the impact on mechanical properties and the glass transition temperature. FTIR-ATR analysis was done on different ratios to observe the polymerisation of samples; and compared to samples without hardener (epoxy-TBD only) which was compared with two other anionic initiators: 2-phenylimidazole and accelerator 960-1.

Swelling shows that varying the sebacic acid content keeps the integrity of the network. The Young's modulus is greatly increased ($\geq 10\,000$ times compared to ratio 1:1). Moreover, activation energy of samples is kept even at low ratios of sebacic acid, showing that the network can relax stress with temperature. The different anionic initiators show that TBD favours ester formation over ether formation in vitrimers. This study shows the potential to manufacture off-stoichiometric acid-epoxy vitrimers to greatly enhance the mechanical properties of vitrimers, while keeping their attractive properties of reprocessable covalent network.



POLY 53: Efficient shockwave energy dissipation in dynamic covalent PDMS rubber

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Polymer networks containing transient bonds have received increasing attention over the past decade. Depending on the specific interaction (ionic, H-bonding, dynamic covalent), a certain amount of energy is required for the bonds to undergo an exchange process. We hypothesize and demonstrate that dynamic covalent bonds in polydimethylsiloxane (PDMS) networks can be used as an effective mechanism for shockwave energy dissipation (SWED). To test this, polymer networks were synthesized from boric acid and commercially available dimethylsiloxane diols of varying length. The density of dynamic boronic ester linkages can be controlled by varying the diol molecular weight while the network chemistry is invariant. Using a classical laser induced shockwave technique, we demonstrate superior energy dissipation in a PDMS boronic ester dynamic rubber (PDMS-B-DR) compared to the benchmark polyurea. The dynamic PDMS also outperforms covalent PDMS (cured via thiol-ene click chemistry) and shows a monotonic improvement in dissipation performance with increasing density of dynamic boronic ester bonds. For all boronic ester densities, the T_g is invariant ($-125\text{ }^\circ\text{C}$) implying a minimal role of segmental dynamics on the variations in dissipation performance of these networks. Our results indicate that dynamic networks are a promising route to engineering improved SWED materials which are lightweight, flexible, and able to withstand repeated shocks. X-ray scattering and rheology have also been performed to relate dissipation performance to structure and relaxation timescales of the material.

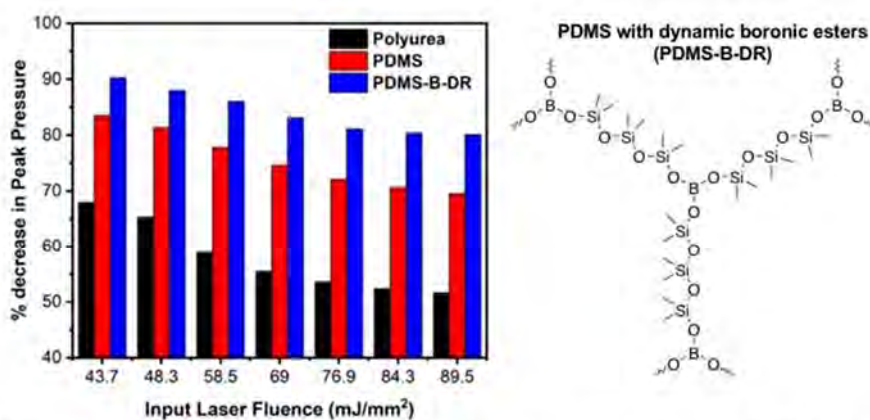


Figure 1. Reduction in peak pressure of a laser induced shockwave by polyurea, permanent PDMS, and a PDMS with dynamic covalent bonds (PDMS-B-DR). The sample with dynamic bonds is the most effective as dissipating energy for all input fluences.

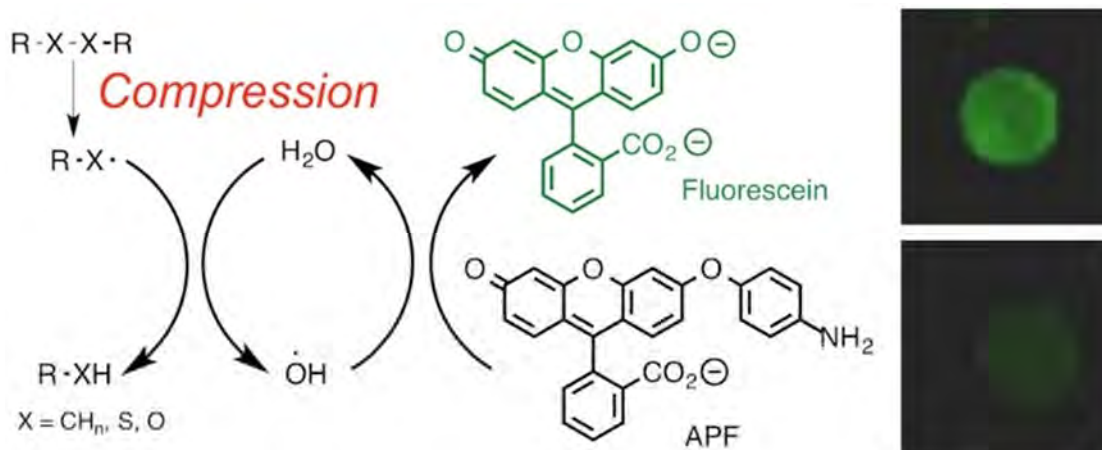
POLY 54: Identifying covalent bond breakage in materials under strain: Mechanochemistry without mechanophores

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This talk will focus on our recent efforts regarding the characterization of mechanochemical bond breakage in soft materials. Hydrogels are promising substrates and frameworks for cell growth and tissue engineering, particularly for cardiovascular repair and cartilage replacement. For these applications, it is important to maintain careful control over gel mechanical properties so that these hydrogels not only match the properties of the desired tissue for replacement but also retain their integrity for extended periods. Since the failure of hydrogels begins with the breakage of crosslinks within the structure, methods are needed to sense this initial breakage. However, most strategies that utilize mechanochemistry require large strain deformations to obtain a detectable signal.

In this talk I will discuss two methods for quantifying bond breakage. In the first, the breakage of covalent bonds in water leads to the formation of radicals, followed by reaction with water to produce reactive oxygen species, which in turn could activate fluorophores sensitive to oxidation. First, it was found that gels loaded with the masked fluorophore 3-(aminophenyl)-fluorescein became fluorescent during compression, even with as little as 5 kPa of pressure. The effect of compression on fluorescence activation was found to depend primarily on the strength of the crosslinking functional group in hyperbranched PEG hydrogels.

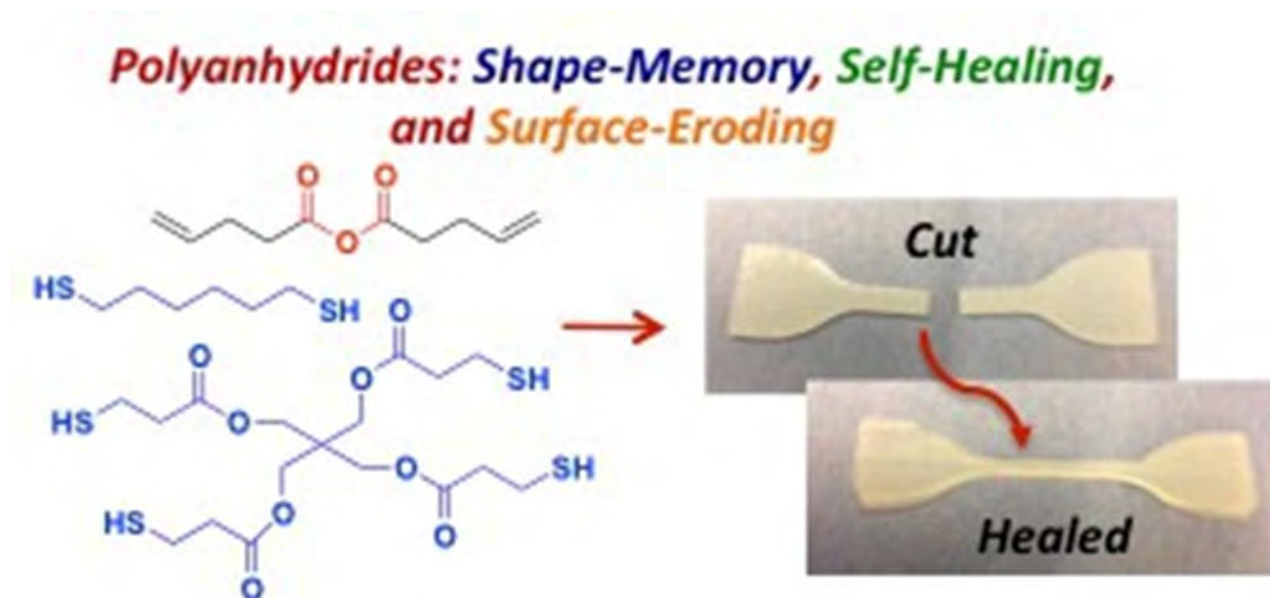
Next, we found that because hydrogen peroxide was the dominant species produced by this process, the enzyme horseradish peroxidase could catalyze mechanochemical reactions resulting from strain on the hydrogels. As a result, new colorimetric and fluorimetric studies were developed that could quantify hydrogen peroxide production, and thus chemical bond breakage, with micromolar sensitivity. Finally, I will also discuss more recent work relying on bond breakages for localized labeling of areas of strain as a tool for identifying incipient fracture in soft materials.



POLY 55: Dynamic covalent exchange in polyanhydrides

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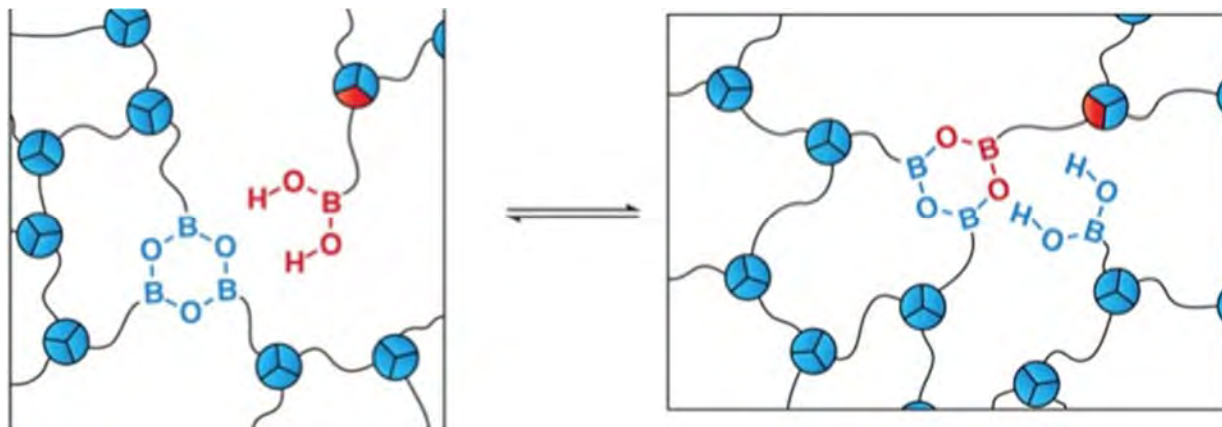
We have recently demonstrated the shape-memory and self-healing characteristics of poly(thioether-anhydrides) when heated above and then cooled below the crystalline melt temperature (T_m) of the polymer. In particular, polyanhydride-poly(ϵ -caprolactone) composites are capable of exhibiting shape memory properties, although dynamic covalent exchange between anhydride moieties occurs at temperatures above ~50-60°C. This allows for permanent shape reconfiguration of the crosslinked polymer. More recently, we have aimed to create an all-anhydride reconfigurable shape-memory polymer made using thiol-ene monomer combinations that produce a semi-crystalline polyanhydride with a T_m of approximately 30-40°C in order to form a polymer that will successfully exhibit shape memory behavior. Self-healing is also evident at elevated temperatures because of anhydride dynamic covalent exchange. Additionally, polyanhydrides undergo surface erosion, allowing the mechanical strength of the material to remain intact. This leads to the possibility of using polyanhydrides that have shape memory properties and a predictable erosion profile that can be tuned to allow use of the material as drug delivery vehicles.



POLY 56: Strong, malleable, and recyclable thermosets via robust dynamic covalent

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In this talk I will share our recent progress in developing strong, malleable, and recyclable thermoset polymers using various dynamic covalent bonds. While permanently cross-linked polymers (i.e., thermosets) have excellent mechanical properties, creep resistance, and chemical/solvent resistance, they cannot be reshaped, reprocessed, or recycled by heat or with solvent. In contrast, thermoplastic polymers can be reshaped and reprocessed, but they normally have lower mechanical strength, lower structural stability at elevated temperature, and poorer chemical/solvent resistances. To combine the excellent attributes of both thermoplastics (reprocessability, recyclability) and thermosets (mechanical strength, creep and solvent resistances), a new strategy has succeeded by introducing dynamic covalent bonds into thermosets. Our laboratory is particularly interested in developing robust dynamic covalent interactions that can lead to thermosets that are mechanically strong, highly malleable, and fully reprocessable and recyclable. Specifically, we have successfully developed robust malleable thermoset polymers via carbon-carbon double bond exchange, boron-oxygen bond exchange, and silicon-oxygen exchange reaction. Successful demonstration of robust, malleable, and reprocessable/recyclable thermosets will have major impact on new materials development, polymer recycling and sustainability, and modern technologies including additive manufacturing.

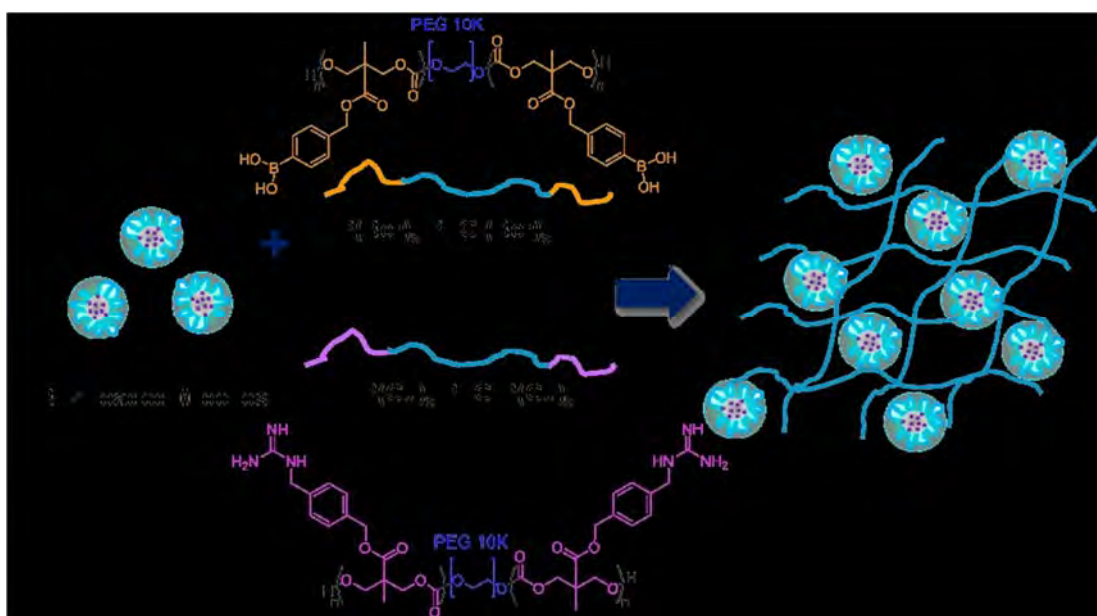


Strong, malleable, and fully recyclable thermosets via B-O crosslinks

POLY 57: 'ABA' hydrogels designed as active therapeutics agents and as therapeutic delivery scaffolds

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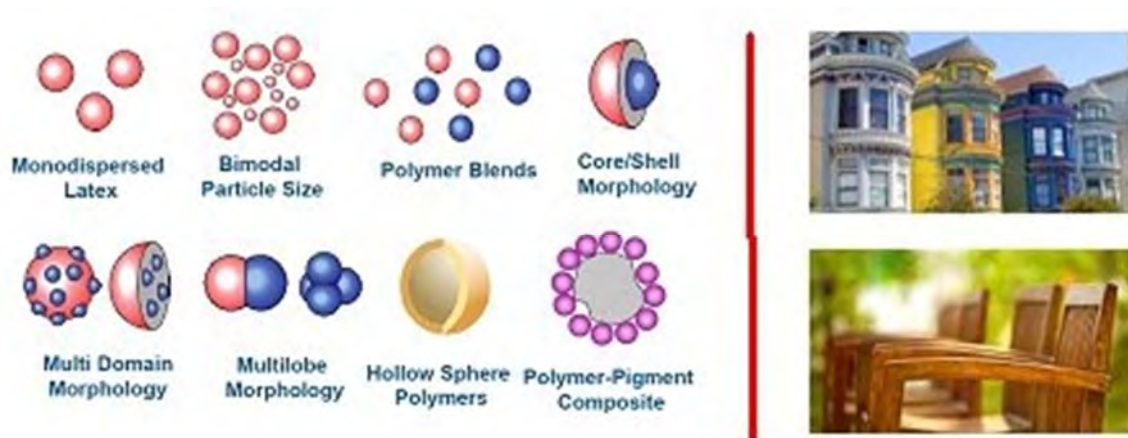
Hydrogels produced from the self-assembly of synthetic polymers have tremendous potential to serve as either a scaffold for delivery of pharmaceuticals or as an active therapeutic. Recent developments in polymer chemistry including organic catalysis and functional monomer platforms have enabled polymers to be synthesized with well-controlled architecture and defined functionalities. Particularly, this functionalization strategy allows for gelation of the 'ABA' copolymers and containment of drug payload through one or a combination of the following association mechanisms such as dynamic covalent bond, hydrophobic interaction, ionic interactions, hydrogen bonding, physical entanglement of macromolecules and chemical cross-linking of the matrix. A series of amphiphilic 'ABA' triblock copolymers, consisting of a hydrophilic PEG middle block flanked on both ends by either boronic acid-functionalized polycarbonate blocks or guanidinium- or thiuronium-functionalized polycarbonate blocks, were synthesized. The boronic acid-containing polymers are capable of forming hydrogels depending on the hydrophobic/hydrophilic balance and concentration of the polymers, where gelation is solely based on dynamic covalent bond. Viscoelastic behavior of the gels can be tuned by blending with guanidinium- or thiuronium-containing polymers to form injectable coacervate gels. Through careful selection of suitable constituent blocks, the loading and effective delivery of diverse variety of drug payloads or drug-loaded nanoparticles has been achieved both *in vitro* and *in vivo*. In addition to serving as a depot for therapeutic delivery, we have shown that the gel can also serve as the therapeutic. Antimicrobial hydrogels have been shown to have broad-spectrum antimicrobial activity as well as the ability to eradicate biofilms.



POLY 58: Overview of emulsion polymerization technology for the preparation of industrially-relevant polymers for health, the home and smart living

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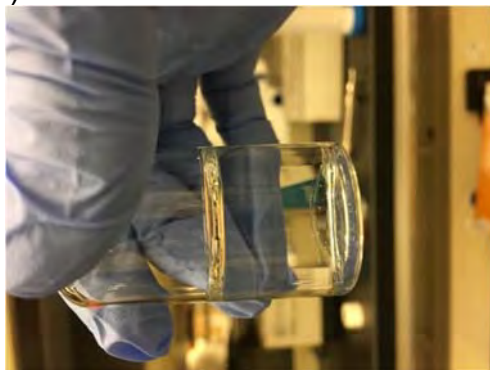
Emulsion polymerization is an important process for manufacturing a wide variety of polymers for use in multiple applications, including coatings, home and personal care, electronics, construction, adhesives and applications in biomedicine. In its most basic form, emulsion polymerization requires four ingredients: water, monomer, surfactant, and initiator. Preparing latex polymers and by extension coatings with the desired balance of properties for the specific application is challenging, however, this waterborne technology facilitates the preparation of a wide range of polymers with non-linear morphology (hard and soft composites, hollow spheres, etc.) thereby providing distinct coatings performance platforms. Now discussed are the syntheses and formulation of acrylic polymers and their use in multiple applications.



POLY 59: Chemical and physical changes in a variety of contact lenses during the wastewater treatment processes

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Contact lens use has increased steadily over the last decade. The usage of soft contact lenses specifically has grown in popularity driven by research on the physiological demand of the cornea and comfort of use. These attributes include higher oxygen permeability, typically attained by use of plastic hydrogel soft lenses which are replaced and disposed of either daily, bi-weekly, monthly, or yearly. Much is unknown about the practices of contact lens disposal by consumers and their fate as contaminants in domestic wastewater. If flushed down the sink or toilet, these lenses will travel to local wastewater treatment plants (WWTPs) where treatment processes may lead to material degradation and fragmentation of macroplastics into microplastics. Over 45 million people use contact lenses in the US, and the number of users of so called 'daily disposable lenses' is constantly increasing. To better understand disposal and fate of lenses in WWTPs, we created a three-part study consisting of (1) an anonymous survey of 139 individuals, wearers and non-wearers, to assess disposal techniques. We learned that 19% of the wearers flush their contacts down the sink or toilet. To understand their journey through WWTPs and degradative forces which they may encounter, we (2) conducted density experiments on 11 types of contact lenses and on WWTP solids/wastewater to identify where the contacts will be retained or separated within the treatment process. Lastly, we (3) subjected a variety of contact lenses of different plastic types to unit operations constituting conventional wastewater treatment and observed degradative effects on the contact lenses. Study findings suggest that disposable contact lenses are emerging contaminants of concern that cause environmental pollution, present a potential physical threat to susceptible aquatic biota, may contribute to microplastic pollution, and have the potential to adsorb, accumulate, and transport harmful persistent organic pollutants into aquatic and terrestrial environments via, respectively, sanitary sewer overflows and the application of treated municipal sludge (biosolids) on land.



13 brands of contact lenses were subjected to a density determination experiment with five solutions ranging from 1.0 g/mL to 1.4 g/mL with all contacts sinking implying that they similarly sink within a wastewater treatment plant.

POLY 60: Using polymers to teach concepts in chemistry: A teacher workshop

Sherri C. Rukes, *scrukes@comcast.net*. Libertyville High School, Libertyville, Illinois, United States

Polymers are encountered in everyday life and are used for many purposes. Polymers are chains made of monomer subunits, which is a repeating chemical unit. The structure and chemical composition of the polymer chain determines the physical properties of the material. Polymers are used to make electronic components, paint, plastic bottles, sunglass lenses, DVDs and so much more. Polymeric materials are usually derived from petroleum or oil, but significant research is underway to develop novel methods of producing these materials using renewable energy sources. Materials engineers rely on some polymers for their rigid strength, others for their flexibility, and still others for their resistance to corrosion. For instance, poly(vinyl chloride) is a strong, corrosion-resistant polymer commonly used in plumbing applications, whereas polyethylene is an example of a flexible polymer found in plastic bags.

This presentation / workshop will give teachers many ideas of how to incorporate polymers into their curriculum. The workshop will focus on using the home as the main topic for these activities. The workshop will show how one can apply simple ideas and concepts of polymers into a traditional K - 12 classroom. For example, teachers will see how different forms of energy could be used as topics, coatings to talk about intermolecular forces, and how to create bioplastics as an engineering design project. Teachers will learn, apply and see simple activities that will help students understand the importance of polymers and how they relate to the core topics of chemistry.



POLY 61: Connecting polymers to the health care industry: Multiple hands on activities

Sherri C. Rukes, *scrukes@comcast.net. Libertyville High School, Libertyville, Illinois, United States*

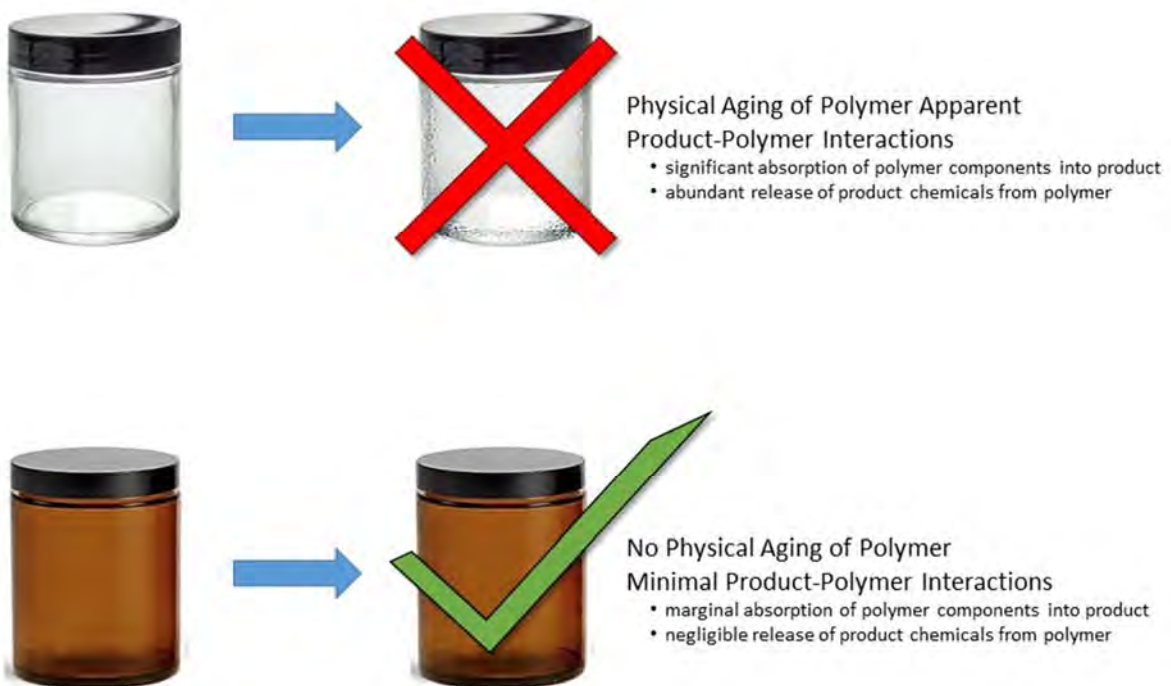
Many polymers are used in the healthcare industry and these applications can be applied to a K - 12 classroom. Using practical applications connecting chemistry to what the community sees is one way to get students hooked and understand the importance to the concepts. This presentation / workshop will give teachers many ideas of how to incorporate polymers into their curriculum using everyday common items. The workshop will focus on using the healthcare industry as the main topic for these activities. For example, teachers will learn how to use hot and cold packs, adhesives and sutures as tools to teach first year chemistry topics. Topics will include are intermolecular forces, properties and types of bonds. The workshop will show how one can apply simple ideas and concepts of polymers into a traditional K - 12 classroom. Teachers will learn, apply and see simple activities that will help students understand the importance of polymers and how they relate to the core topics of chemistry.



POLY 62: Case study of polymer compatibility with ingredients in cosmetic products

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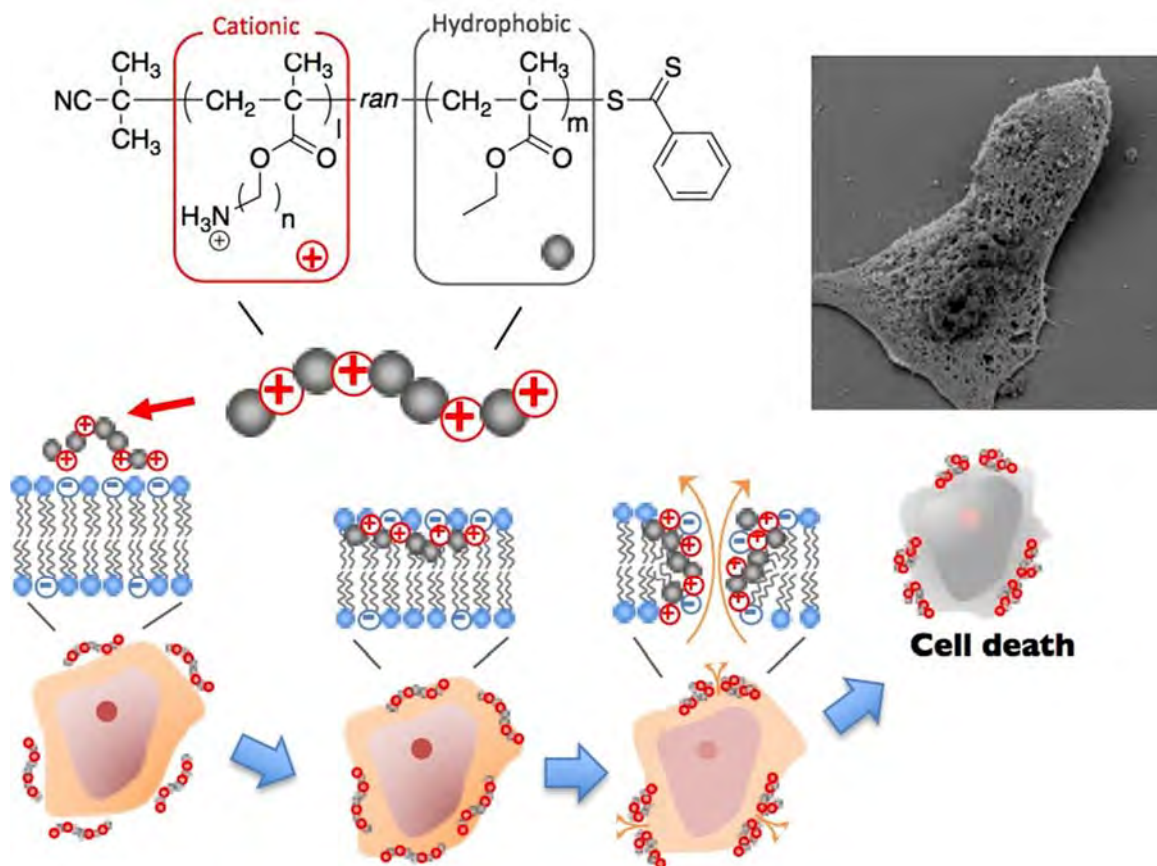
Many manufacturers across various industries have sought to use plastic packaging to replace glass in order to save on costs. However, a majority of cosmetic products utilize organic solvents and oils in their ingredients, which interact with polymers. In doing so, they impact the mechanical strength and transparency of the packaging. Copolyesters provide the necessary transparency and mechanical properties for many cosmetic packaging applications, but their chemical resistance to products varies across a wide range, depending on the polymer composition and the ingredients of the product. Three cosmetic products of different compositions with the same end use were selected to evaluate the effects of major ingredients on different polymers. Three copolyesters were selected based on their desirable properties to pair with the products, making for nine combinations altogether. Each polymer was exposed to its paired product and put under accelerated aging conditions. Then the mechanical properties, morphological properties, and chemical composition were evaluated using tensile testing, differential scanning calorimetry, and gas chromatography-mass spectrometry, respectively. In each scenario, ingredients of significance were identified and their effect on each polymer's properties are presented.



POLY 63: Amphiphilic methacrylate copolymers with anticancer activity

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In this study, we developed new synthetic polymer-based anticancer agents that mimic the mode of action of anticancer peptides. The anticancer polymers designed here are low molecular weight methacrylate copolymers with random-sequences of cationic and hydrophobic side chains, serving as a model platform to test our approach, which capture the cationic, amphiphilic properties of anticancer peptides. These polymers target anionic lipids exposed on the cancer cell surfaces and disrupt the cancer cell membranes. The polymers exhibited cytotoxicity to proliferating prostate cancer cells and selectivity over normal cells. Many synthetic polymers used in anticancer therapeutics are drug delivery carriers in the forms of drug conjugates or drug-encapsulated particles where the anticancer activity originates primarily from the drugs, not the polymers. However, the proposed anticancer polymers are designed to directly act by targeting cancer cell membranes.

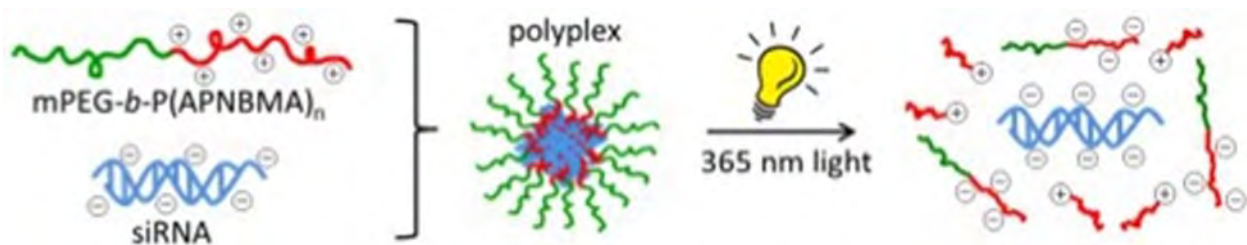


The design and mode of action of anticancer peptide-mimetic polymers.

POLY 64: Photo-responsive polymeric nanoplexes for gene therapeutics delivery and wound healing applications

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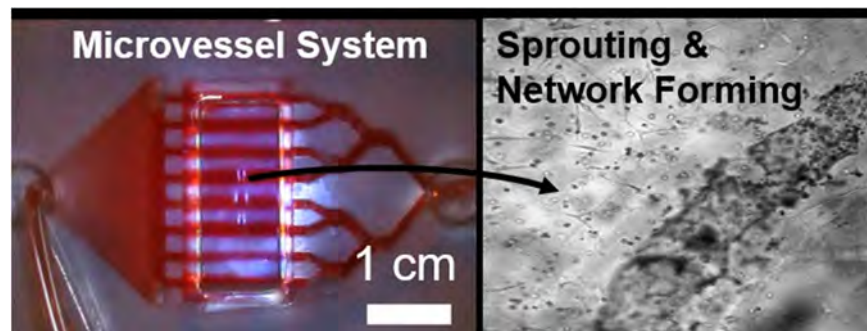
Vascular bypass grafting is a routine treatment for cardiovascular diseases; however, nearly 50% of bypass grafts fail within a few years following surgery due to cellular inflammatory responses at the suture sites. To overcome this problem, we synthesized novel diblock polymers to deliver nucleic acid therapeutics capable of promoting healing in a spatiotemporal manner. A key component of our design is a monomer containing photocleavable *o*-nitrobenzyl moieties linking cationic groups to the polymer backbone so that light irradiation can induce polymer hydrolysis and charge reversal. The polymers self-assemble with anionic nucleic acids in solution to form nanoparticle complexes with a PEG “stealth” coating. Application of a photo-stimulus disrupts the electrostatic interactions to trigger the release of bound nucleic acids, such as siRNA, from the nanocomplexes. More significantly, our soft nanoparticles maintained stability in serum, exhibited robust cellular uptake, facilitated nanocarrier imaging, and were capable of photo-responsive on/off control over gene expression. These formulations enabled the knockdown of two key functional genes, IL1 β and CDH11, that are implicated in inflammatory responses in human aortic adventitial fibroblasts. The complete knockdown of both genes, in combination, resulted in significant attenuation of TGF- β 1-triggered fibroblast proliferation and differentiation into myofibroblasts, two of the primary hallmarks of fibrosis. Further attenuation over clinically relevant time scales was achieved by modulating the polyplex dosing regimen by taking input from a recently developed kinetic model, whose created was enabled by our polymer design.



POLY 65: Polymer-protein composites from microfluidics to manufacturing human blood vessels

Michael A. Daniele^{1,2}, michaelangelo.daniele@gmail.com, Ashlyn T. Young², Kristina Rivera², Patrick Erb². (1) Electrical & Computer Engineering, NC State University, Raleigh, North Carolina, United States (2) Biomedical Engineering, UNC/NC State, Raleigh, North Carolina, United States

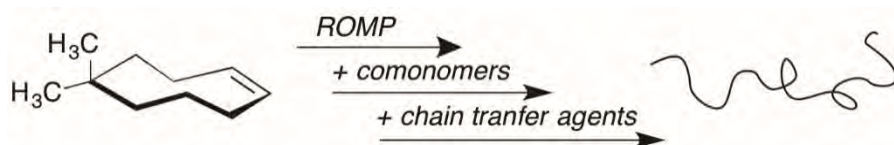
We are rapidly approaching the time when synthetic substitutes of human organs will be viable for transplant. Significant breakthroughs in stem cell biology, tissue engineering and microfabrication have laid the foundation for microsystems to build such viable human tissues. Despite recent scientific breakthrough, however, current tissue engineering lacks the capability to generate large (>1 in³) tissues that can sustain viability. Without an integrated blood vessel network, in fact, large tissue samples lose viability and die from the inside out. Here we present our work on engineered tissue scaffolds and microsystems to optimize the growth of continuous blood vessel networks, and thus large tissue models, grafts, and transplants. Enabling the generation of patent, high-volume blood vessel networks will provide a route to engineer “human-sized” tissues and organs.



POLY 66: Oxidatively robust polymers for implantable biomedical devices

Marc A. Hillmyer, *hillmyer@umn.edu*. University of Minnesota, Minneapolis, Minnesota, United States

Polyurethanes and polyolefins are examples of useful polymers for various implantable biomedical devices. To ensure long term performance and help prevent explantation, these materials should be very stable when implanted in the body as, for example, insulation of leads associated with implantable cardioverter-defibrillators. The two main chemical processes that compromise the integrity of implantable polyurethanes are hydrolysis and oxidative degradation. Both of these reactions ultimately lead to molar mass loss and concomitant degradation of material properties. Cracking, erosion, and ultimate device failure can result. In this talk I will present our work on new hydrolytically and oxidatively stable polymers using ring-opening metathesis polymerization strategies. The talk will focus on the design of a new monomer, its polymerization in the presence of a chain transfer agent and/or other comonomers, and characterization of the resultant polymers. The stability of these materials and related ring-opening metathesis routes to other interesting polymers from substituted cyclooctenes will also be covered.



POLY 67: Integrin-targeting materials in regenerative medicine

Elizabeth Cosgriff-Hernandez¹, cosgriff.hernandez@tamu.edu, Allison Post², Prachi Dhavalikar², Thomas Wilems¹, Ziyang Lan¹. (1) Biomedical Engineering, The University of Texas at Austin, Austin, Texas, United States (2) Biomedical Engineering, Texas A&M University, College Station, Texas, United States

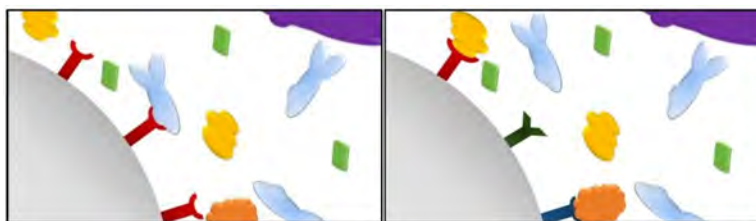
The ability to direct cell behavior has been central to the success of numerous therapeutics to regenerate tissue or facilitate device integration. Collagen often serves as a design basis for bioactive materials due to its putative role in regulating cell adhesion and phenotype, which occurs in part through $\alpha1\beta1$ and $\alpha2\beta1$ integrin adhesion signals it presents to cells. These integrins are involved in an array of cell activities including angiogenesis, cell migration, adhesion, and proliferation. However, all collagen-containing products on the market today utilize materials from slaughterhouses with the associated disadvantages including no means to optimize the molecular composition of the collagen to guide regeneration. We propose to circumvent these limitations by generating novel bioactive materials using a collagen-mimetic protein engineered to have enhanced therapeutic action and improved scale-up potential. Initial sequence design was based on the collagen-like protein, Scl2 in *Streptococcus pyogenes*. Whereas native collagen has numerous binding sites for integrins present on a wide range of cells, the Scl2 protein acts as a biological blank slate that only displays the selected receptor-binding sequences programmed in by site-directed mutagenesis. We used site directed mutagenesis to introduce human integrin binding sites into this protein and have provided evidence that human integrin binding sites function within the engineered protein bind and activate $\alpha1\beta1/\alpha2\beta1$. To generate robust materials based on this technology, the collagen-mimetic protein was conjugated into a poly(ethylene glycol) (PEG) based hydrogel to generate bioactive hydrogels. This platform technology is currently being explored in several tissue engineering applications including chronic wound dressings, bone grafts, and vascular grafts. It also provides a unique opportunity to investigate the contribution of collagen binding integrins in a variety of regenerative processes and disease pathogenesis.



POLY 68: Peptide-toyopearl adsorbents for removing CHO host cell proteins from cell culture supernatants

Ashton Lavoie, Alice Di Fazio, Kevin Blackburn, Ruben G. Carbonell, **Stefano Menegatti**, stefano.menegatti@gmail.com. North Carolina State University, Raleigh, North Carolina, United States

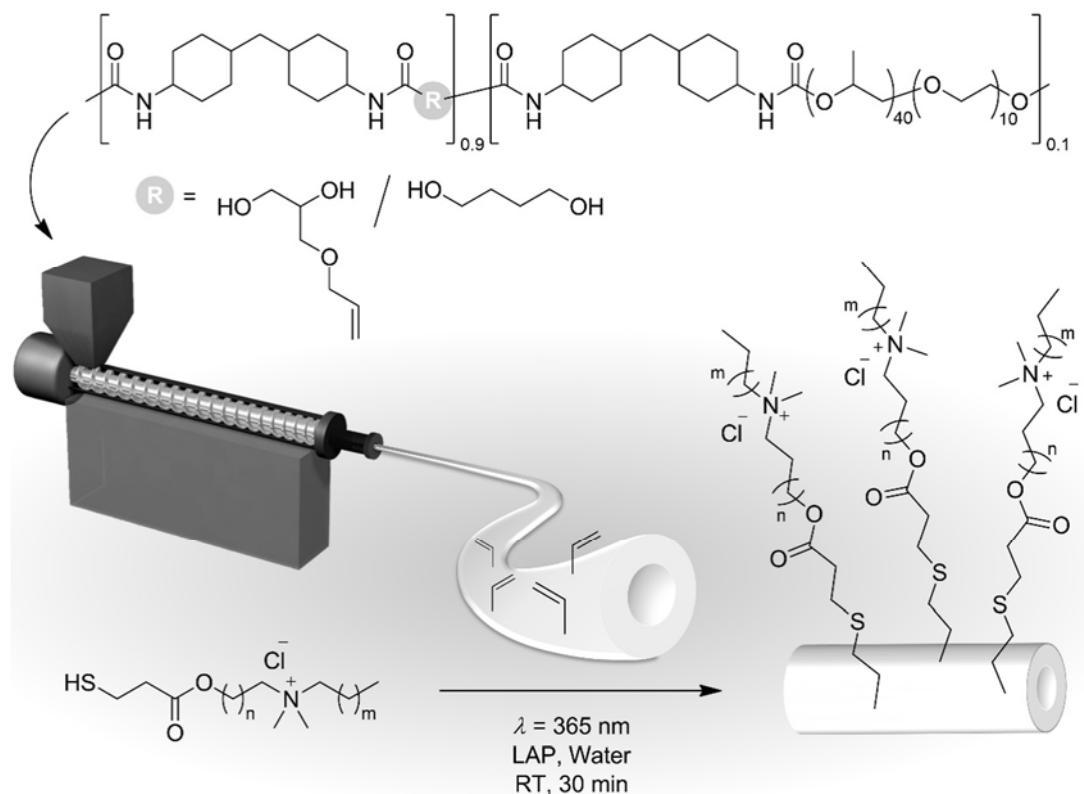
The removal of host cell protein (HCP) impurities represents a major challenge to purification processes in biomanufacturing given their diverse composition, structure, abundance, and potential similarity to the target product. Currently, HCP clearance relies on chromatographic adsorbents designed for either direct product binding or capture of HCPs in flow-through mode with broad specificity (e.g., ion exchange or mixed-mode). While this approach has proven effective at attaining high purity biotherapeutics, product-bound HCPs and HCPs that affect product stability continue to pose significant challenges. We propose a new approach for removing HCPs from cell culture supernatants in flow-through mode using new-generation multimodal adsorbents developed by our group on Tosoh resins. Our proteomic study of the HCPs present in the cell culture fluid and chromatographic fractions indicated that, while many were found to bind to commercial resins, a group of 24 HCPs are not captured effectively by any. With the growing interest in flow-through approaches to HCP removal, we resolved to improve upon commercial media by developing new small synthetic peptides that specifically capture CHO HCPs. First, **(1)** HCP-binding candidates were identified by screening solid-phase peptide libraries to select leads that bind HCP, yet not IgG. HCP-binding candidates showed enrichment towards hydrophobic-positive and zwitterionic sequences. We **(2)** initially evaluated these peptides synthesized on Toyopearl resin by measuring their static binding of HCPs from a CHO culture harvest containing IgG. We observed equivalent or higher binding of HCPs, with minimal IgG binding, on our peptide-Toyopearl adsorbents as compared to commercial resins. We finally **(3)** selected ligands to be conjugated to chromatographic resins at optimal density, and be evaluated by dynamic HCP removal. The results of this work can transform HCP removal in flow-through mode for downstream processing by addressing “problematic” HCPs and making downstream more robust in clearing HCPs from different cell line sources.



POLY 69: Post-fabrication QAC-functionalized thermoplastic polyurethane for contact-killing catheter applications

Matthew Becker, becker@uakron.edu. University of Akron, Akron, Ohio, United States

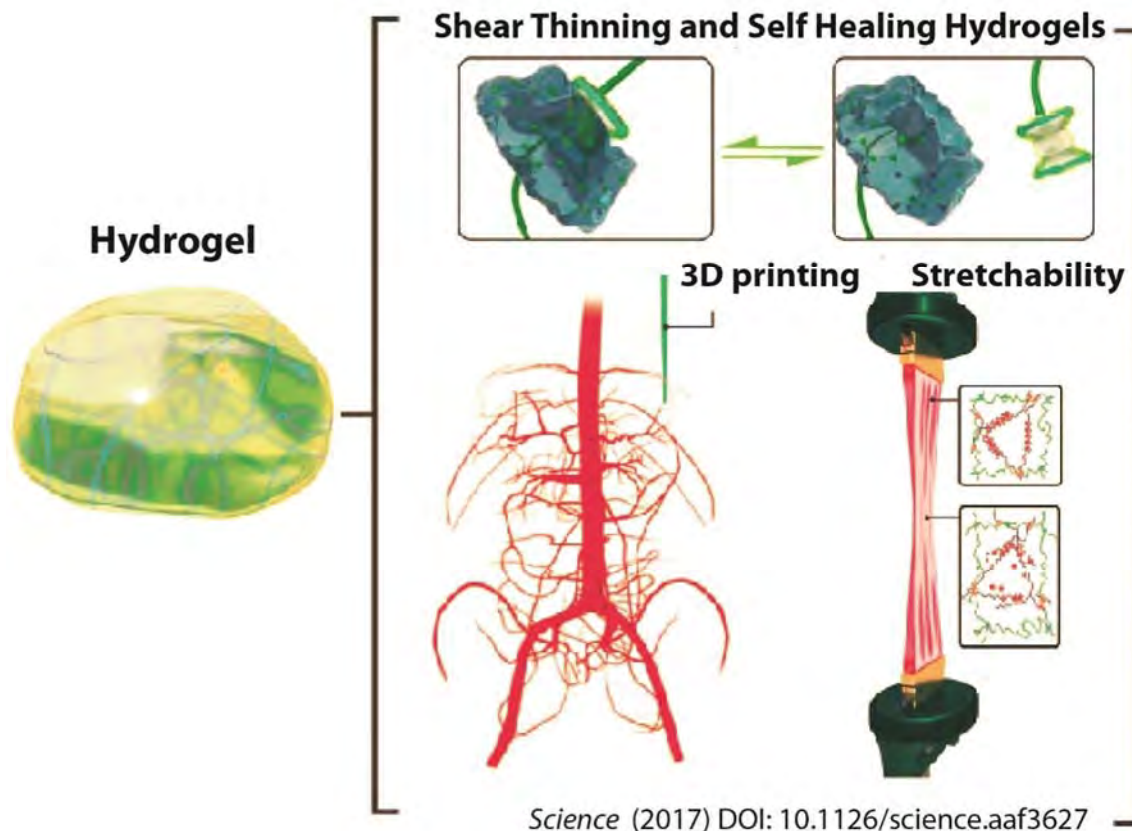
The use of catheters is ubiquitous in medicine and the incidence of infection remains unacceptably high despite numerous advances in functional surfaces and drug elution. Herein we report the use of a thermoplastic polyurethane containing an allyl ether side-chain functionality (allyl-TPU) that allows for rapid and convenient surface modification with antimicrobial reagents, post-processing. This post-processing functionalization affords the ability to target appropriate TPU properties and maintain the functional groups on the surface of the device where they do not affect bulk properties. A series of quaternary ammonium thiol compounds (Qx-SH) possessing various hydrocarbon tail lengths (8 – 14 carbons) were synthesized and attached to the surface using thiol-ene “click” chemistry. A quantitative assessment of the amount of Qx-SH available on the surface was determined using fluorescence spectroscopy and X-ray photoelectron spectroscopy (XPS). Contact-killing assays note the Q8-SH composition has the highest antimicrobial activity, and a live/dead fluorescence assay reveals rapid contact-killing of *Staphylococcus aureus* (> 75% in 5 min) and *Escherichia coli* (90% in 10 min) inocula. Scale-up and extrusion of allyl-TPU provides catheter prototypes for biofilm formation testing with *Pseudomonas aeruginosa*, and surface-functionalized catheters modified with Q8-SH demonstrate their ability to reduce biofilm formation.



POLY 70: Nano- and microfabricated hydrogels for regenerative engineering

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Engineered materials that integrate advances in polymer chemistry, nanotechnology, and biological sciences have the potential to create powerful medical therapies. Our group aims to engineer tissue regenerative therapies using water-containing polymer networks, called hydrogels, that can regulate cell behavior. Specifically, we have developed photocrosslinkable hybrid hydrogels that combine natural biomolecules with nanoparticles to regulate the chemical, biological, mechanical and electrical properties of gels. These functional scaffolds induce the differentiation of stem cells to desired cell types and direct the formation of vascularized heart or bone tissues. Since tissue function is highly dependent on architecture, we have also used microfabrication methods, such as microfluidics, photolithography, bioprinting, and molding, to regulate the architecture of these materials. We have employed these strategies to generate miniaturized tissues. To create tissue complexity, we have also developed directed assembly techniques to compile small tissue modules into larger constructs. It is anticipated that such approaches will lead to the development of next-generation regenerative therapeutics and biomedical devices.



POLY 71: Poly(vinylidene fluoride) based multiferroic composites

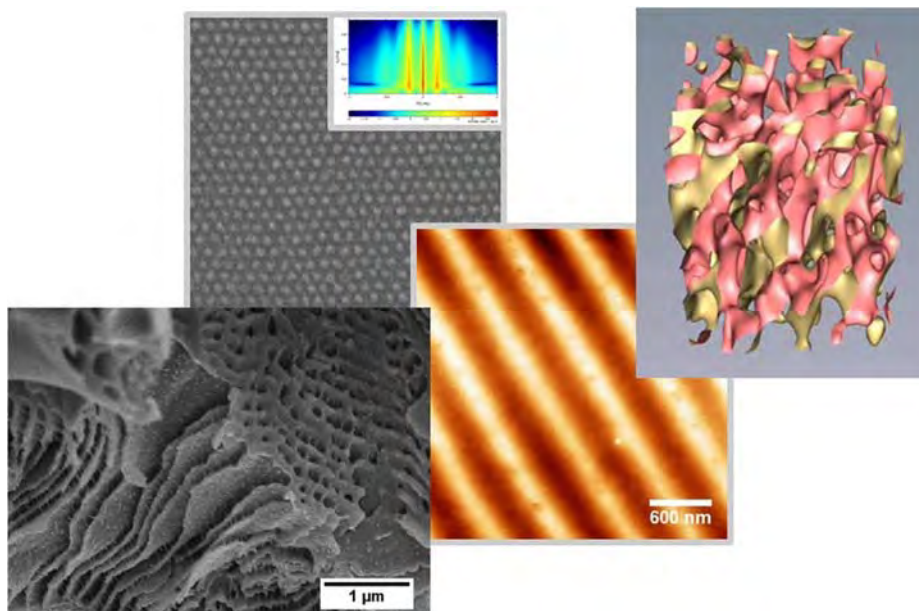
Katja Loos, *k.u.loos@rug.nl*. Univ of Groningen Poly Chem, Groningen, Netherlands

Advanced memory devices with high data storage capacity are highly demanded in many technology fields. Magnetolectric materials have attracted much attention for this type of application as the coexistence of ferroelectricity and ferromagnetism in these materials is able to provide four physical polarization states, i.e., two electric polarization and two magnetic polarization states, offering an opportunity to achieve four-state memory devices.

Magnetolectric materials exhibit a unique coupling effect (ME effect) between the magnetic and the electric properties, *i.e.* a magnetic response induced by an applied electric field and an electric polarization variation caused by an external magnetic field. Besides FSM devices this effect opens a door to new generations of devices exhibiting multifunction, such as microwave devices, sensors, transducers, magnetic-field sensors that could replace low-temperature superconducting quantum interference devices etc. Unfortunately single-phase magnetolectric compounds are rare, and their magnetolectric responses are either relatively weak or occur at temperatures too low for practical applications. A solution seems to be composites that incorporate both ferroelectric and ferromagnetic phases. Several of such composites were already reported that yielded giant magnetolectric coupling responses above room temperature.

In these composites the elastic coupling interaction between the magnetostrictive phase and piezoelectric/ferromagnetic phase leads to giant magnetolectric responses. In these composites precise control of the individual components and morphologies with nanometer-size dimension is critical to optimizing their performance.

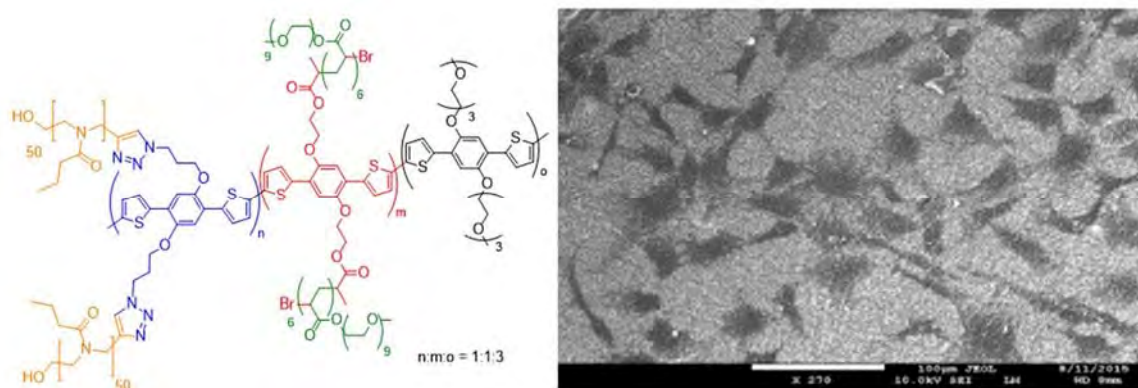
Here we present approaches towards such well-defined composites from (block co)polymer precursors using semicrystalline polymers such as poly(vinylidene fluoride) (PVDF), that have strong piezo-, pyro- and ferroelectric properties.



POLY 73: Highly functionalizable polypyrrole phenylenes and polythiophene phenylenes: Synthesis and application in a range of biological applications

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School of Chemical Sciences, University of Auckland, Auckland, New Zealand

Functionalisation of conducting polymers is an important area of research in the interest of increasing the processability of the material and bestowing additional properties. We have shown that polypyrrole phenylenes (PPyPs) polythiophene phenylenes (PThPs) allow a wide range of functionalities to be easily incorporated in its structure. This includes side chains that can undergo pre- or post-polymerisation modification using Atom transfer radical polymerisation (ATRP) grafting and through azide-alkyne Huisgen cycloaddition 'click' chemistry. ATRP can be used to graft copolymers to the conducting PThP backbone, modifying the physical properties while still retaining the original electroactivity of the backbone. 'Click' chemistry enables the attachment of a wide range of compounds such as peptides and other biomolecules allowing the systems to be biocompatible and/or act as biosensors. We report on the synthesis and properties of highly functionalised PThPs; for example the copolymer shown below, which has been modified to be water soluble and displays thermoresponsive properties. Alternatively an RGD-peptide ligated derivate has been used as a growth scaffold for human skin cells (HDFa) (see figure).

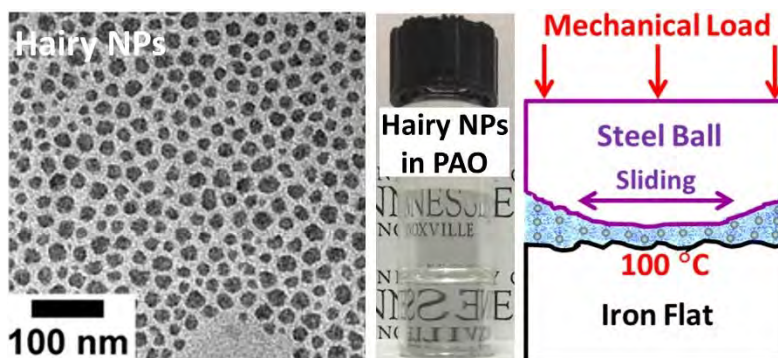


Functionalized polythiophene phenylenes and HDFa cells growing on a PPyP fibre mat

POLY 74: Hairy nanoparticles for lubrication

Bin Zhao, zhao@ion.chem.utk.edu. Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

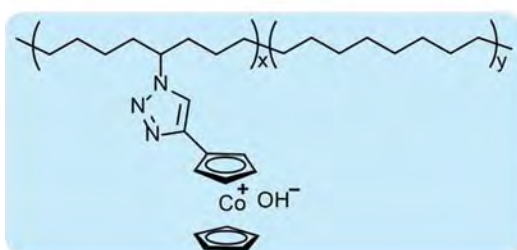
Nanoparticles (NPs) are potentially effective oil lubricant additives for reducing friction and wear. A variety of NPs, including metals, metal oxides, and metal sulfides, have been studied and shown to exhibit excellent abilities to form protective tribofilms on the substrates and decrease friction and wear volume. However, a major issue with the use of these NPs is their high tendency to undergo aggregation and precipitation in nonpolar base oils, such as polyalphaolefin (PAO), due to the large difference in chemical composition between oils and NPs and the van der Waals attractive forces between NPs. Using surface-initiated polymerization from metal oxide nanoparticles, we have synthesized oil-soluble polymer brush-grafted NPs (hairy NPs) and demonstrated their excellent dispersibility and stability in PAO in a wide temperature range. Addition of 1 wt% hairy NPs in PAO resulted in significant reductions in both friction and wear. We further prepared a family of hairy nanoparticles to investigate the effects of various parameters on lubrication performance. The tribological properties of these hairy NPs were evaluated by high contact stress ball-on-flat tribological tests, and the tribofilms formed on the substrates were characterized by transmission electron microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. The results showed that hairy NPs are promising additives for PAO for friction and wear reduction.



POLY 75: Designing chemically inert metallo-polyelectrolytes as anion-exchange membranes in alkaline fuel cells

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Cationic polyelectrolytes are widely pursued as anion-exchange membranes (AEMs) in alkaline fuel cells for converting fuels into electricity. We conceptualized chemically inert, mechanically tough, cationic metallo-polyelectrolytes as durable AEMs, which are centered on cationic cobaltocenium. This presentation will discuss organic polymer chemistry approaches toward various compositions of polyelectrolytes. One of particular designs involves ring-opening metathesis polymerization (ROMP) of cobaltocenium-containing cyclic olefins. Followed by backbone hydrogenation, it led to a new class of AEMs with a hydrocarbon framework and alkaline-stable cobaltocenium cation for ion transport. These AEMs exhibited excellent thermal, chemical and mechanical stability, as well as high ion conductivity.



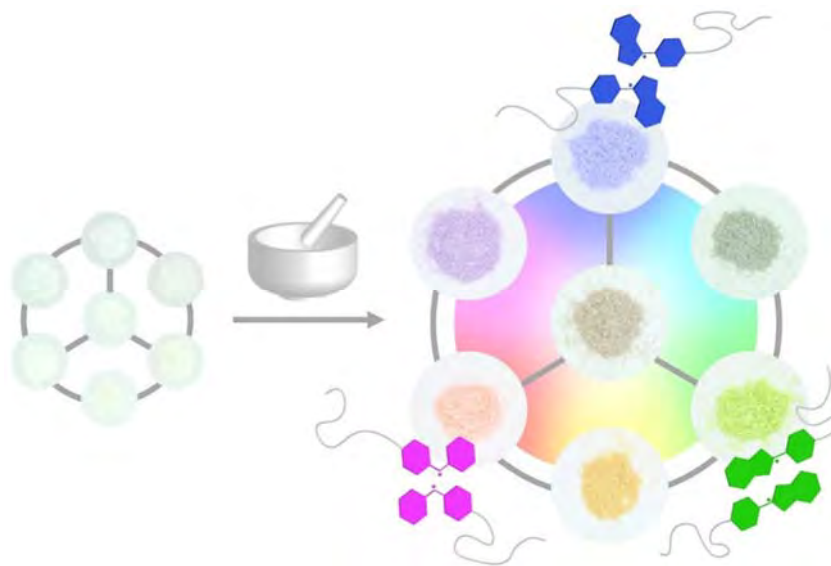
H-AEM-OH



POLY 76: Radical-type rainbow mechanochromic polymers

Daisuke Aoki, daoki@polymer.titech.ac.jp, Kuniaki Ishizuki, Raita Goseki, Hideyuki Otsuka. Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan

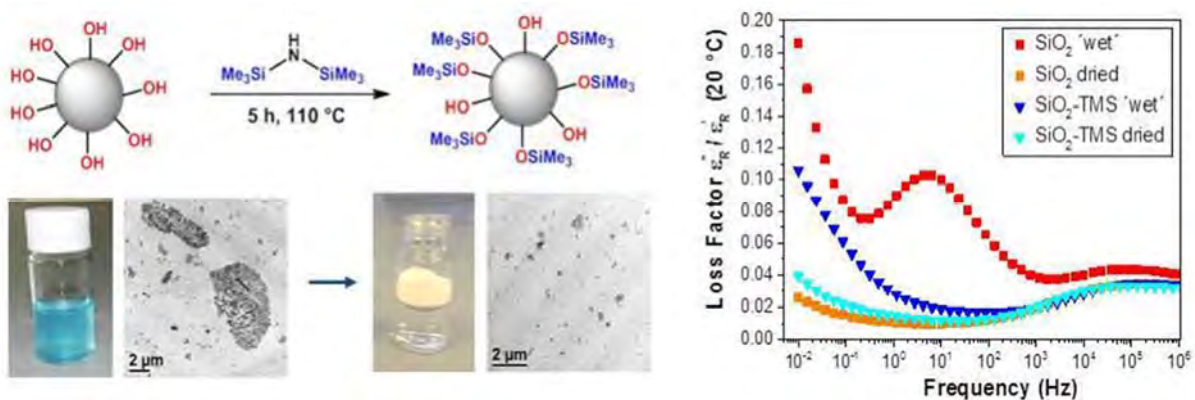
Mechanochromic polymers, i.e., polymers sensitive to mechanical impact, promise great potential for applications in damage sensors. In particular, radical-type mechanochromic polymers, which produce colored radical species in response to mechanical stress, may enable not only the visualization of mechanical stress, but also its quantitative evaluation by electron paramagnetic resonance analysis. In this work, a radical-type mechanochromic polymer that exhibits a color change from white to green upon dissociation of a diarylbibenzothiophenyl moiety at the mid-point of a polystyrene chain is presented, and its mechanochromic behavior examined. Mechanochromic materials that show a variety of colors ('rainbow colors') in response to mechanical stress were prepared by simply mixing radical-type mechanochromic polymers of primary colors.



POLY 77: Effect of surface interactions on the insulating properties of epoxy composites

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In high-voltage engineering, epoxy resins are the most commonly applied polymer class for insulating compounds. In order to enhance their dielectric properties, composites of an epoxy/amine resin and one type of nano-scaled filler (SiO_2 , surface-silylated SiO_2 , Al_2O_3 , surface-silylated Al_2O_3 , and BN) were prepared. The nanocomposites were tested as dielectric materials with a focus on the surface functionalization of the nanoparticles and the water absorption of the material. Permittivity measurements revealed that the composites containing pristine silica showed the lowest permittivity. This phenomenon can be explained by polar interactions between the nanoparticles' surfaces and the adjacent polymer matrix (Tanaka model), which result in a decrease of the mobility and the polarizability of the polymer network. The dried samples acted as good dielectrics (loss factors of 0.010-0.013), while water absorption under ambient conditions deteriorated the insulating properties, especially at frequencies below 100 Hz. This effect was most pronounced in case of particles that bear hydroxy groups on their surfaces (SiO_2 and Al_2O_3), which increase the interfacial polarization by interaction with water. On the contrary, the composites containing nanoparticles with a hydrophobic surface (such as surface-silylated silica) showed good dielectric properties, even upon the absorption of water.



Left: Surface functionalization of silica and alumina nanoparticles with hexamethyl disilazane; right: Loss factors of pristine and surface-silylated silica nanoparticles ('wet' and dried samples).

POLY 78: Harnessing click chemistry to diversify the functionality of anisotropic colloids

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Rising interests in the use of particles as solid surfactants in multiphasic systems has been motivated by prospects to increase emulsion stability and introduce stimuli-responsive properties. While many systems have utilized homogeneous particles to form Pickering emulsions, amphiphilic Janus particles offer enhanced attachment energies and opportunities to tailor the functionality to specific fluid phases. Current methods for the fabrication of Janus particles in bulk solutions rely on phase separation mechanisms which are highly dependent on the interaction energies between precursors, requiring unique synthesis conditions. In order for Janus particles to be viable solid surfactants on a large scale, it is necessary to develop versatile methods of fabrication that provide straightforward tunability in the chemical composition. Inspired by recent advances in click chemistry for particle synthesis, we developed clickable Janus particles containing alkyne pendant groups that can participate in thiol-yne click reactions to transform the chemical functionality and surface charge. Integration of alkyne pendant groups allows us to take advantage of the suite of thiols already commercially available. We demonstrate functionalizing clickable Janus particles to be amphiphilic by introducing either carboxyl, hydroxyl, or amine moieties. Click chemistry not only allows us to tailor the chemical functionality and surface charge of Janus particles, but also enables us to control the extent of modification which we show influences the particle morphology and emulsion stability. Furthermore, multi-functional composite Janus particles can be easily synthesized by performing sequential click reactions. The use of thiol-yne click chemistry offers a fast-reacting and scalable method to tailor the chemical functionality of Janus particles for specific applications.

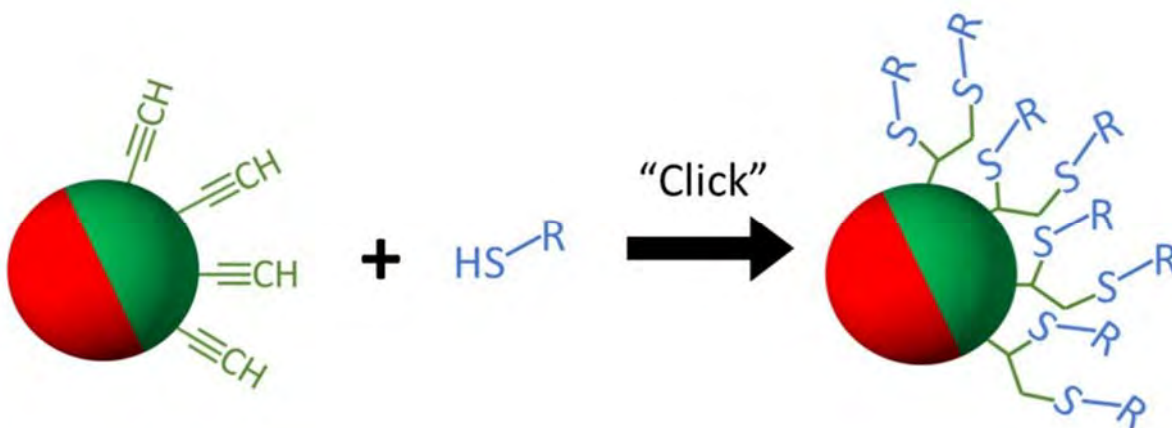
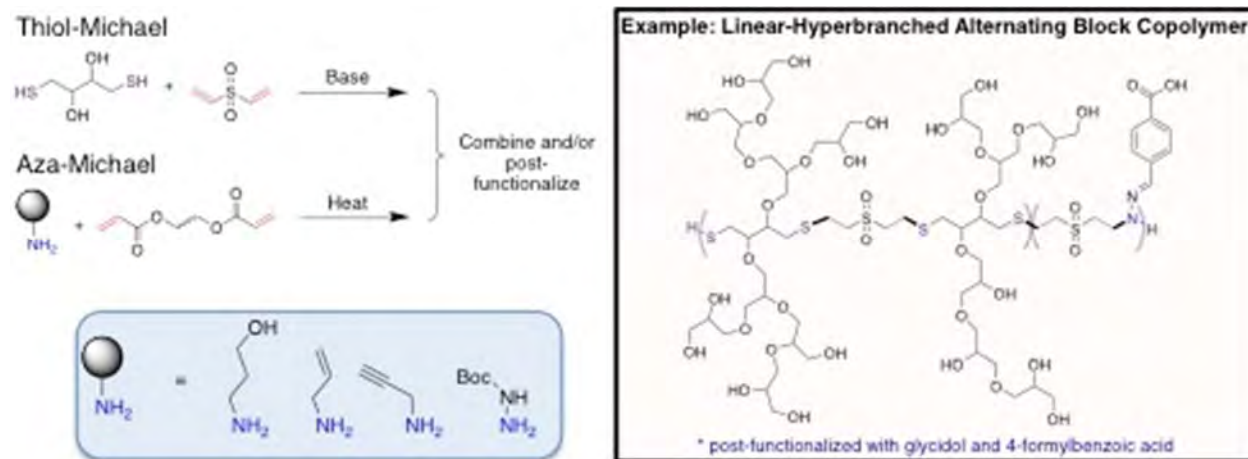


Illustration of modifying the chemical functionality of Janus particles using thiol-yne click chemistry.

POLY 79: Combinatorial synthesis of functional polymers with complex architectures using thiol-Michael and aza-Michael chemistries

Dillon Love¹, *dilo7362@colorado.edu*, **Dylan Domaille**², **Benjamin Fairbanks**¹, **David Klug**¹, **Christopher Bowman**¹. (1) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States (2) Chemistry, Colorado School of Mines, Golden, Colorado, United States

Our research focuses on the development of chemical strategies for the scalable synthesis of biomimetic, functional polymers using orthogonal “click” reactions. The thiol- and aza-Michael reactions in combination present a unique platform for the rapid generation of polymers with a broad range of complex architectures, such as alternating multiblock copolymers, networks, bottle-brush polymers, linear-hyperbranched block copolymers, and combinations thereof. The wide range of commercially available primary amines, dithiols, and dienes also allows for the introduction of many functional group chemistries onto the polymer backbone, e.g. alkenes, alkynes, alcohols, hydrazines, that may undergo further reactions to incorporate a specific polymer functionality or to modulate the polymer architecture. Current work is focused on using these reaction schemes to combinatorially synthesize, with aid of a high throughput automated synthesizer, polymers with a broad range of properties for applications including: rewritable/dynamic copolymers, self-assembly, molecular recognition, and covalent adaptable networks.

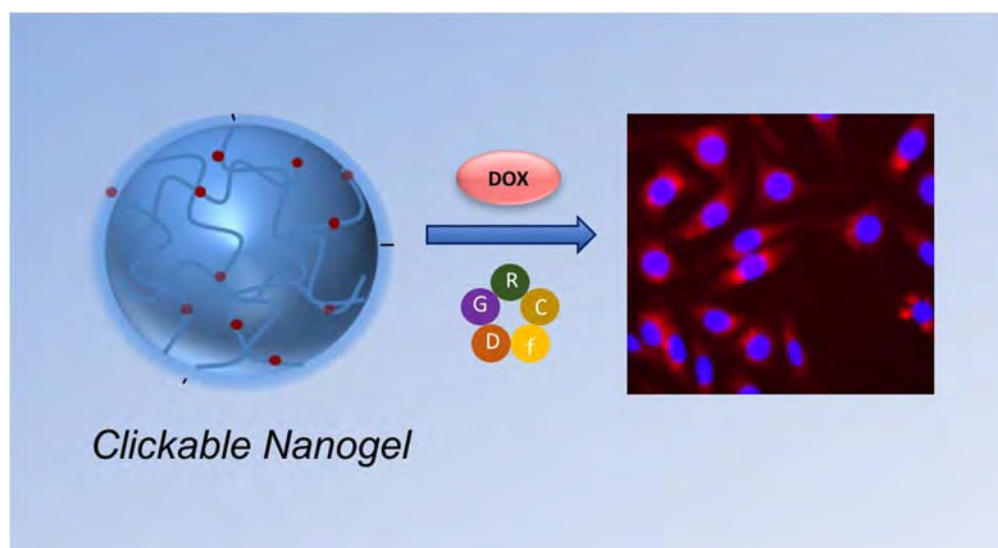


Michael reactions of dithiols and primary amines with electron-deficient dienes are used to prepare linear polymers with variable side-chain chemical functionalities. Polymers can be combined with another polymer to generate alternating block copolymers and the sidegroups can undergo further functionalization to more complex architectures and functional polymers.

POLY 80: Fabrication of clickable nanogels from reactive copolymers: Novel nanocarriers for targeted therapy

Laura Chambre¹, *lchambre2008@my.fit.edu*, **Bugra Aktan**¹, **Aysun Degirmenci**¹, **Rana Sanyal**^{1,2}, **Amitav Sanyal**^{1,2}. (1) Chemistry, Bogazici University, ISTANBUL, SARIYER, Turkey (2) Center for Life Sciences and Technologies, Istanbul, Turkey

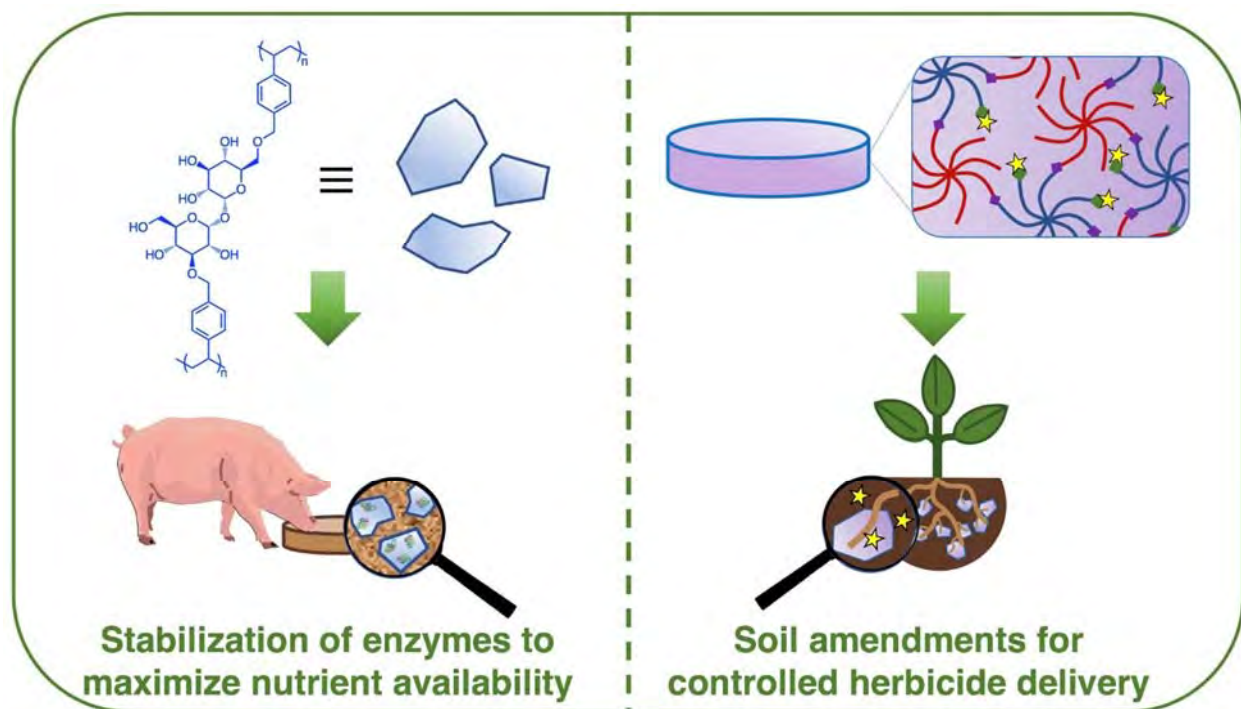
Polymer based nanotheranostic agents have attracted a lot of interest in recent years because of their capability to simultaneously diagnose and treat the disease. Such constructs also enable monitoring of the treatment in real time. Polymer based theranostic agents comprise of three main components: a biocompatible polymeric construct that acts as a vehicle, a therapeutic agent to treat the disease, and an imaging agent to monitor the localized delivery of the drug. Nanogels, with their excellent stability and biocompatibility, serve as ideal nanocarriers. Moreover, their small size allows preferential accumulation at the tumour site through enhanced permeability and retention effect. This presentation will outline different approaches for fabricating poly(ethylene glycol) based multi-functionalizable nanogels containing maleimide and amine-reactive moieties. Since the maleimide functional group is reactive toward thiols and dienes through the Michael and Diels-Alder reactions, respectively; copolymers were crosslinked in aqueous media using dithiol, diamines or bis-furan based linkers to yield reactive nanogels. Nanogels were conjugated with drug and targeting units to achieve selective delivery to breast cancer cells. Doxorubicin, a widely used chemotherapeutic agent, was attached to the nanogels through the labile carbamate linker, allowing its release at acidic pH. Indeed, Doxorubicin, with its inherent fluorescence can be also used as a theranostic agents. To enhance the selectivity of the nanocarrier and provide targeted delivery, a cyclic peptide with high affinity toward integrin receptors overexpressed on various cancer cells was linked to the nanogel. Cellular internalization experiments showed increased uptake of targeted constructs compared to the non-targeted nanocarriers. It can be envisioned that facile fabrication and modular functionalization of these nanogels would promote their utilization as promising theranostic platforms to treat various diseases.



POLY 81: Synthetic hydrogels tailored for stabilization and sustainable release of agricultural and animal feed cargo

Priera Panescu¹, ppanescu@ucla.edu, Jeong Hoon Ko¹, Heather D. Maynard². (1) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States (2) UCLA, Los Angeles, California, United States

Hydrogels offer an attractive scaffold for the encapsulation, stabilization, and controlled release of precious resources. Moreover, synthetic hydrogel preparation and cargo release can be easily optimized through tuning gel properties, such as stiffness and linker degradability. Two hydrogels were synthesized and were specifically constructed to maintain the activity of and sustainably release important vulnerable payloads. The first hydrogel was synthesized to covalently incorporate trehalose. These gels were used to stabilize the three most widely used animal feed enzymes, which are a necessary additive to enhance the nutritional value of grains, but are deactivated by high temperatures during the feed pelleting process. All three enzymes retained greater than 90% activity after heating to 90°C when non-covalently encapsulated in the hydrogel. The second hydrogel was created through dynamic click chemistry to allow the gradual release of mesotrione, a triketone herbicide that rapidly breaks down in acidic soils. Hydrazone linkages were implemented to reversibly conjugate and encapsulate mesotrione into a slow degrading hydrogel, ultimately decreasing the off-target effect of the free herbicide and increasing its efficiency. The synthesis, optimization, and agricultural application of these hydrogels will be presented.



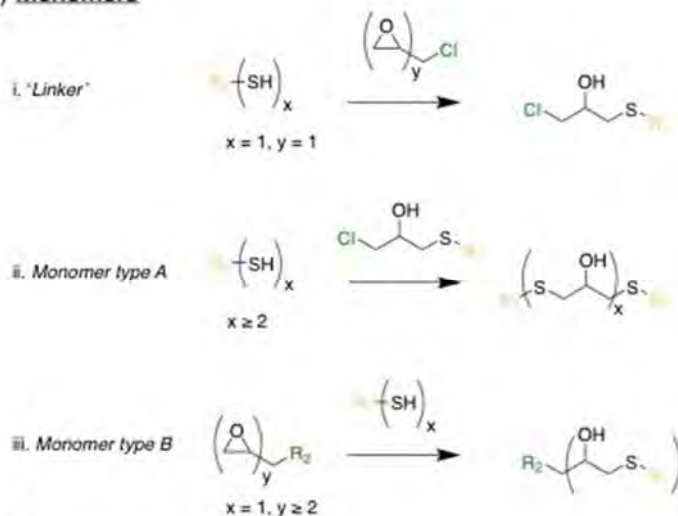
POLY 82: Realizing high refractive index materials from thiol-X polymers: A general synthetic strategy

Marvin Alim¹, marvin.alim@colorado.edu, **Sudheendran Mavila**², **Robert R. McLeod**^{4,1}, **Christopher Bowman**^{3,1}. (1) Materials Science & Engineering, University of Colorado Boulder, Boulder, Colorado, United States (2) Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States (3) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States (4) Electrical, Computer & Energy Engineering, University of Colorado Boulder, Boulder, Colorado, United States

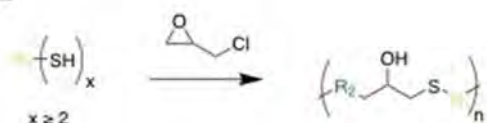
While the virtues and capabilities of the thiol-X ‘click’ chemistry paradigm are well-known, a critical gap in the monomer toolbox persists with regards to achieving the potential of high refractive index ($n > 1.6$) thiol-X polymeric materials. We report a general synthetic strategy to achieve high refractive index monomers and/or oligomers compatible with thiol-X polymerizations using substrates with a vast library of structures and functionality – thiols and epoxides. Specifically, a set of novel diallyl ether monomers were synthesized using 1-chloro-3-(phenylthio)-2-propanol (CPTP) with systematic structural variation in the high refractive index dithiol ‘core’ employed (i.e. 1,4-benzenedithiol, 4,4’-thiobisbenzenethiol and 2,7-thianthrenedithiol) to produce liquid monomers (n_D at 20°C ranging from 1.617 to 1.66) of relatively low viscosity with excellent solubility in various neat thiol-ene resins. Photopolymerized crosslinked networks prepared with 1,3,5-benzene trimethanethiol (BTMT) produced optically transparent films with refractive index values exceeding 1.68 at 589 nm.



a) Monomers



b) Oligomers

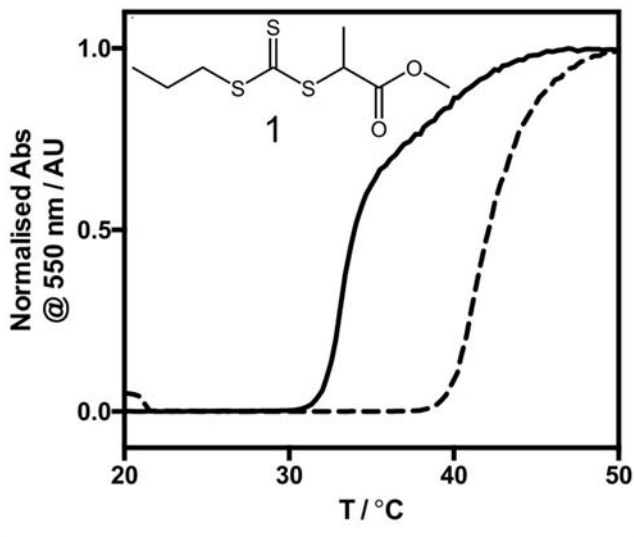


POLY 83: Development of oxidation-responsive polymers for targeting inflammation

Emma Owens, **Seb G. Spain**, sebastian.spain@gmail.com. Department of Chemistry, University of Sheffield, Sheffield, South Yorkshire, United Kingdom

Inflammatory diseases, such as multiple sclerosis and rheumatoid arthritis, are characterised by relapses with increased symptoms and degenerative disease progression. During these relapses, an abnormal concentration of reactive oxygen species (ROS) are produced by the immune system. Although ROS are a normal part of the immune system's response to invading pathogens, excess production of ROS leads to irreversible tissue damage and further disease progression. Consequently, materials that respond to ROS (e.g. change in solubility or morphology) may provide a mechanism for the detection and treatment of immune diseases.

We have recently discovered that the thiocarbonylthio end group installed in a conventional RAFT polymerization can be utilised as an oxidation-sensitive moiety to modulate the lower critical solution temperature (LSCT) of the archetypal thermoresponsive polymer poly(*N*-isopropylacrylamide) (pNIPAM). The hydrophobicity of the RAFT agent used allows some control over the change in with increases of up to 8 °C demonstrated. We are currently investigating this as a mechanism for isothermal globule-to-coil transitions in pNIPAM to allow release of drugs.



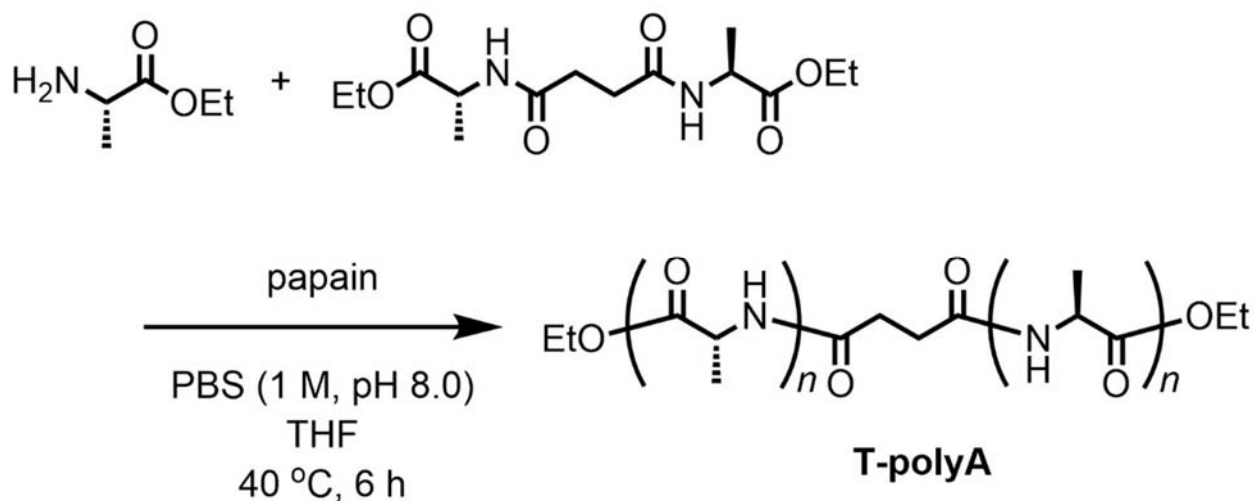
Cloud points measurements for poly(*N*-isopropylacrylamide) synthesised with RAFT agent **1** before (solid line) and after (dashed line) oxidation with H₂O₂.

POLY 84: Chemoenzymatic synthesis of telechelic polyalanine and its use as a reinforcing agent for silk materials

Kosuke Tsuchiya, *kosuke.tsuchiya@riken.jp*. Enzyme Research Team, RIKEN Center for Sustainable Resource Science, Wako, Saitama, Japan

In order to construct unique polypeptide architectures with a specific functionality, papain-catalyzed polymerization of alanine ethyl ester in the presence of a bifunctional amino acid ester derivative was performed to obtain a telechelic-type polyalanines. The formation of the telechelic polypeptides was confirmed by ^1H NMR and MALDI-TOF mass spectroscopies. It was revealed by AFM observation that long nanofibrils were formed from the telechelic polyalanine, whereas a conventional linear polyalanine with a similar degree of polymerization showed granule-like structures. It was demonstrated that this method to synthesize the telechelic-type polypeptides would potentially open up a pathway to construct novel hierarchical structures by self-assembly.

The telechelic polyalanine was found to be an effective reinforcing agent for silk materials (silkworm and spider silks) by inducing β -sheet crystal structures via the specific self-assembling nature. Silk materials have attracted intensive attention as eco-friendly tough materials because of their excellent mechanical property and biomass-based origin. Composite films based on a recombinant spider dragline silk protein (ADF3) from *Araneus diadematus* were prepared by doping with linear or telechelic polyalanine (L- or T-polyA, respectively) as a reinforcing agent. Higher tensile strength and toughness of the composite films were achieved with the addition of T-polyA compared with the tensile strength and toughness of the silk-only film. The difference in the reinforcing behavior between L- and T-polyA was associated with their primary structures, which were revealed by wide angle X-ray diffraction analysis. L-polyA showed a tendency to aggregate in the composite films and induce crystallization of the inherent silk β -sheet to afford rigid but brittle films. By contrast, T-polyA dispersion in the composite films led to the formation of β -sheet crystal of both T-polyA and the inherent silk, which imparted high strength and toughness to the silk films.



Chemoenzymatic synthesis of telechelic polyalanine (T-polyA).

POLY 85: Synthesis of cell penetrating peptide containing α -aminoisobutylic acid using chemoenzymatic polymerization

Yu Miyagi¹, yu.miyagi@riken.jp, **Kosuke Tsuchiya**², **Keiji Numata**³. (1) enzyme research team, RIKEN, Saitama, Japan (2) Enzyme Research Team, RIKEN Center for Sustainable Resource Science, Wako, Saitama, Japan (3) RIKEN, Saitama, Japan

Cell penetrating peptides (CPPs) containing unnatural α,α -disubstituted amino acid form the stable amphiphilic helical structures and show high cell penetrating ability. In the present study, we synthesized CPPs containing lysine and α -aminoisobutylic acid (Aib) by using chemoenzymatic polymerization and examined the secondary structures and the cell penetrating activities. The chemoenzymatic reaction of tripeptides (Lys-Aib-Xxx, Xxx = Glycine, Alanine, Leucine, Lysine, Phenylalanine) was performed using papain or protenase K in a buffer at 40-60 °C for 1 h. We analyzed the properties of the obtained peptides by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and circular dichroism (CD) spectroscopy. The peaks assigned to the dimer and trimer of the Lys-Aib-Xxx unit were observed, indicating the successful polymerization of Lys-Aib-Xxx esters using papain and protease K. We measured the CD spectroscopy of the obtained peptides in various buffer solutions. The CD spectra did not show any specific secondary structures in phosphate buffer (pH 8.0), whereas these peptides form the helical-rich secondary structures in 0.1% sodium dodecyl sulfate solution. This result indicates that these peptides can form the suitable helical-rich secondary structures to penetrate the cell membrane in a physiological condition. Finally, we evaluated the cell penetrating activity of the obtained peptides by confocal microscopic observation. Cell penetrating activity of the novel peptides was confirmed by the internalization of fluorescence dye, which is connected to the N-terminal of the peptides (Figure), in human embryonic kidney 293 (HEK) cells.

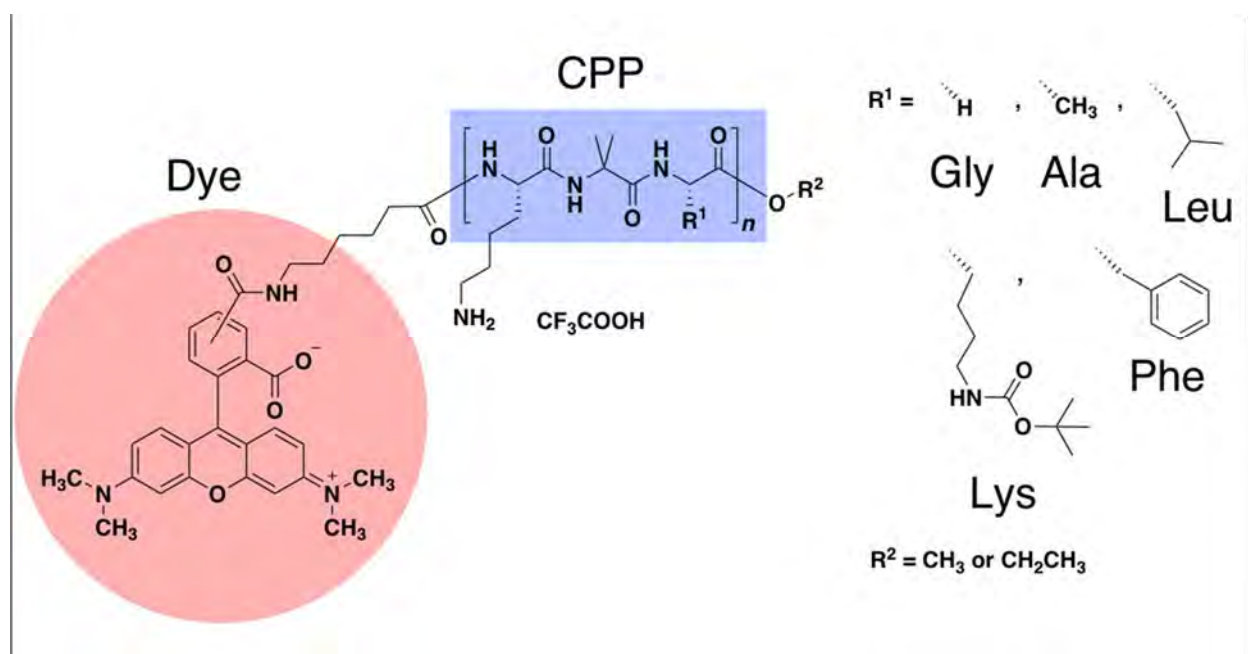
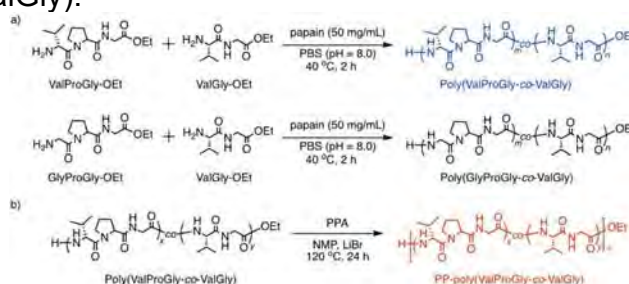


Figure. Chemical structures of cell penetrating peptides with fluorescence dye

POLY 86: Synthesis of elastin mimicking polypeptide consisting of periodic di- and tri-peptide motifs by chemoenzymatic polymerization

Prashant G. Gudeangadi¹, pgudeangadi@gmail.com, Kosuke Tsuchiya², Keiji Numata³. (1) Enzyme Research Team, CSRS, RIKEN, Wako Shi, Saitama, Saitama-Ken, Japan (2) Enzyme Research Team, RIKEN Center for Sustainable Resource Science, Wako, Saitama, Japan (3) RIKEN, Saitama, Japan

Polypeptides are building blocks in various natural proteins. Elastin is an important structural protein with an amino acid sequence valine-proline-glycine-valine-glycine (ValProGlyValGly) in its hydrophobic region. Due to its remarkable elasticity and stimuli-responsive properties, recently elastin and elastin-like polypeptides (ELPs) have been actively studied as biomaterials for various biomedical applications. Both proline and valine are key for such an elasticity. Chemoenzymatic polymerization of amino acids using proteases is eco-friendly, atom-economical method of polypeptide synthesis. In order to synthesize periodical amino acid sequence, the ValProGly-OEt and GlyProGly-OEt tripeptide ester were prepared as a monomer. These tripeptides were chemoenzymatically homopolymerized in phosphate buffer solution (1 M, pH 8.0) using papain at 40 °C for 2h. The tripeptides were also copolymerized with ValGly-OEt as a counterpart. All the obtained polypeptides were characterized by MALDI-TOF mass spectroscopy and ¹H NMR spectrometry. The Circular dichroism (CD) spectra of poly(ValProGly-co-ValGly) revealed temperature dependent, reversible structural transition similar to that of tropoelastin (soluble precursor of elastin). Furthermore, post-polycondensation reaction of poly(ValProGly-co-ValGly) in the presence of polyphosphoric acid as a condensing agent at elevated temperature resulted in a higher molecular weight product, PP-poly(ValProGly-co-ValGly). PP-poly(ValProGly-co-ValGly) showed different secondary structure and thermal properties compared to poly(ValProGly-co-ValGly).



Scheme. 1 a) Chemoenzymatic copolymerization of Pro- and Val-containing di- tri-peptides using papain and b) post-polycondensation of poly(ValProGly-co-ValGly).

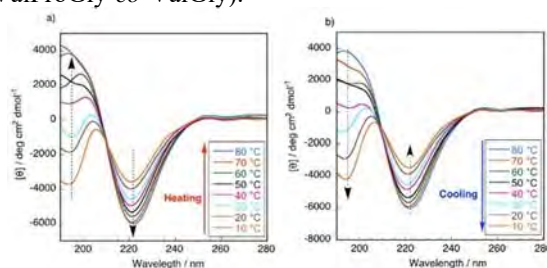
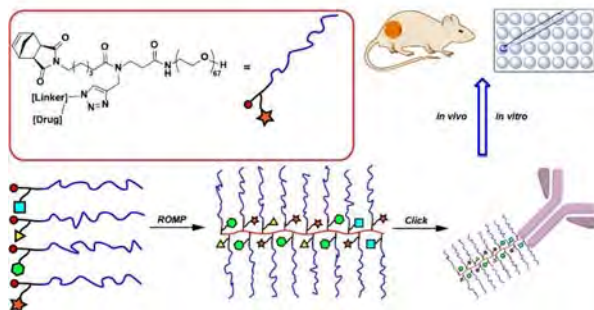


Fig. 1 CD spectra of poly(ValProGly-co-ValGly) in water in the second a) heating and b) cooling cycle at different temperatures between 10 and 80 °C. The concentration of the polypeptide was 1 mM.

POLY 87: ROMP-enabled combination cancer therapy—toward a single-carrier platform with precise ratio control, tunable therapeutic release, and specific targeting

Hung V. Nguyen¹, *hvt191@mit.edu*, **Alex Detappe**², **Yivan Jiang**⁴, **Nolan Gallagher**³, **Clelia Mathieu**², **P. Peter Ghoroghchian**², **Irene Ghobria**², **Jeremiah A. Johnson**⁵. (1) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Department of Medical Oncology, Dana-Farber Cancer Institute, Harvard Medical School, Boston, Massachusetts, United States (4) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (5) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Recent decades have witnessed incredible advancements in the field of drug discovery, especially in cancer chemotherapy, resulting in novel therapeutic agents with intricate mechanisms of action towards specific cellular pathways, targeting certain types of cancer. Furthermore, the use of multiple therapeutic agents—combination therapy—has become increasingly important; this is due to their potential synergistic activities, orthogonal toxicity profile, or simply being required to eradicate single-drug-resistant tumors. Nonetheless, in their free forms, problems such as non-specific biodistribution, off-target toxicity, poor *in vivo* circulation, and limited stability, remains major challenges. To circumvent these weaknesses, nanoparticle-based cancer therapies, most commonly micelles and liposomes, are deployed to improve therapeutic index. However, incorporation of multiple therapeutic agents into a single delivery vehicle at optimal ratios are challenging. To exacerbate the problem, their release kinetics are highly dependent on the nature of the drug molecules, making delivery platform development highly dependent on the identity of each chemotherapy agent. We report here our progress towards engineering a single-carrier system that simultaneously addresses all these challenges. Utilizing ring-opening metathesis polymerization, we can prepare bottlebrushes (BP) or brush-arm star polymers (BASP) containing, to date, up to four components of choice at precise ratios. This inherent convergence is the result of our macromonomer (MM) building block library, where each MM is designed to carry one payload of either a therapeutic agent or an imaging probe. Moreover, these MMs possess tunable release rates based on their designated linker, whether pH-, redox-, or UV-responsive at pre-determined rates, as well as non-cleavable. To further address passive and active accumulation, the resulting BPs or BASPs can be further conjugated with targeting moieties. As a case study, we present here one such system with a clinically relevant therapeutic 3-drug combination, a near-infrared fluorescence probe, and active-targeting capability via antibody-conjugation.

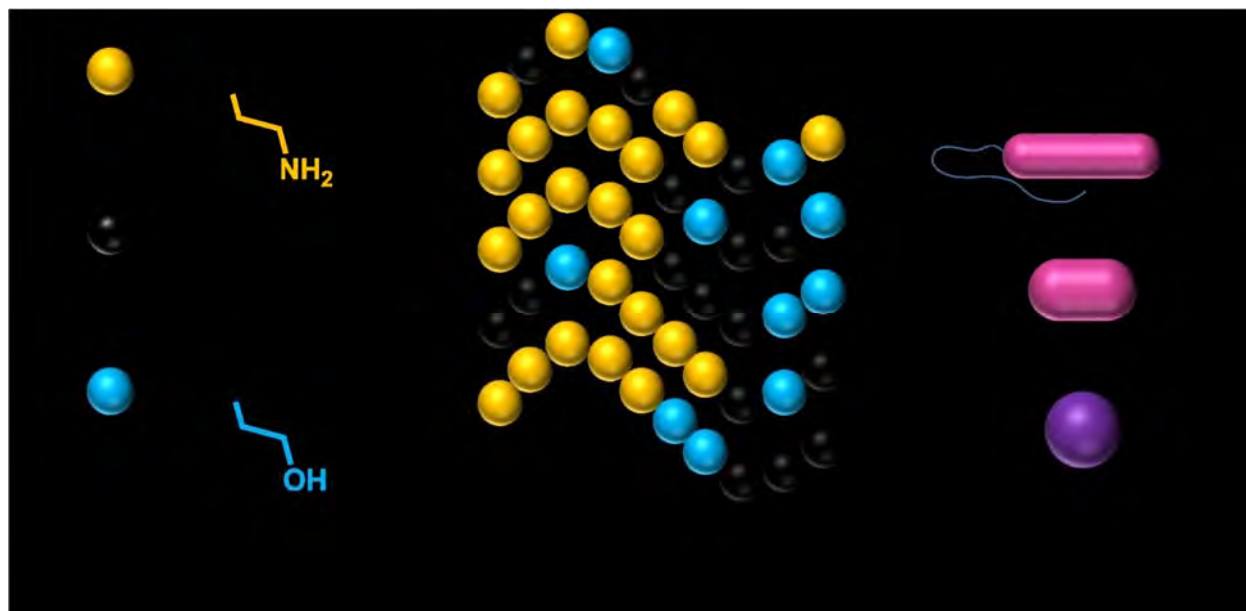


POLY 88: Towards sequence-controlled antimicrobial polymers using PET-RAFT polymerization

Peter Judzewitsch, Edgar Wong, **Cyrille Boyer**, cboyer@unsw.edu.au. Chemical Engineering, UNSW, Sydney, New South Wales, Australia

Synthetic polymer structures have shown promise in the biological domain in recent years. Specifically, the use of polymers in combatting the rise in multidrug-resistant bacterial infections is a focus of many groups.^[1] In this arena, one such topic is in mimicking naturally occurring antibiotic agents termed Antimicrobial Peptides (AMPs).^[2] As part of the innate immune system, AMPs have been shown to act in a manner preventing easy bacterial adaptation and resistance development, although production of such molecules remains laborious.

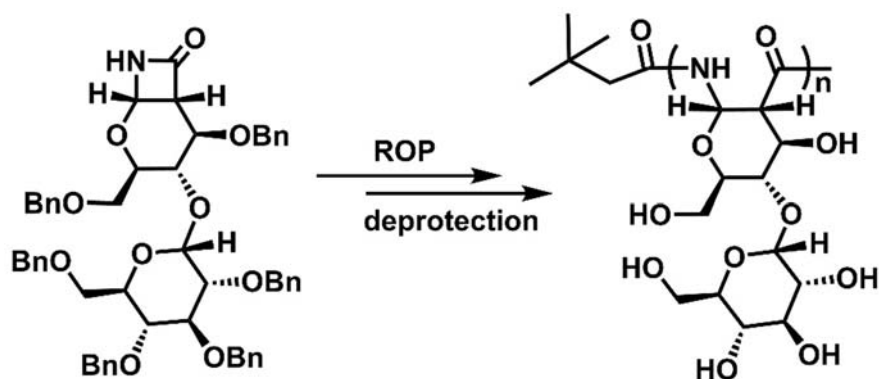
Recent developments in controlled/living radical polymerization (CLRP) techniques have enabled production of more complex synthetic polymers in the last few decades.^[3] This provides a wider variety of relatively easy to produce synthetic macromolecular structures, allowing for AMP mimetic structures to be explored more easily. Using photoinduced electron transfer-reversible addition-fragmentation chain transfer (PET-RAFT) developed previously by our group,^[4] we have recently investigated the impact of monomer placement within block terpolymers of a singular composition on antimicrobial activity. We have discovered that, through such variations in monomer order addition, antimicrobial activities of polymers differ despite a constant global composition. This has enabled the production of polymers with targeted antimicrobial activity.



POLY 89: Synthesis of biologically active branched polysaccharide mimetics by ring-opening polymerization of a maltose-based β -lactam

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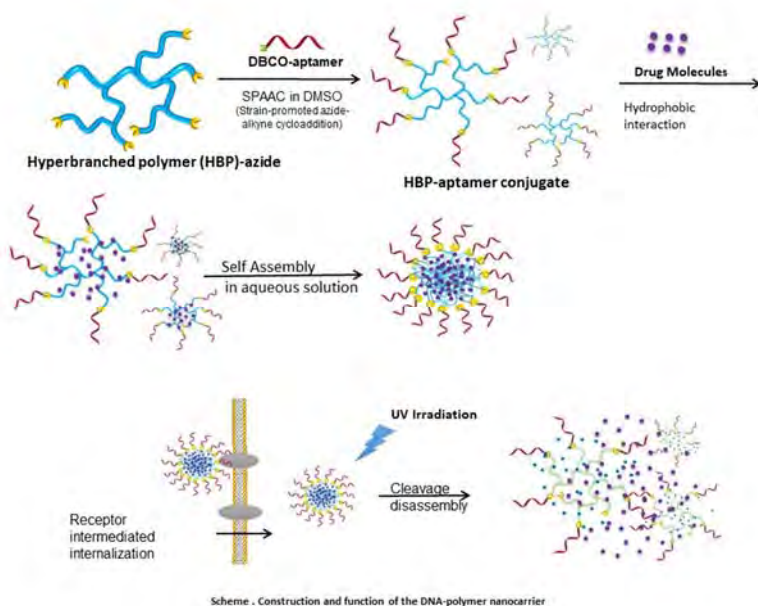
Many polysaccharides existing in nature have branched structures, in which the composition, position, and frequency of branches play key roles in determining the physicochemical and biological properties. However, due to the structural complexity of branched polysaccharides and the difficulty in isolation of pure products, it is challenging to decipher the structures and elucidate the structure-function relationships. Therefore, the synthesis of stereoregular branched polymers that structurally and functionally mimic complex natural polysaccharides are of significant interest. As a conventional method to synthesize branched polysaccharides, cationic ring-opening polymerization of anhydrodisaccharides suffers from the low polymerizability of these disaccharide monomers, and thus cannot provide branched polysaccharides with high molecular weights. Herein, we report a novel polymerization method to prepare branched polysaccharide mimetics by ring-opening polymerization of a disaccharide-based β -lactam monomer. Using this method, stereoregular poly-amido-saccharides (PASs) bearing α -glucopyranose branches (mal-PASs) are synthesized by anionic ring-opening polymerization of a maltose-based β -lactam followed by debenzoylation. The polymerization affords high molecular weight branched polymers (up to 31,510 g/mol) with narrow dispersities (PDI < 1.1). The debenzoylation of these polymers proceeds smoothly without degradation of the polymer backbone. PASs with different branching frequencies are prepared by copolymerization of maltose β -lactam monomer and glucose β -lactam monomer followed by deprotection. The branching frequencies calculated from nuclear magnetic resonance spectroscopy (NMR) are consistent with the feeding ratio of monomers during copolymerization. Mal-PASs and copolymers are highly soluble in water and adopt a left-handed helical conformation in aqueous solutions, according circular dichroism (CD) analysis. Turbidimetric assays show that, despite the rigid polymer backbone, branched PASs are multivalent ligands to plant lectin Concanavalin A.



POLY 90: DNA grafted hyperbranched polymer as smart drug delivery system for target binding and photoresponsive drug release

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A new photo-responsive hyperbranched polymer was designed and synthesized by introducing UV-sensitive *o*-nitrobenzyl functionalities into the backbone of the polymer. This hydrophobic polymer was grafted with hydrophilic PEG and DNA aptamer by “click” chemistry, giving rise to an amphiphilic polymer-DNA conjugate which could further self-assembled into uniform nanoparticles. The nanostructure acting as a “smart” delivery system would be able to target on specific cells and disassemble instantly under UV irradiation, promoting the release of loaded molecules. The formation and disassembly of nanoparticles have been fully characterized by DLS, TEM, and UV-Vis absorption. Targeting ability contributed by aptamer (sgc8) towards specific cancer cells (CEM) and receptor assisted internalization have been proved by flow cytometry and confocal microscopy. To further evaluate its expected exceptional loading efficiency introduced by the inherent cavity of hyperbranched polymer and releasing efficiency due to hydrophobicity change triggered by UV light, encapsulation of a model drug Nile red was performed. The release profile of Nile red was then examined by fluorescence spectroscopy, demonstrating a fast release behavior upon UV irradiation. Now we are applying this platform to other water-insoluble anticancer drugs such as DOX and Taxol, so that we can testify the stability, internalization pathway, and cytotoxicity of this nanocarrier loaded with drug molecules in cell studies to prove its promising therapeutic effect as a “smart” drug delivery system.



POLY 91: Cartilage dynamics and function

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Articular cartilage exhibits excellent load bearing properties owing to its hierarchical organization at both molecular and supramolecular levels. It also provides joints with a nearly frictionless articulating surface. It is known that the extracellular matrix (ECM) of cartilage is a composite gel-like material consisting of approximately 60–70% water, 20–30% collagen (mainly type II collagen), 10–15% proteoglycans (PGs) and small quantities of other materials, e.g., proteins and DNA. The most abundant PG is the bottle-brush shaped aggrecan, which consists of a central core protein to which many glycosaminoglycan (GAG) chains (mainly chondroitin sulfate and keratan sulfate) are covalently attached. In cartilage ECM aggrecan molecules are non-covalently bound to long hyaluronic acid (HA) molecules (like bristles to the backbone in a bottlebrush). The complex formation between aggrecan and HA is facilitated by link proteins. The ratio of aggrecan to HA is approximately 100:1. These highly charged microgel-like PG assemblies occupy the pores of the collagen matrix, generate a large osmotic swelling pressure and provide osmotic resistance to deswelling under external load. We investigate the structure and dynamic behavior of the major macromolecular components of cartilage ECM as well as their assemblies, using complementary microscopic (small-angle neutron scattering, neutron spin echo, static and dynamic light scattering, atomic force microscopy) and macroscopic techniques (osmotic swelling pressure measurements, rheological measurements). The results reveal how the hierarchical bottlebrush organization of cartilage PGs defines the load bearing properties of the tissue.

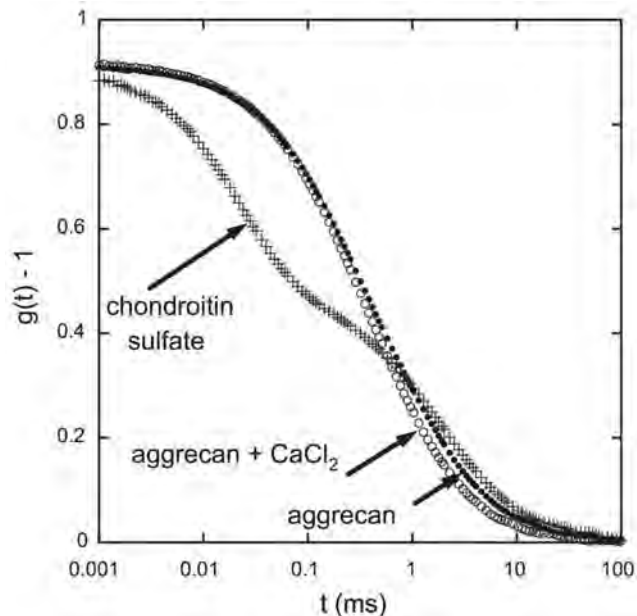
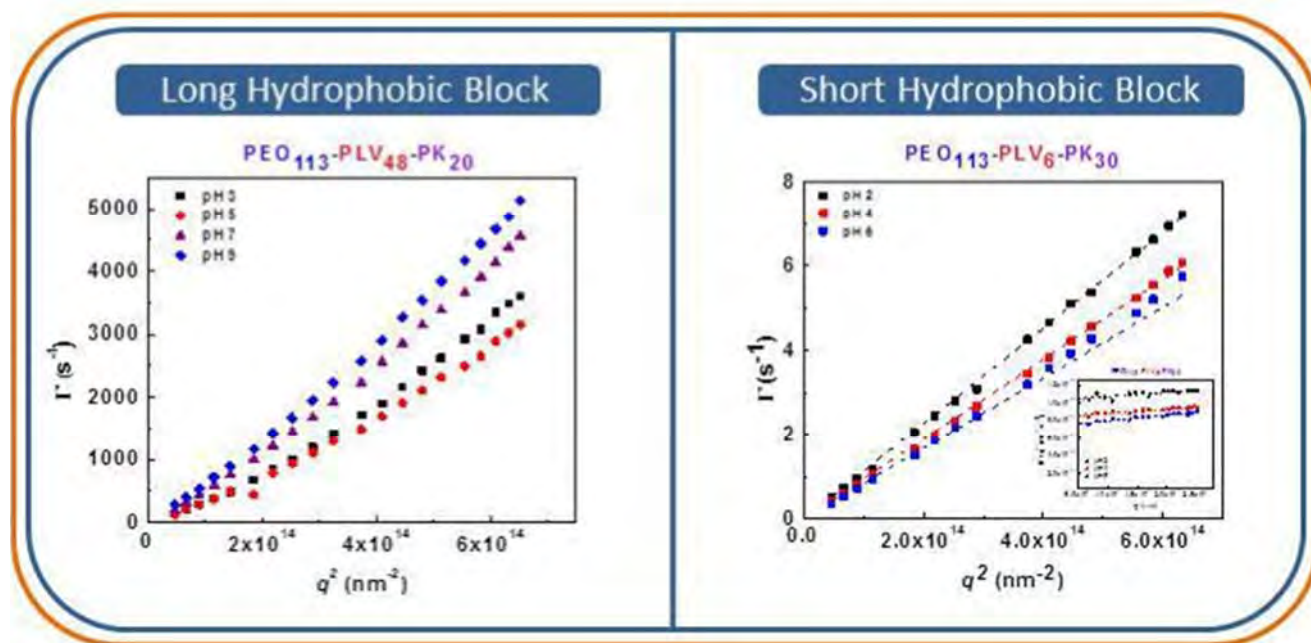


Figure 1. Intensity correlation functions $g(t) - 1$ for aggrecan solutions (0.6 % w/w) in 100 mM NaCl without CaCl₂ and with 25 mM CaCl₂, and for a 2% w/w chondroitin sulfate solution at scattering angle 150°.

POLY 92: Synthesis and characterization of self-assembling ABC triblock copolypeptides

Brooke Barnes, *bbarnes@ufl.edu*, Lauren M. Stein, Daniel A. Savin. Chemistry, University of Florida, Gainesville, Florida, United States

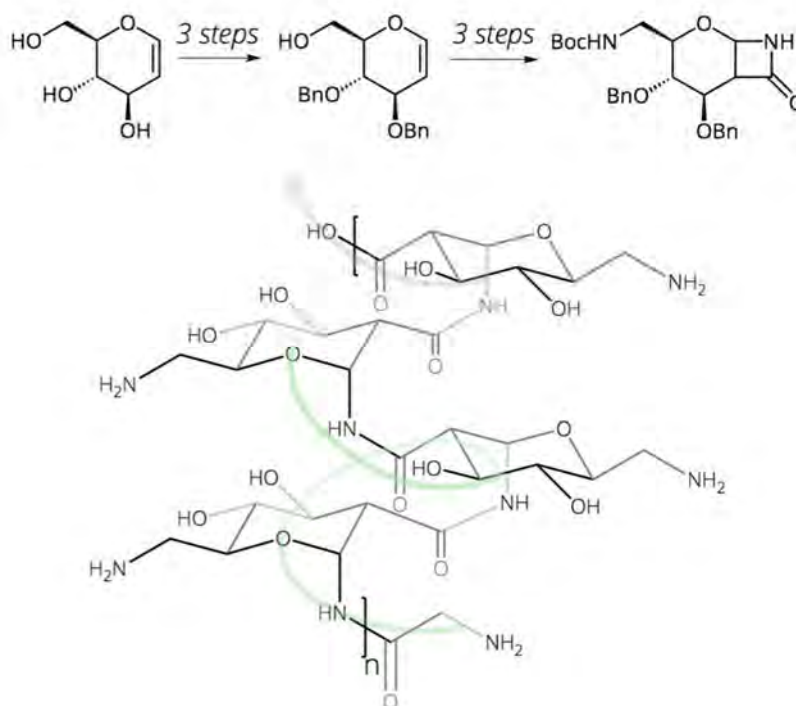
Herein we report the synthesis and solution characterization of an ABC triblock consisting of poly(ethylene oxide-*b*-(leucine-*s*-valine)-*b*-lysine). It is hypothesized that this polymer will self-assemble into unilamellar, size monodisperse vesicles in dilute aqueous solution, independent of preparation methods. Poly(leucine) is a hydrophobic, alpha helix forming polypeptide that has been shown to exhibit a “zipper effect” in coiled-coil dimers. This specific interaction afforded by the poly(leucine) block will be able to dominate the thermodynamics of polymer self-assembly through side-by-side ordering of alpha helices, which helps drive vesicle formation. Initial studies suggest that polymers with a longer hydrophobic block form irregular, size polydisperse assemblies ranging from 60- 200 nm. Upon shortening the hydrophobic block, size monodisperse assemblies with vesicle morphologies are achieved. Further work is being performed to elucidate the effect of polypeptide specific interactions on self-assembly behavior.



POLY 93: Synthetic, enantiopure, and well-defined carbohydrate polymer with an amino sugar backbone

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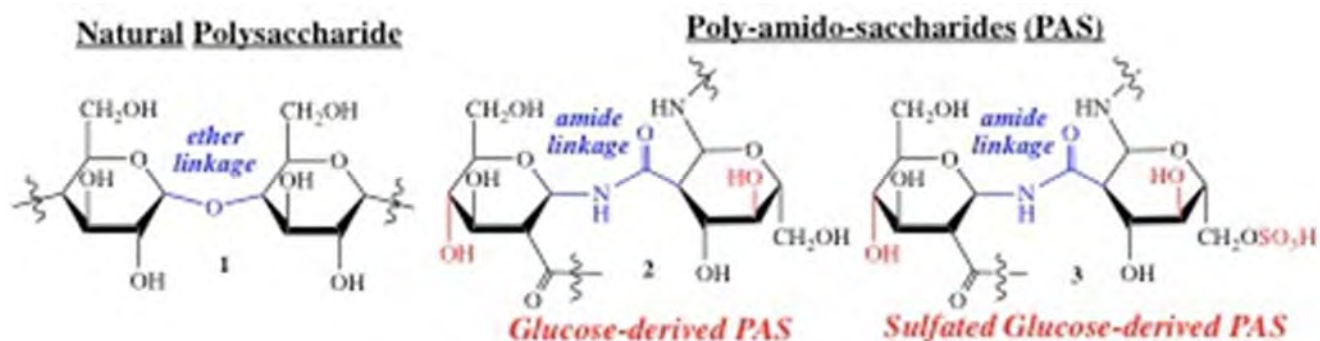
Carbohydrate polymers comprised of amino sugar subunits exist in nature in roles ranging from structural integrity to cell adhesion and anticoagulation, yet there are few synthetic amino sugar polymers available to leverage their properties in biomedical applications. In contrast to nucleic acids and polypeptides, polysaccharides are challenging synthetic targets as they possess remarkable diversity in their stereochemistry, functionality, linkage types, and degree of branching. Despite these hurdles, synthetic polysaccharides offer flexibility in the incorporation of abiotic components, control of macromolecular properties to suit the application, and importantly, the strict chemical definition not found in material extracted from natural sources. Herein, we report the synthesis and characterization of a new biomimetic carbohydrate-based polymer comprised of a repeating amino sugar backbone (AmPAS). AmPAS are enantiopure, can be obtained with controlled molecular weight and narrow size distribution, and possess a number of unique chemical and physical properties that are suitable for biomedical applications. AmPAS are linked by a 1,2-amide bond that confers resistance to enzymatic and hydrolytic degradation and adopt a helical conformation in solution irrespective of pH, salt concentration, and the presence of denaturants. These polymers are water soluble, cationic at neutral pH, and densely functionalized with hydroxyl and amine groups for further chemical modifications such as cross-linking or conjugation.



POLY 94: Synthesis, characterization and computational studies on sulfated poly-amido-saccharides

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Sulfated polysaccharides play critical and important clinical roles in a number of physiological and patho-physiological processes to include, the coagulation cascade, viral transmission, and anti-oxidation. However the synthesis of polysaccharides and their synthetic analogs is challenging due to the large number of stereocenters and similar functional groups. Herein, we report the synthesis of sulfated poly-amido-saccharides (sulPAS) structures, via SO₃-NMe₃ treatment of the synthesized polymers. The sulPASs were characterized by NMR, IR, and GPC. SulPASs at concentrations up to 100 µg/ml show anticoagulation activity in a colorimetric antithrombin binding activity assay and are non-cytotoxic to NIH 3T3 cells. Computational studies comparing the sulPASs with their non-sulfated PAS counterparts reveal the structural changes in the polymer backbone induced by the sulfate groups, depending on the sulfation position(s). The results of this study provide support for further investigation of sulPAS as an anticoagulant and alternative to the clinically used heparin.



A natural polysaccharide **1**, and glucose derived poly-amido-saccharides (PASs) with the more stable amide linkage, nonsulfated **2** and sulfated **3**.

POLY 95: Understanding our collection: A survey of plastics at the Harvard Art Museums

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Claes Oldenburg's False Food Selection comprises a collection of ready-made plastic food items housed in a wooden box. The once relatively realistic food is degrading with items now discolored, deflated and exhibiting bloom. The spoiling of the food is undoubtedly due to its materials; a combination of polyurethane, poly(vinyl chloride) and rubber – three of the most at-risk plastics in museum collections. Other instances of plastic degradation highlighted the need for a comprehensive survey of the polymeric materials in the Harvard Art Museums collection. Since mid-2016 nearly 400 objects containing plastic have been examined as part of the survey. Identification of the polymeric materials, obtained through the tandem use of FTIR and pyrolysis-GCMS, enabled recommendations to be made regarding treatment, handling, display and storage to improve the longevity of plastic objects in the collection. This paper will outline the survey process and results, including technical studies of the polymeric materials in a number of works in the collection with degradation issues.



Claes Oldenburg, False Food Selection (1966). Harvard Art Museums/Fogg Museum, Barbara and Peter Moore Fluxus Collection, Margaret Fisher Fund and gift of Barbara Moore/Bound & Unbound

POLY 96: Treatment and drying challenges in the conservation of waterlogged rubber gaskets and seals from the Civil War submarine *H.L.Hunley*

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The *H.L.Hunley* is the world's first successful combat submarine and also one of the most unique time capsules of our time. The pioneering Civil War submarine made history in 1864 when it sank the *USS Housatonic*. Shortly after, the *Hunley* and its crew of eight vanished. Lost at sea for over a century, the submarine was located in 1995 and raised in 2000. The *Hunley* was delivered to the Warren Lasch Conservation Center in Charleston, South Carolina for study and treatment. The interior excavation uncovered the remains of the crew and a wide array of artifacts that reflect life in the 19th century.

In order for the submarine to be completely water tight it was fitted with a series of rubber gaskets and seals. Due to the current conservation treatment of the submarine hull and desalination in alkaline solutions, the removal of any organic component including rubber was imperative.

To date, the conservation and archaeological teams have excavated an estimated 80 gaskets and seals from different sections of the submarine: viewing ports, flanges, pumps, hatches etc. These rubber components have been in direct contact with the iron plates and gear from the submarine thus the rubber have been found to be covered with iron corrosion products.

Analysis using Fourier Transform infrared spectroscopy (FT-IR) and Scanning electron Microscope (SEM) showed that the rubber gaskets and seals are in fact lined with cotton. In addition, components that are part of the vulcanization process were also identified using SEM-EDS and X-ray fluorescence (XRF). The conservation treatments and drying techniques challenges will be presented and discussed.



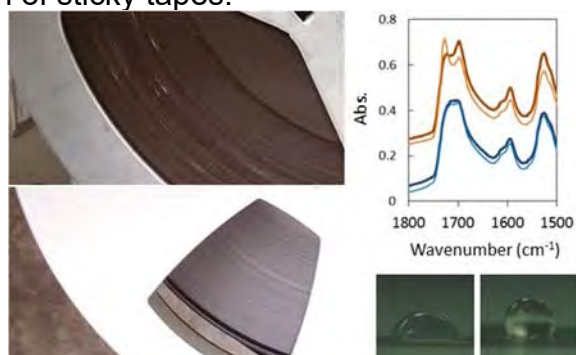
POLY 97: Thermal effects on the degradation and restoration of polyurethane-based magnetic media

Andrew Davis¹, adavi@loc.gov, **Eric B. Monroe**², **Fenella G. France**¹. (1) Preservation Research & Testing, Library of Congress, Catonsville, Maryland, United States (2) Preservation Research and Testing Division, Library of Congress, Gaithersburg, Maryland, United States

Researchers, audio engineers, and tape users have studied polyurethane-based magnetic audio tape degradation for decades, but uncertainties remain in the understanding of physical tape degradation and how to treat degraded tapes to enable their playback. Problems of squealing and shedding in old tapes, generally termed “sticky shed syndrome”, are most frequently remedied by prolonged baking at elevated temperatures. Despite its prevalence, many audio preservationists still express uncertainty about precise baking requirements and the full long-term effects of baking. This work builds on prior knowledge of tape degradation processes by assessing degraded and non-degraded polyurethane-based test tapes available at the Center for the Library’s Analytical Scientific Samples.

The material-level and physicochemical properties were evaluated for a range of at-risk tapes, including major and popular tape brands, both before and after exposure to typical baking conditions. Of particular interest were sticky/non-sticky “twins” of the same tape model. Thermal analysis tools were used to examine the glass transition temperatures, polymer/lubricant crystallinity, and additive volatilization in polyurethane-based tape binders and backings. Additional measurements assessed the volatile organic compounds within the tapes using mass spectroscopy, chemical functionality using reflectance spectroscopy, and surface energy effects using water contact angle. These properties served as an indicator of the condition of the tapes’ urethane binder layer and were found to have some similarities and some unexpected differences following thermal treatment.

While certain models of tape are known to be particularly vulnerable to degradation, the exact condition and playback performance still varies between individual tapes. Learnings from these lab-scale experiments are now being paired with playback and on-deck evaluation of test tapes in order to provide practical guidance in persevering audio materials. In particular, these efforts aim to inform improved methods for the rapid non-destructive identification of sticky tapes.



POLY 98: Extinct and endangered polymers in cultural heritage materials

Elissa O'Loughlin, newpondstudio@gmail.com. Private consultant, Seaford, Delaware, United States

The potential loss of some polymeric materials, their sources and methods of manufacture, is a little recognized but consequential occurrence. Examples of polymeric materials are presented as extinct or endangered substances. Chemical and working properties of the "lost" polymers are unmatched with today's equivalents. War, economics, scarcity of raw materials and loss of expertise are factors in the trend. Some rare polymers exist only in research settings. Nikawa, an animal glue, is vital to Japanese artistic production. Mechanization changed production methods; alternatives supplanted traditional raw materials. In 2014 the last traditional maker ceased production. Modern production methods both remove components and introduce contaminants that affect valued working properties. The technology is now thought to be lost. Isinglass is a proteinaceous substance derived from the swim bladders of Baltic sturgeon. Extirpated in its home waters, small extant populations are endangered. Used in icon production, as an adhesive and a binder, it is used by art conservators for the consolidation of flaking surfaces. Sources are extremely limited, of varying quality, and have been adulterated with synthetic resins. It is prized for its adhesive strength, optical properties, and long term stability. Dragon's blood, a tree resin, renowned for its brilliant red transparent color, was used in many artistic forms. Specimens from the island of Socotra are threatened by the current war in Yemen. Also used as a medicinal and described by Pliny, current pharmacoepic research may bolster its survival. Cellulose acetate, a modified cellulose, will change irrevocably in composition. Phthalate plasticizers are being replaced with less toxic equivalents. It was used as a lamination film and in animation art. Polymers are themselves cultural heritage materials; their loss diminishes our understanding of many forms of human endeavor.



POLY 99: Teaching polymer chemistry to art conservation graduate students

Rebecca Ploeger, ploeger@buffalostate.edu. *Art Conservation, SUNY Buffalo State, Buffalo, New York, United States*

A common concern expressed by incoming art conservation graduate students is the disconnect they felt between their traditional undergraduate chemistry courses and the field of art conservation, and how this would be addressed in the science curriculum. All art conservation graduate programs in the United States require chemistry prerequisites; the program at Buffalo State requires both organic and inorganic chemistry I and II (including lab) coursework for chemistry majors. All programs have their own strategies for dealing with this disconnect, and this paper will focus on how this issue has been tackled at Buffalo State, in specific reference to the Polymers in Art and Conservation course.

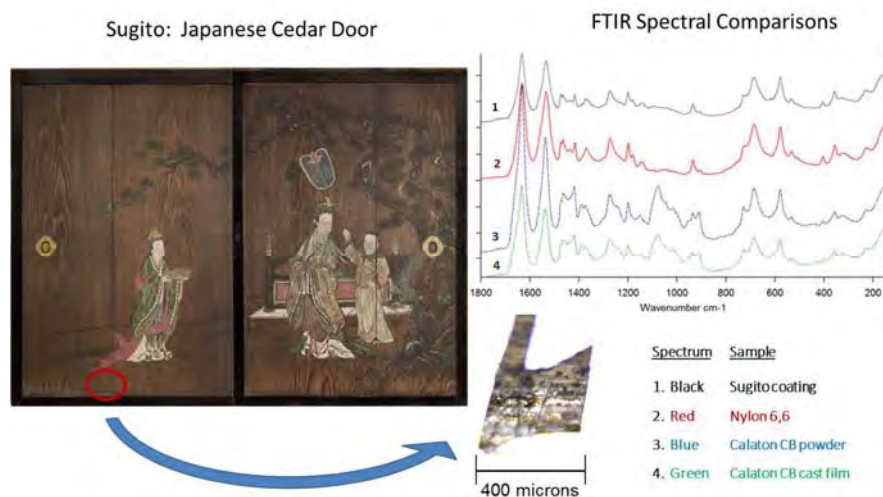
Although the Buffalo State graduate program does not have a specialization in conservation science or imaging and documentation, both underpin and run parallel to all conservation training disciplines throughout the entire program. Polymers in Art and Conservation is their first science class, and is a fast-paced introduction to polymers, including nomenclature, chemistry, physics, degradation, identification, and characterization of polymers used to create and treat works of art. Conservation students are often tactile learners, so whenever possible, hands-on demonstrations are incorporated in the lectures, and concepts are further solidified in the lab. There is also a term-project – the “mystery polymer project” where in the first week students select a degraded polymeric object and carry it with them over the term, and link lecture topics to the state of the object. By the end, they will have identified the polymer using scientific analysis, analyzed the type of degradation (and why it occurred), and suggest conservation treatment options. The mystery polymer project has been successful in making the visual and tangible connections between chemistry and cultural heritage that the students were lacking in their pre-program coursework, and every year has generated positive feedback from the students.



POLY 100: Investigation of a soluble nylon applied to Japanese *sugito*

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A polymer coating was applied to 20 Japanese *sugito* (cedar doors) in the Philadelphia Museum of Art (PMA) during the 1960s to protect and consolidate their elaborate painted decorations. The pair shown below, titled *Queen Mother of the West*, measure 161.9 × 219.7 cm. The polymer used is referred to as soluble nylon in the art conservation literature; one product was sold by Imperial Chemical Industries, Ltd. (ICI) under the tradename Calaton CB. Although soluble nylon was favored for its flexibility, clarity and adhesive properties, it is no longer used as it ages poorly and becomes insoluble. Coating and paint samples from the doors were studied by FTIR, Raman and other techniques. Calaton CB is a derivative of nylon 6,6. Partial N-methoxymethylation of nylon 6,6 results in a polymer soluble in methanol in contrast with the highly insoluble nylon 6,6. Calaton CB samples were obtained from the Winterthur Museum, Getty Conservation Institute, and other sources. Calaton CB cast films also are being investigated and compared with both commercial nylon 6,6 and the *sugito* samples. The four infrared spectra shown below illustrate both major similarities and minor (but significant) spectral differences between nylon 6,6; Calaton CB powder; Calaton CB cast film; and the soluble nylon on the *sugito*. There is little change between the powder and cast film (to date); aging studies are in progress. The spectral changes observed in the *sugito* samples may be influenced by the underlying binder and/or pigments, but the spectral similarity to nylon 6,6 is clear. This investigation also is of significance internationally as comparable *sugito* in Nagoya and Nijo Castles, Japan are national treasures and therefore their decorations cannot be sampled.

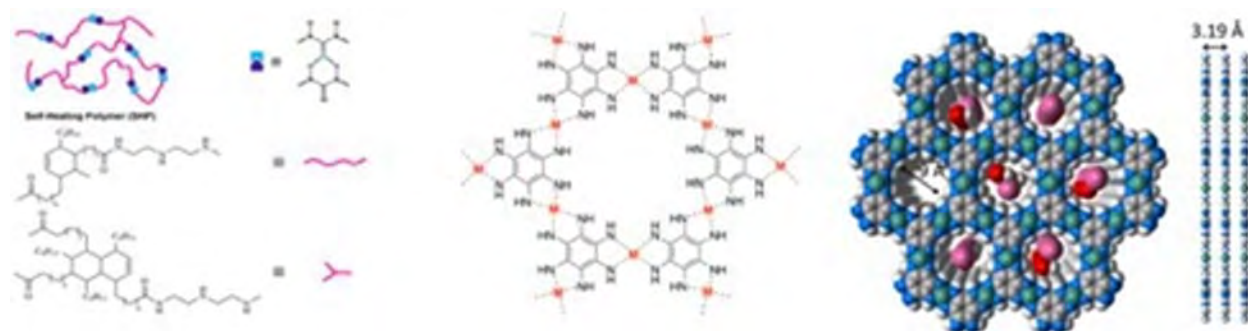


Above left: *Queen Mother of the West* (PMA: 1966-211-17a,18a, purchased with the Fiske Kimball Fund & the Marie Kimball Fund, 1966). Sampling area (red circle) and sample (400 microns). Right: FTIR spectra (1800 - 150 cm^{-1}) of 1) *sugito* polymer coating (black/dot line), 2) nylon 6,6 (red/solid line), 3) Calaton CB powder (blue/dot-dash line), and 4) Calaton CB cast film (green/dash line).

POLY 101: Organic materials for energy storage

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In this talk, I will present self-healing materials and conductive metal-organic framework design, synthesis and application in energy storage.



POLY 102: Transport in confined polymer films: How chemically amplified photoresists at IBM spawned a decade of thin film transport research at NIST

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A little over a decade ago Dr. Qinghuang Lin from IBM came to NIST with concerns about the performance of their chemically amplified photoresist systems. At the time, the thickness of these polymer based films was starting to push below 200 nm and there were significant concerns about deviations in their performance / resolution as the film thickness continued to drop. This was a time when in the scientific literature that there was significant debate over deviations in the glass transition temperature for polymer films thinner than 100 nm. The lithographic community was worried about the ramifications that this might have on the patterning resolution of their critical photoresist formulations. In response, through a DARPA grant with IBM, NIST helped to develop a suite of tools that could quantify both the spatial and temporal extend of photoacid reaction and diffusion in these thin film photoresist tools, thereby establishing quantitative platform to understand thin film effects on photoresist performance. This was a seminal catalyst for the NIST research programs, shifting our focus from simple transition effects in thin film to more complicated transport properties. In the decade and a half that followed, NIST has leveraged these tools to address transport problems in confined polymer films and interfaces in not just chemically amplified photoresists, but also water transport in polymer films and interfaces for membranes and composites, viscous flow in nanoimprint lithography, ion diffusion in polyelectrolyte interfaces, and even the freeze-drying processes used to preserve proteins in viscous sugars and alcohols. In this presentation, I will review several of these advances and highlight some of the general observations that we have learned about transport in confined polymers that was spawned by Dr. Qinghuang Lin's initial inquiry.



POLY 103: Lyotropic liquid crystalline conjugated polymers with directed self-assembly and alignment capability for plastic electronics

Jinsang Kim¹, *jinsang@umich.edu*, **Bong-Gi Kim**², **Kyeongwoon Chung**¹, **Da Seul Yang**¹, **Jongho Kim**³, **Geun Seok Jang**³, **Jong Won Chung**⁹, **Eun Jeong Jeong**¹, **Min Sang Kwon**⁴, **Bonwon Koo**⁹, **Sungbaek Seo**⁸, **Maciej Barlog**⁵, **Taek Seung Lee**⁶, **Mohammed Al-Hashimi**⁷. (1) University Michigan, Ann Arbor, Michigan, United States (2) Organic & Nano System Engineering, Konkuk University, Seoul, Korea (the Republic of) (3) Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon, Korea (the Republic of) (4) Materials Science and Engineering, Ulsan National Institute of Science and Engineering, Ulsan, Korea (the Republic of) (5) Chemistry, Texas A&M University at Qatar, Education City, Qatar (6) Chungnam Natl Univ, Daejeon, Korea (the Republic of) (7) 351I Texas AM Eng Bldg, Texas AM University at Qatar, Doha, Qatar (8) Biomaterials Science, Pusan National University, Miryang-Si, Korea (the Republic of) (9) Samsung Advanced Institute of Science and Technology, Suwon, Korea (the Republic of)

Conjugated polymers have been used for various optoelectronic applications, such as organic solar cells, thin film transistors, and light emitting diodes. Their optical and electronic properties, such as absorption, emission, and conductivity, are highly anisotropic due to the 1-dimensional p -orbital overlap along the conjugated polymer backbone. Therefore, unless conjugated polymers are assembled and aligned with a well-defined structure, their optical and electronic properties cannot be fully realized in their device applications. In reality, however, the directed assembly and particularly macroscopic alignment of CPs is a challenging task. Recently, our group investigated molecular design for directed alignment of CPs, and realized anisotropic optoelectronic properties from aligned CP films. When CPs satisfied three identified design rules; (1) concentration-induced planarization unit, and (2) bulky side chains linked to (3) a tetrahedral carbon, CP chains are readily aligned to the direction of flow field and exhibit a high dichroic ratio. The developed molecular design principle and application of lyotropic liquid crystalline conjugated polymers (LC CPs) having directed self-assembly and alignment feature will be discussed. Thin film transistors built on highly aligned such CP films showed more than three orders of magnitude faster carrier mobility along the CP alignment direction than the perpendicular direction. The established molecular design principle for directed alignment of CPs is readily applicable to many useful CP developments for various optoelectronic devices and to achieve the full realization of the anisotropic properties of CPs in devices such as photovoltaic cells.

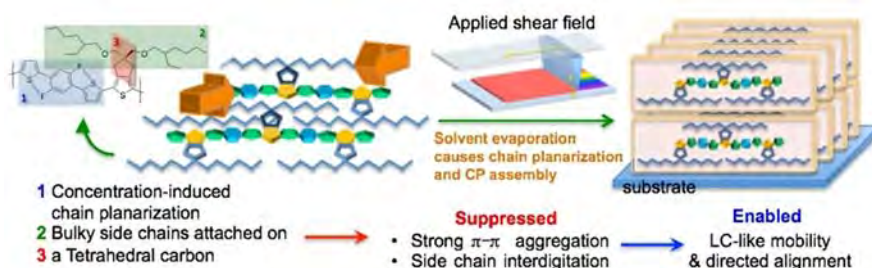
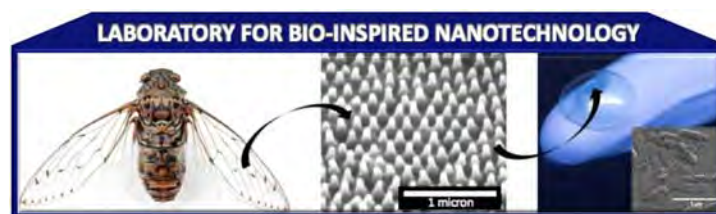


Fig. 1. Schematic illustration of the directed alignment mechanism through the regulated chain planarization, self-assembly, and directed alignment along shear direction. Reference: B.G. Kim et al Nature Materials 2013, 12, 659 & Kyeongwoon Chung et al Manuscript submitted.

POLY 104: Investigating antimicrobial properties of nanotextured surfaces for wound bandages against resistant infections

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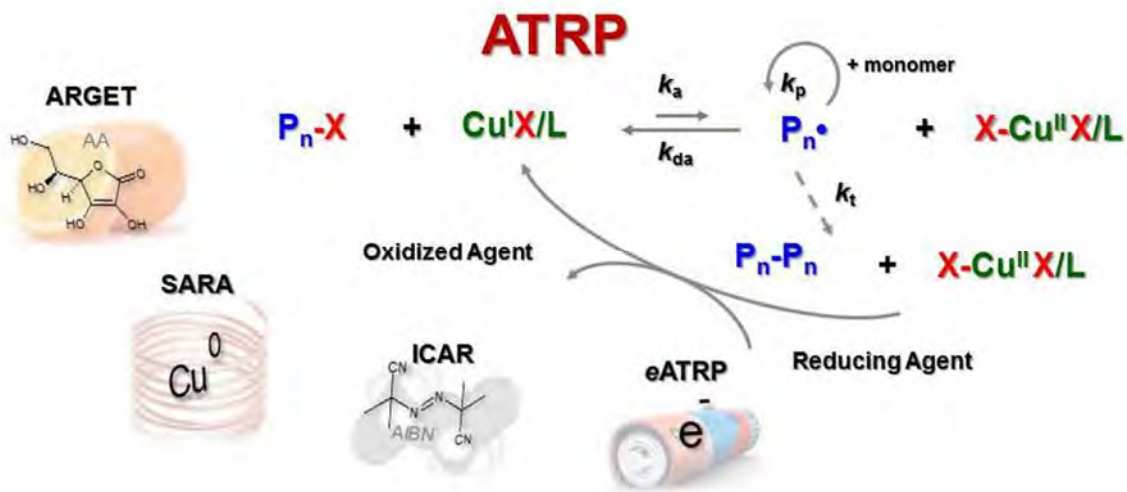
Some of the new research that Qinghuang Lin is proposing to embark on are biocompatible packaging materials and transport of biopolymers through nanoporous media. The research I present may have synergism. Human pathogenic bacteria and fungi often populate environments where nutrient rich fluid is present in the static and flow state. Invasive bacterial and fungal infections were observed among US military personnel with combat-related injuries in the past decades. These infections develop after a traumatic blast-related penetrating injury and, for treatment, are shielded with dermal or ocular bandages coupled with antimicrobial agents. During treatment, bacteria and fungi can develop resistance against antibiotics and antifungals causing further infections. In this research, we culture antimicrobial resistant bacteria, *P. aeruginosa*, and clinical isolates of fungi, *A. fumigatus* and *F. oxysporum*, *in vitro*, on flat and engineered nanotextured surfaces on materials used in medical devices such as bandage contact lenses. Nanotextured surfaces of pillar arrays with varying periodicities were fabricated using nanoimprint lithography. Both static and fluid flow environments for drug resistant microbes were replicated using culture dishes and microfluidic channels respectively. In static environments, a decrease in *P. aeruginosa*, *A. fumigatus*, and *F. oxysporum* cell growth and an increase in cell death were observed on the nanotextured surfaces compared the flat. In fluid flow environments where *P. aeruginosa* upstream cell motility and infectious biofilm formation occur, a decrease in cell motility and attachment were observed on the nanotextured surfaces compared to flat. These antimicrobial properties of the nanotextured surfaces present a promising coating for dermal and ocular wound bandages against resistant bacterial and fungal infections.



POLY 105: Commercial aspects of ATRP

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu*. CMU, Pittsburgh, Pennsylvania, United States

Atom transfer radical polymerization (ATRP) is a versatile controlled radical polymerization procedure employed to prepare new block, gradient, graft, star, brush and branched functional copolymers that find applications as various new advanced functional nanostructured materials. Some examples of commercial applications of ATRP in large and small companies will be presented.

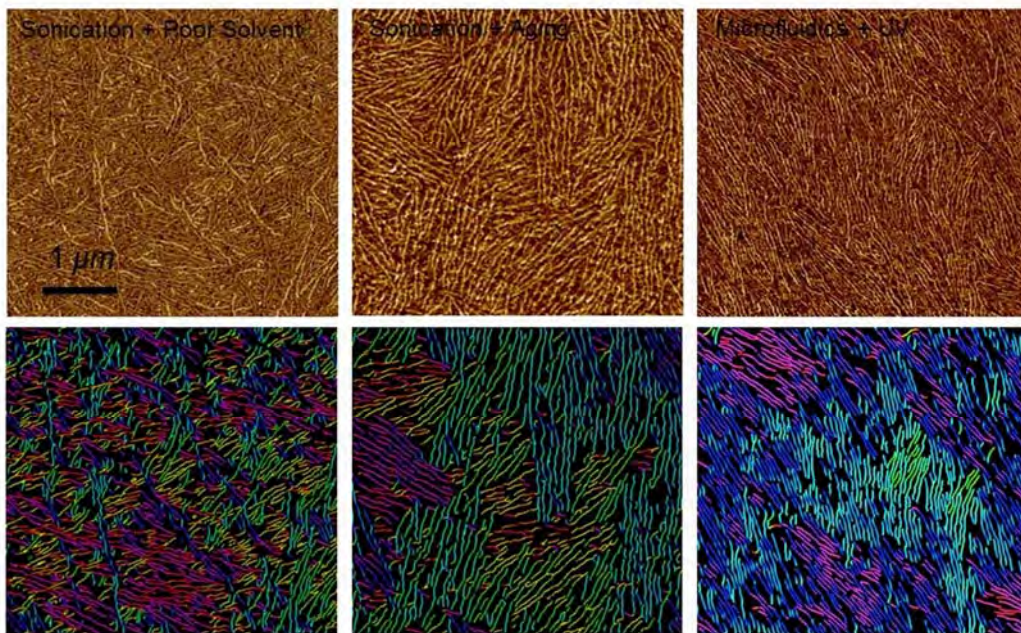


POLY 106: Polymer fibrils, transport pathways and stretchable electronics

Elsa Reichmanis, elsa.reichmanis@chbe.gatech.edu, Guoyan Zhang, Michael McBride. Georgia Institute of Technology, Atlanta, Georgia, United States

Simultaneous enhancement of the electrical performance, mechanical stretchability, and optical transparency of conjugated polymers may significantly broaden the spectrum of realizable applications for these materials in future intelligent optoelectronics, i.e., wearable devices, electronic skin, stretchable displays, and a vast array of biomedical sensors. The successful introduction of these devices however, relies on the design and development of sustainable, robust and reliable materials and processes. Studies have shown that not only does device performance depend critically on semiconductor alignment at many length scales, materials' mesostructure can be manipulated in solution prior to device fabrication. Observations surrounding the behavior of these materials suggest that requisite macroscopic long-range order required for high performance devices may be achieved through process optimization coupled with quantitative analysis of processed semiconducting thin film images. This approach allows development of robust materials structure-process-property relationships that can then be used to guide subsequent materials selection and process approaches. This presentation will explore how we can derive critical insights into the structure-process-property space using well-coupled modeling and experimental approaches, and how those can impact the design and development of all-printed, stretchable electronic devices.

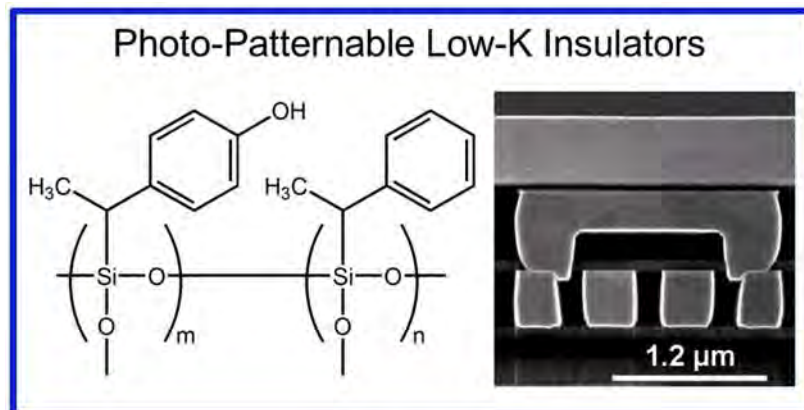
Solution assembly and impact on morphology



POLY 107: Industrial Polymer Research for Nanoelectronics

Qinghuang Lin, qhlin@us.ibm.com. MS 6-250, IBM T J Watson Rsrch Ctr, Yorktown Heights, New York, United States

Modern semiconductor microchips are the brain of the Information Age and the engine of new knowledge-based economy. These ubiquitous and sophisticated microchips have fundamentally changed how we live, work, learn, communicate, do business, and interact with government. The steady increase in computing power resulting from these microchips, coupled with big data and advances in algorithms, has ushered in a new artificial intelligence (AI) era in the last few years, with stunning performances of some artificial intelligence computing systems, e.g. AlphaGo by DeepMind. Polymers have played a crucial role in enabling the ever smaller, faster and cheaper and more efficient transistors for over fifty (50) years. In this talk, I will discuss a class of polymers called silicon-containing polymers as an enabling material platform for modern microchip manufacturing. I will present synthesis of silicon-containing polymers and their applications as three types of electronic materials: (1) photosensitive polymeric materials, called photoresists, used to “print” modern microchips; (2) on-chip electrical insulators prepared either by a dry chemical vapor deposition or a wet spin-on process; (3) photo-patternable on-chip low dielectric constant electrical insulators. These silicon-containing polymers have been commercialized and adopted for high-volume manufacturing of several generations of microchips. They have also enabled new chip-making technologies that are indispensable for making some of the most popular electronic devices in the world today.

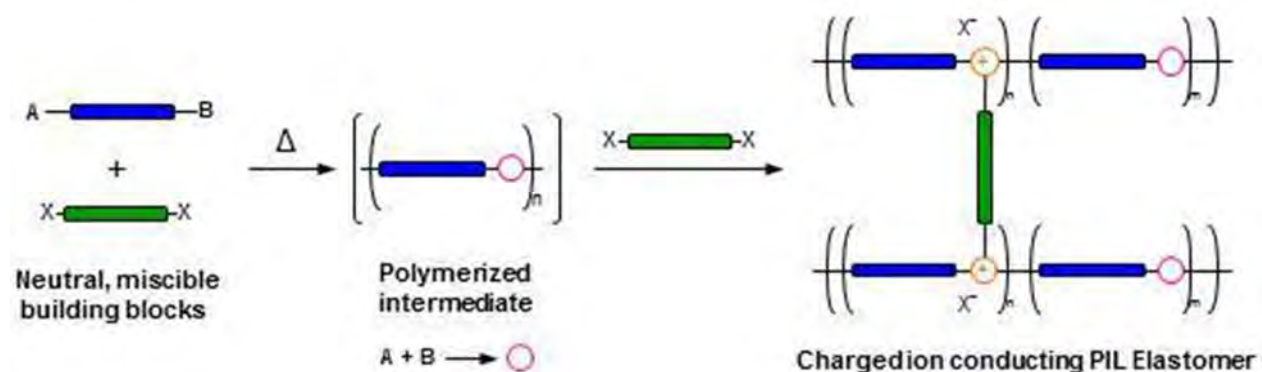


POLY 108: Ionic vitrimers through trans-*N*-alkylation covalent exchanges

Mona Obadia¹, Antoine Jourdain¹, Damien Montarna², **Eric Drockenmuller¹**,
eric.drockenmuller@univ-lyon1.fr. (1) IMP@LYON1, Lyon, France (2) C2P2,
Villeurbanne, France

We have developed ionic vitrimers that take inspiration from poly(ionic liquid)s which are unique polyelectrolytes with cationic and anionic groups included in the repeating unit. A broad library of ionic vitrimers have been prepared by the solvent- and catalyst-free polymerization of different α -azide- ω -alkyne monomers and concomitant *N*-alkylation of the resulting poly(1,2,3-triazole)s with a series of difunctional cross-linkers.

Temperature-induced trans-*N*-alkylation exchanges between 1,2,3-triazolium cross-links and halide-functionalized dangling chains enable to recycle and reprocess these highly cross-linked permanent networks. These vitrimers can also be recycled by depolymerization with specific solvents able to displace the trans-*N*-alkylation equilibrium, and display a great potential for applications that require solid electrolytes with excellent mechanical performances and facile processing such as supercapacitors, batteries, fuel cells and separation membranes.



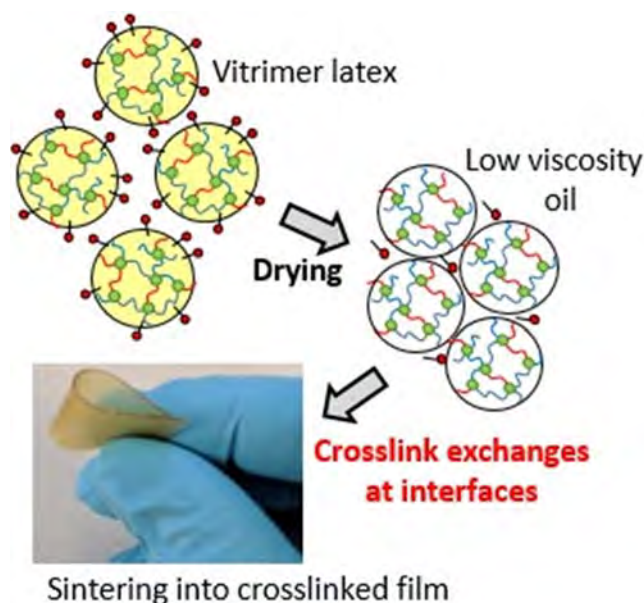
POLY 109: Formation of crosslinked networks through sintering of vitrimer nanoparticles

Damien Montarnal, damien.montarnal@univ-lyon1.fr, Elodie Bourgeat-Lami, Thi Tran, Eleanor Rawstron. University of Lyon - CNRS - CPE Lyon - Laboratory of Chemistry, Catalysis, Polymers and Processes., Lyon, France

Crosslinked networks constitute an outstanding class of polymer materials in which chemical bonds maintain a tri-dimensional permanent structure anchoring the polymer chains together. In comparison to thermoplastics made of linear polymers, crosslinked polymers display therefore far superior thermo-mechanical properties and solvent resistance, but are essentially intractable: after curing they adopt a permanent shape and cannot be further processed nor recycled. Vitrimers invented in 2011 aim at overcoming these drawbacks by incorporating in the networks dynamic covalent crosslinks governed by reactions in chemical equilibrium.[1] At high temperatures or in the presence of catalysts, chemical equilibria are fast enough to enable large scale reorganisation of the network and therefore stress relaxation and plastic deformation of the polymer. Yet, the network remains permanently crosslinked at all times.

This very versatile concept has been successfully applied to different polymer systems taking advantage of a variety of well-known equilibrated reactions.[2] Yet, polymerization methodologies and processing of vitrimers are currently limited to bulk materials.

We will discuss the first syntheses of vitrimer latexes by waterborne miniemulsion polymerization. This versatile strategy enables obtaining stable polyhydroxyester-based cross-linked particles from epoxy-acid, initially incompatible precursors, while minimizing hydrolysis of the ester bonds formed during the curing. After drying of the latexes, trans-esterification exchanges occurring at high temperatures through interparticle interfaces induces an efficient sintering into homogeneous cross-linked polymer films[3]



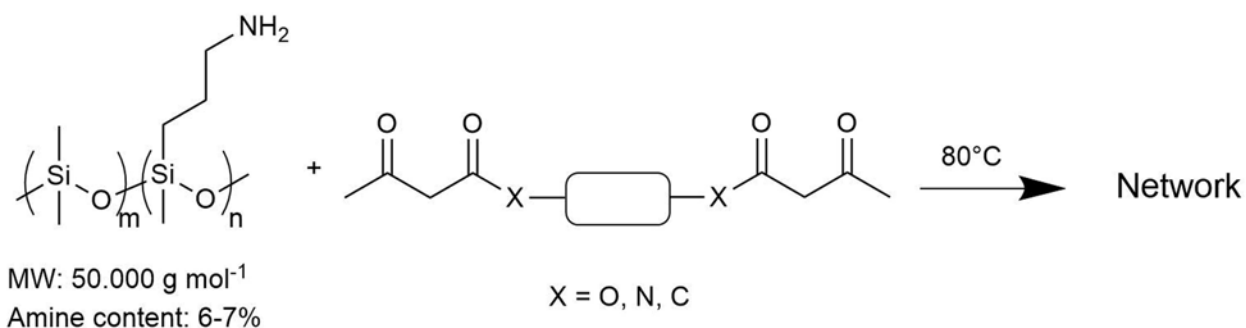
POLY 110: Reprocessable rubbers from PDMS vitrimers

Yann Spiesschaert, Yann.spiesschaert@UGent.be, Lucie Imbernon, Filip E. Du Prez.
Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Ghent, Belgium

Vitrimers are a new class of crosslinked polymeric materials that can be thermally processed in a viscous liquid state (through network rearrangements) without losing network integrity. This feature renders the materials processable like vitreous glass, without the need for moulds or precise temperature control. In this context, the vinylogous acyl exchange reaction has proven to be a robust, catalyst-free reaction that results in exceptional high- T_g vitrimer materials. The possibility to utilize the vinylogous urethane chemistry in PDMS was already proven, however, the obtained properties were still sub optimal. Here, the influence of the different vinylogous acyl exchange reactions was investigated as to have a better control on creep and on the processing conditions (Figure 1), followed by the investigation of fillers in order to improve the obtained mechanical properties.

First, a model study was performed to investigate the influence of an additive on the rate of the exchange reaction. Secondly, vinylogous acyl containing crosslinked PDMS rubbers were synthesized. Different characterization methods such as tensile test, IR or rheology were used to study those networks' mechanical properties and ability to undergo network rearrangements.

The obtained results could be an important step towards the spreading of vitrimer-like properties throughout other known crosslinked materials.

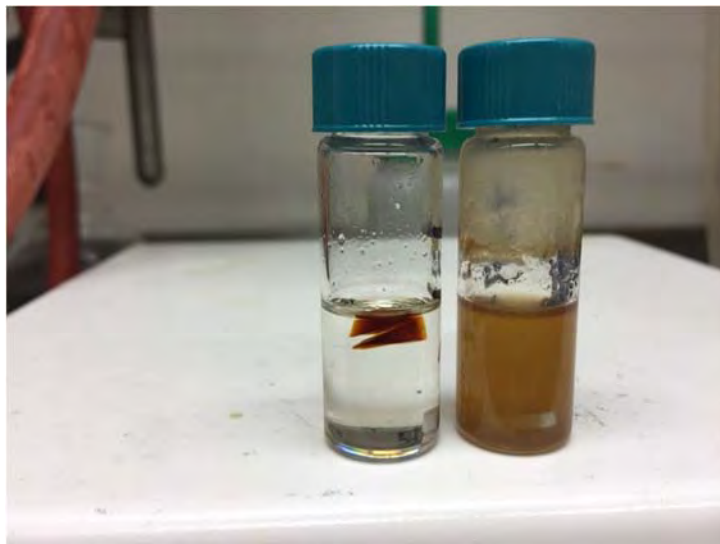


Strategy for the synthesis of PDMS vitrimers.

POLY 111: Vitrimers can be dissolved into cyclic molecules via dynamic bond exchange

Junpeng Wang¹, wangjp.duke@gmail.com, Jeremiah A. Johnson². (1) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Vitrimers are a type of thermoset materials whose stress-relaxation behavior can be controlled from the dynamic bond exchange at elevated temperature. Because of the associative nature of the bond exchange reactions, vitrimers are typically considered to be insoluble even at high temperature. Here we demonstrate that a vitrimer, whose dynamics is contributed by transesterification, can be dissolved at elevated temperature when sufficient catalyst for transesterification is added. Large amount of cyclic molecules can be found in the dissolved product. We anticipate the formation of loops via dynamic bond exchange can be applied to tune mechanical properties of thermoset materials.

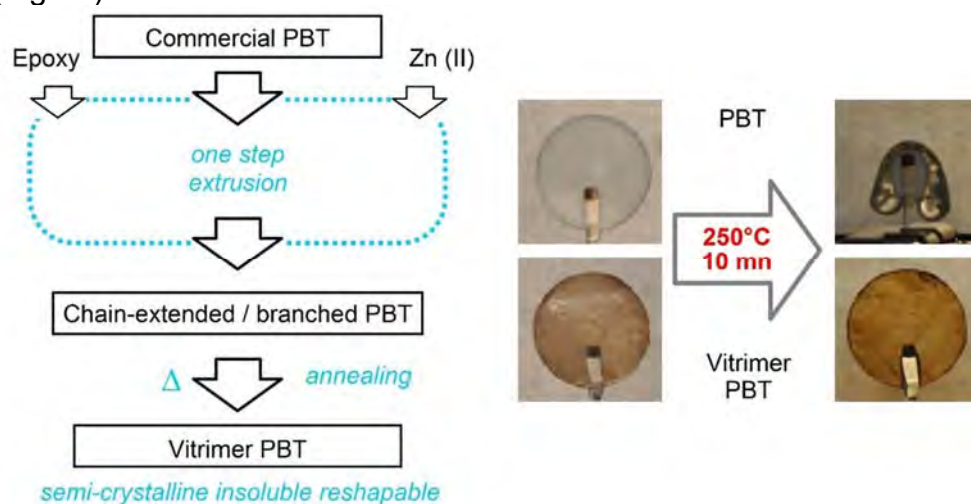


POLY 112: Epoxy and polyester-based vitrimers and composites

Francois Tournilhac, francois.tournilhac@espci.fr. Soft Matter and Chemistry, ESPCI - Paris, Paris, France

Vitrimers, invented in 2011 by the group of Leibler, were first based on exchangeable links by transesterification and implemented by using classical epoxy chemistry. As epoxies are ubiquitous in high performance composites, a first question addressed here is to examine to what extent the original properties of vitrimer are maintained in materials containing more than 50% by weight of reinforcing fibers. To answer this question, we analyze quantitatively the bond strength of epoxy vitrimer based composite plates made by resin transfer molding and compare them to their non-vitrimer counterparts made of a standard thermoset epoxy, It is demonstrated that only epoxy vitrimer samples show substantial bond strength and the ability to be repeatedly welded thanks to the exchange reactions which promote improved surface conformity and chemical bonding between the adherands at the joint interface. This opens the way towards joining composite parts without adhesives nor mechanical fasteners.

Polybutylene terephthalate, PBT is characterized by a high degree of crystallinity, a high melting point and rapid crystallization. One of its limitations is that just above the melting point (230°C) any mechanical strength disappears and the polymer tends to drip under its own weight. In demanding applications, it is necessary to use crosslinked PBT but the existing crosslinking processes are complex and the polymer obtained is not recyclable. In the process that we envisioned, PBT is modified by epoxy resins in the presence of a transesterification catalyst, directly into an extruder. To devise an effective formulation we studied in detail the exchange reactions and catalysis in model systems and in the polymer. The polymer thus obtained maintains the essential properties of a semi-crystalline thermoplastic polymer and acquires the new properties of vitrimers such as heat resistance, mechanical strength and solvent resistance. Transformation of ordinary PBT into a vitrimer could open up new areas of application for PBT (Figure).

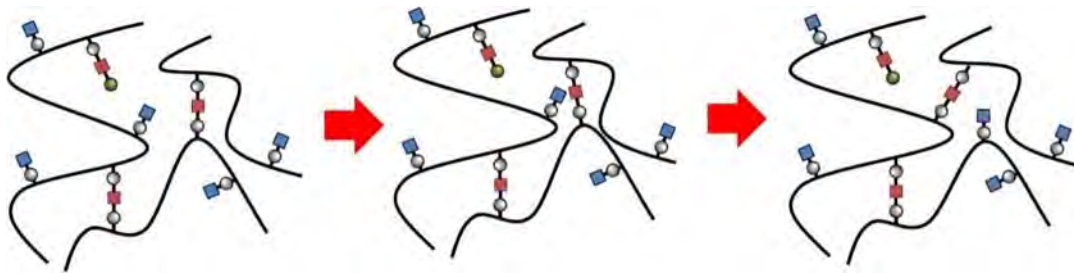


Transformation of standard PBT into a vitrimer showing improved of thermal resistance.

POLY 113: Transforming thermoplastics into vitrimers

Renaud Nicolay, renaud.nicolay@espci.fr. Matière Molle et Chimie, ESPCI ParisTech, Paris, France

Vitrimers are chemically cross-linked networks that can rearrange their topology without decreasing their cross-linking density thanks to exchangeable links present in the network. As a result, vitrimers can be reshaped and recycled at will while being insoluble at every temperature. In this presentation, the design and synthesis of vitrimers made of polymers prepared by chain-growth polymerization will be discussed. Their synthesis in solution or in the melt, using reactive processing, as well as their ability to be processed multiple times with thermoplastic techniques will be presented. Finally, the thermomechanical and chemical resistances of these vitrimers will exemplified and compared to that of their thermoplastic precursors.



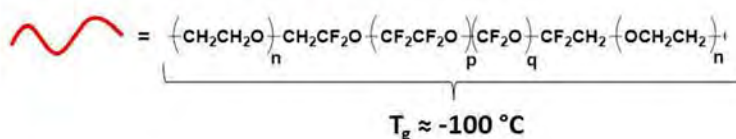
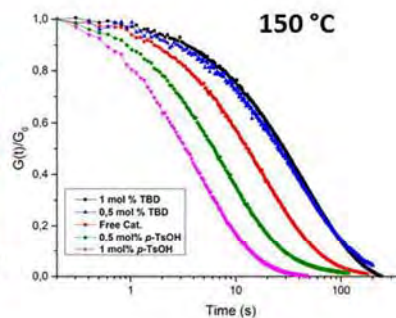
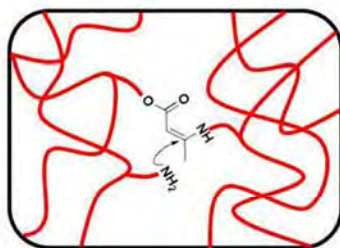
POLY 114: Low T_g fluorinated vitrimers for high performance applications

Marc Guerre, *marc.guerre@UGent.be*, Christian Taplan, Filip E. Du Prez. Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Ghent, Belgium

In 2011, a new type of materials combining both thermoplastic and thermoset properties was invented, *vitrimers*, now already referred to as *the third type of plastics* and receiving world-wide industrial and academic attention. The huge enthusiasm in vitrimers originates from the fact that they combine the best of both polymer classes. By incorporation of exchangeable covalent linkages into a polymer network, *dynamic crosslinks* can be formed above a certain temperature. These vitrimers can therefore be thermally processed, reshaped and recycled without losing network integrity. Besides, the design and synthesis of superior polymeric materials with excellent combination of chemical and physical properties has triggered research on fluorinated polymers, leading to immediate acceptance in commercial products for various markets in which no other polymeric materials can really compete: coatings (Teflon), energy storage (batteries), lithography and many others. Although fluorinated materials are indispensable for certain added value applications, the wider uses of fluorine-containing materials are still hampered by their production cost, complexity of synthesis, toxicity and difficult processability.

Here, the reported materials are the first example of fluorinated low T_g materials (-100 °C) exhibiting vitrimers properties. A catalyst-free transamination of vinylogous urethane has been successfully used as associative dynamic chemistry platform. A straightforward and one-pot solvent-free network synthesis has been reported. Transparent Perfluoropolyether-based vitrimers can be recycled multiple times at 140 °C with extremely short time scale (few seconds), and materials recovered 90 % of the original mechanical properties. Viscoelastic and mechanical properties can also be tuned by the addition of additives and adjusting crosslinking density.

140 °C, 5 min, 1 ton



Transamination of vinylogous urethane of PFPE-based network (recycling and stress relaxation experiments with additives at 150 °C)

POLY 115: Catalyst-free vitrimers from vinyl-derived polymers

Jacob J. Lessard, jjlessard@chem.ufl.edu, Luis F. Garcia, Charles P. Easterling, Michael B. Sims, Kyle C. Bentz, Scarlett Arencibia, Daniel A. Savin, Brent S. Sumerlin. Chemistry, University of Florida, Gainesville, Florida, United States

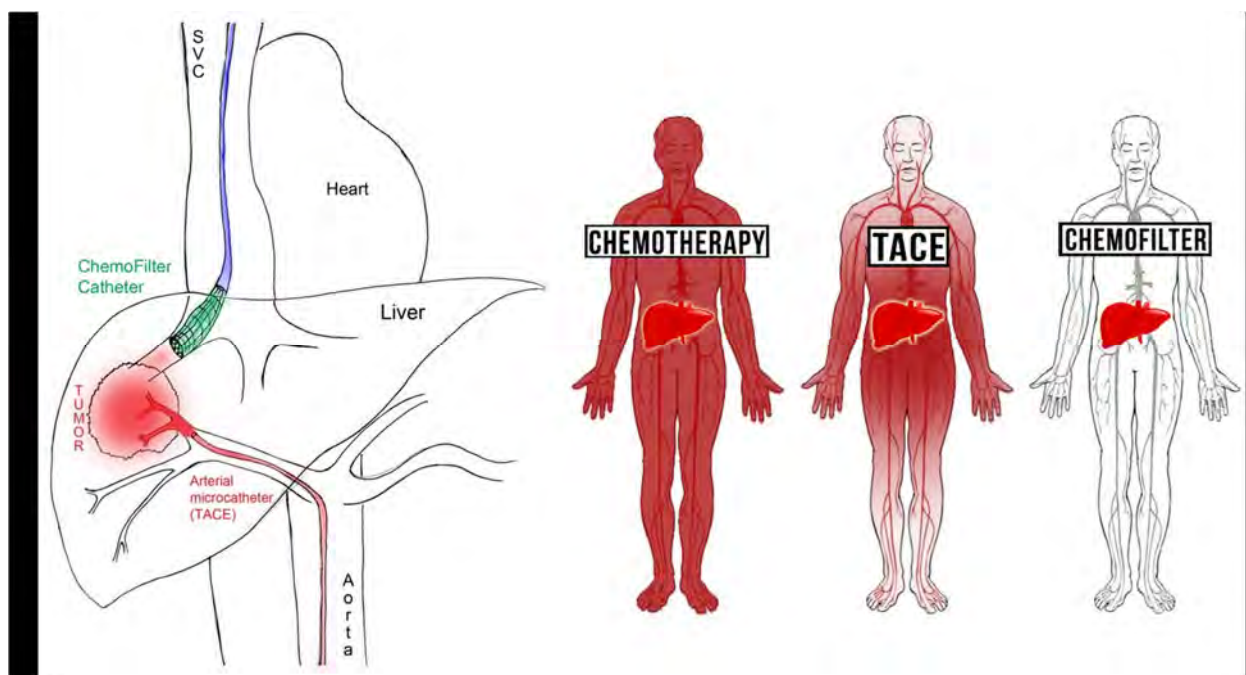
Vitrimers have grown in popularity partly because of their lack of creep at ambient temperatures and remarkable reprocessability. We propose a straightforward approach using commercially available monomers and crosslinker to design vitrimer materials from vinyl-derived prepolymers. The vitrimers we synthesized were (re)processed over a total of 6 compression cycles and were shown to maintain both mechanical and chemical properties.



POLY 116: Developing materials for drug capture: An approach to removing chemotherapy agents from the bloodstream

Michael D. Schulz¹, mdschulz@vt.edu, **Ophelia Wadsworth**¹, **Stephanie Oyola-Reynoso**¹, **Steven Hetts**². (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Radiology, University of California, San Francisco, San Francisco, California, United States

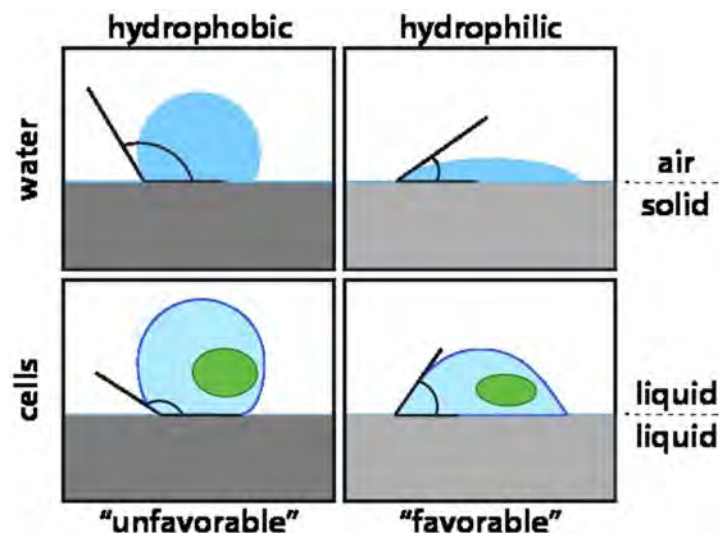
Chemotherapy agents are notorious for producing severe side-effects. One approach to mitigating this off-target damage is to deliver the chemotherapy directly to a tumor via transarterial infusion, or similar procedures such as transarterial chemoembolization (TACE), and then sequestering any chemotherapeutic in the veins draining the target organ before it enters the systemic circulation. To achieve this approach, we are developing materials that are capable of capturing this errant chemotherapy from the bloodstream. Ultimately, these materials will be used to construct a device (a "chemofilter") that can be depolyed via catheter "downstream" from the tumor, enabling off-target chemotherapy to be intercepted and sequestered before entering systemic circulation. Our approach involves the attachment of drug-capture materials to surfaces. One such drug-capture material is genomic DNA, which enables the capture of DNA-targeting chemotherapy agents. We have explored several methods of achieving DNA attachment and have investigated the ability of different materials to remove chemotherapy agents from biologically relevant solutions. We have observed effective drug capture from solution at clinically relevant concentrations and timescales, indicating that drug capture is a viable strategy for mitigating the harmful side-effects associated with chemotherapy.



POLY 117: Analysis and culture of cells at the interface between immiscible solutions of polymers

Christopher J. Luby², **Charles Mace**¹, charles.mace@tufts.edu. (1) Tufts University, Medford, Massachusetts, United States (2) Chemistry, Tufts University, Medford, Massachusetts, United States

Adhesion interactions at a biological interface—one formed between two cells or a cell and material—are influenced by the chemical properties (e.g., the display of functional groups or expression of an adhesion marker) and physical properties (e.g., stiffness of a surface or rheological properties of a cell) of each surface. Because chemistry and physics are intertwined at the cellular level, however, our current understanding of how they contribute to observed phenotypes is limited by the inability to address these properties independently. Further complicating the study of cell adhesion is the relatively narrow scope of materials that are available to biomedical researchers. Solid substrates (e.g., glass or plastic) are inexpensive and provide a number of experimental conveniences, but restrict cell growth and motility to a two-dimensional plane. Hydrogels and semi-solid matrices offer more accurate mimics of the three-dimensional cellular microenvironment, but complicate the recovery of cells and may originate from undefined or xenogeneic sources, which subsequently affects the reproducibility of an observation. Currently, no material exists that combines the advantages of both approaches to enable the broad study of cellular events that occur at and across interfaces. Here, we describe the use of an entirely liquid culture system to study cell adhesion. Aqueous multiphase systems (AMPS) are prepared from immiscible aqueous solutions of polymers, which produce stable liquid/liquid interfaces that act as scaffolds for the isolation, culture, and study of cells. We have developed an imaging technique, lateral microscopy, to facilitate the direct observation of cells at AMPS interfaces. The morphology of a cell at a liquid/liquid interface can be used to describe the relationship between its surface properties and the surrounding microenvironment in an analog to wettability. Overall, the use of AMPS will provide a new paradigm for the study of cell adhesion and the development of applications in cell organization and motility.

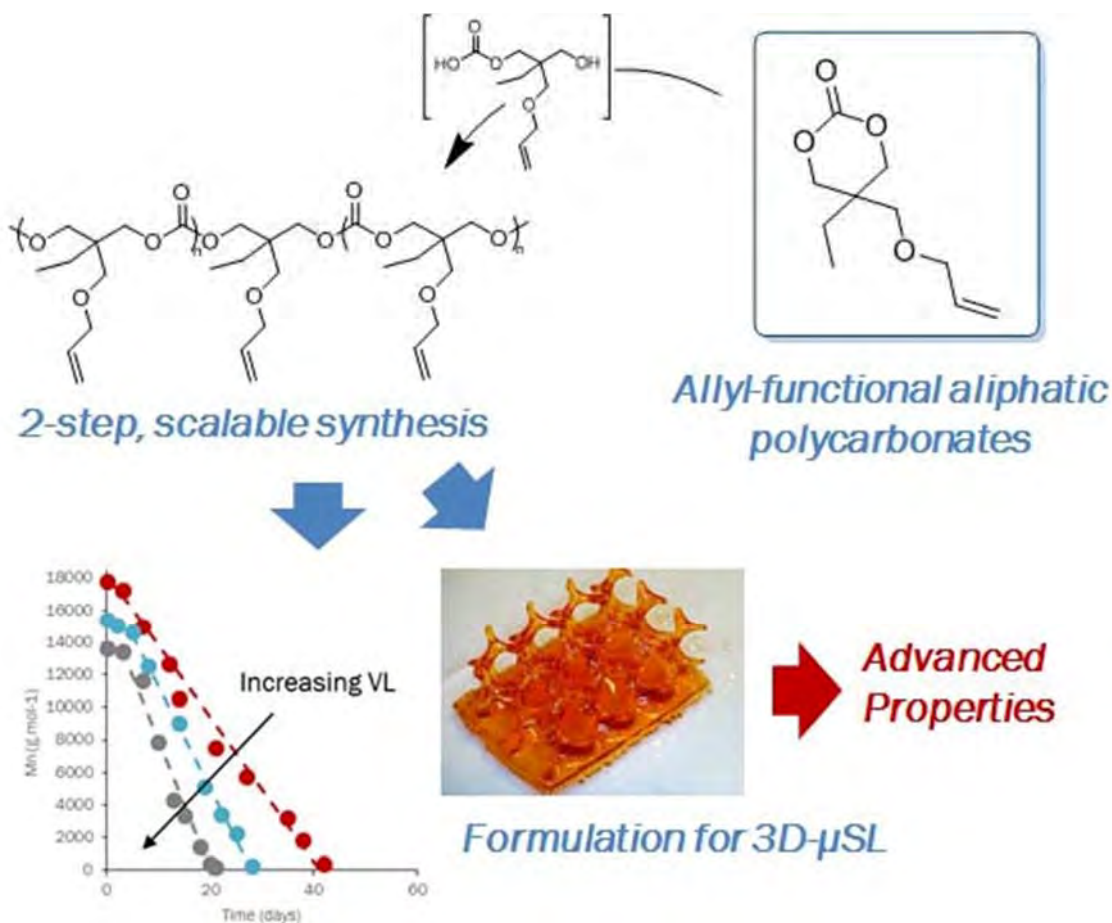


POLY 118: 3D printing of fully degradable materials

Andrew P. Dove, *a.dove@bham.ac.uk*. School of Chemistry, University of Birmingham, Birmingham, United Kingdom

A wide range of polymer materials can be constructed from a vast array of chemical resources. In a biomaterials context, careful design can elicit desired properties to interface with biological systems or even direct their behaviour. Our work focussed on the development and application of degradable biomaterials and sustainable polymers. These areas naturally compliment one-another. The richness of resource in terms of functional group provides ample opportunity to design new degradable materials with novel, targeted properties while simultaneously potentially providing a lower resistance to their eventual application from regulators.

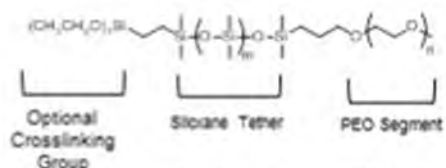
This presentation will focus on the design of aliphatic polycarbonate materials for biomedical applications through 3D printing. Specifically, we report the synthesis of new, functional polymers that can be crosslinked using light-activated chemistries to create printed materials with controlled micron-scale structures. We have focussed our efforts on expanding the scope of these materials to enable post-fabrication modification and infer advanced properties such as shape-memory properties



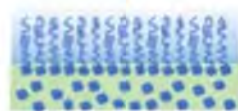
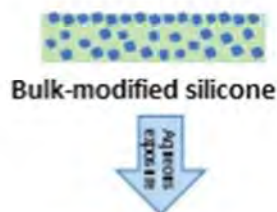
POLY 119: Amphiphilic silicones with broad-spectrum anti-fouling behavior

Melissa Grunlan^{1,2}, mgrunlan@tamu.edu, Bryan K. Ngo¹. (1) Biomedical Engineering, Texas AM University, College Sta, Texas, United States (2) Materials Science and Engineering, Texas A&M University, College Station, Texas, United States

Silicones, particularly silica-reinforced crosslinked polydimethylsiloxane (PDMS), are widely-used for medical and marine applications. However, silicone-based medical devices are prone to thrombosis and infection and silicone foul-release (FR) coatings represent have limited efficacy against marine organisms. The poor anti-fouling behavior of silicones is attributed to their extreme hydrophobicity. Thus, incorporation of a hydrophilic anti-fouling component to silicones may enhance resistance to biological adhesion. Although poly(ethylene oxide) (PEO) is known to be exceptionally anti-fouling (e.g. protein resistant), these observations have been largely made when PEO is grafted to a physically stable substrate (e.g. gold and silicon wafer). In this way, migration of the PEO to the water-surface interface, where biological adhesion occurs, is not required. In this work, we sought to enhance the water-driven surface-migration of PEO incorporated into silicones in order to achieve superior anti-fouling behavior. Conventional PEO-silanes consist of a PEO segment separated from the reactive crosslinkable group by a short alkane spacer. In contrast, we prepared PEO-silane amphiphiles with siloxane tethers of varying lengths and as well as variable PEO segment lengths. Amphiphilic silicone coatings were prepared by blending a silicone with the PEO-silane amphiphiles at different concentrations. The impact of amphiphile architecture as well as level of silica reinforcing filler on water-driven surface restructuring was assessed. The resistance of these amphiphilic silicone coatings to proteins, bacteria and marine organisms was evaluated.



PEO-silane amphiphiles to modify silicones

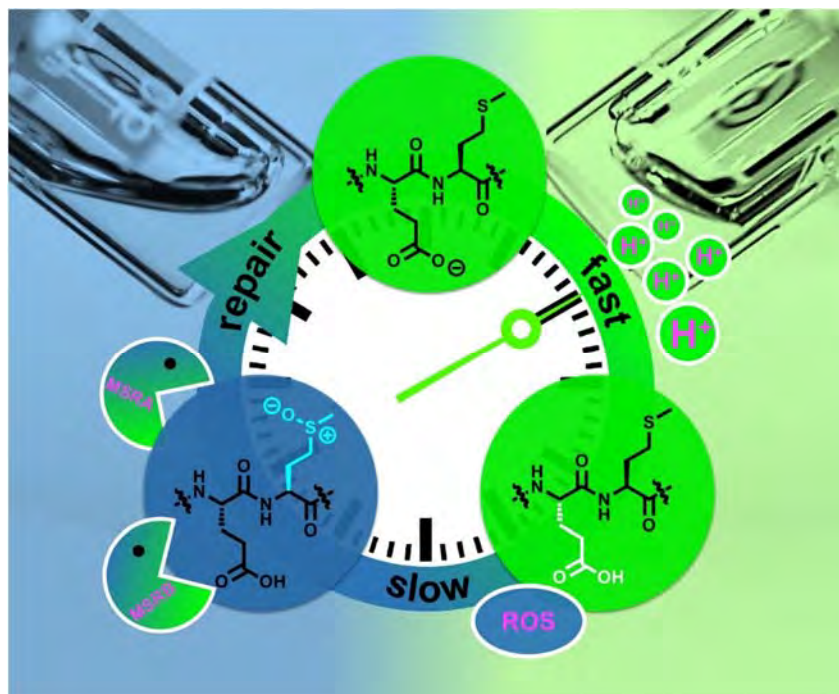


Substantial water-driven PEO migration
High anti-biofouling

POLY 120: Transient hydrogels mediated by redox-responsive supramolecular polymerization

Daniel Spitzer, Leona Lucas Rodrigues, **Pol Besenius**, besenius@uni-mainz.de.
Institute of Organic Chemistry, University of Mainz, Mainz, Germany

Spatial and temporal control in multistimuli-responsive materials are critical properties to advance and optimize functional soft matter in order to mimic key features of living systems. In this contribution, I will discuss our methodology in developing non-equilibrium states in supramolecular polymers and materials. We have expanded our concept of charge regulated β -sheet self-assembly of alternating hydrophilic and hydrophobic amino acids in order to introduce redox-switchable properties. An interplay of pH- and oxidation-stimuli, promoted by the production of reactive oxygen species (ROS) thus leads to transient supramolecular polymerizations of methionine containing amphiphiles, with tuneable lifetimes and stabilities of the hydrogels. The incorporation of triethylene glycol chains introduces thermoresponsive properties to the materials, which operates in a biomedically relevant temperature range of 30 - 40 °C. Excitingly repair enzymes are able to reverse the oxidative damage in the methionine-based thioether side chains and thus reinitiate supramolecular polymerization. Reactive oxygen species play an important role in signal transduction cascades, and our strategy therefore offers great potential for applications in dynamic biomaterials that operate in redox microenvironments.



POLY 121: Polymer-protein conjugates and protein-loaded polymersomes

*Charles A. Figg, Bryan S. Tucker, Tomohiro Kubo, R. N. Carmean, **Brent S. Sumerlin**,
sumerlin@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville,
Florida, United States*

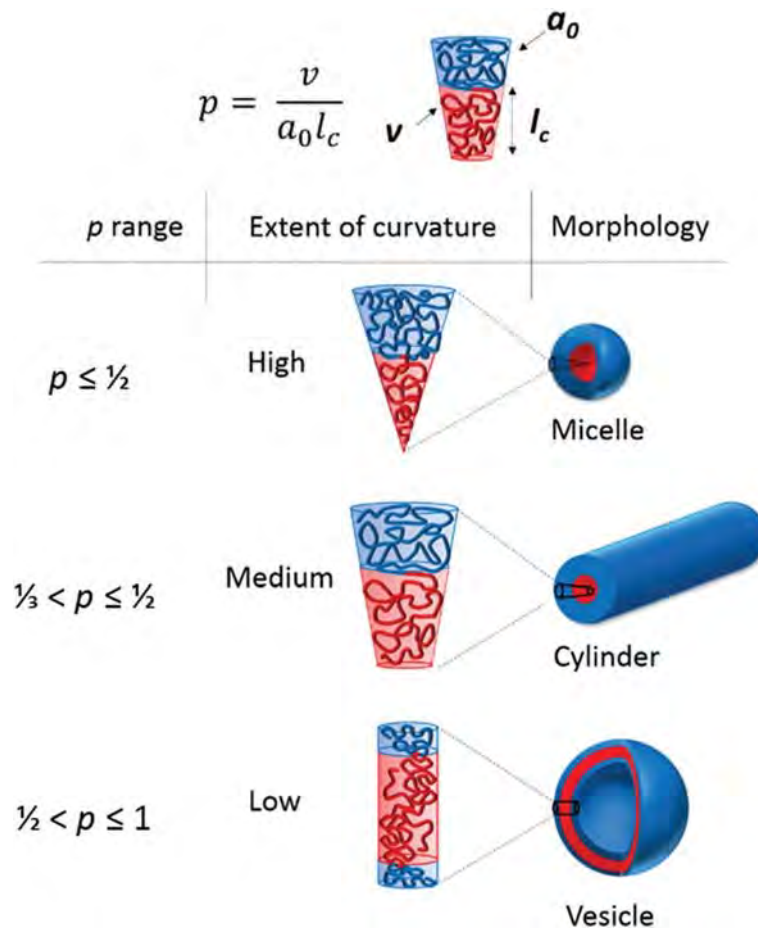
This presentation will describe our recent work in the area of polymer-protein conjugates, protein-loaded polymersomes, and new strategies for polymerization in the presence of sensitive biological macromolecules. Biofriendly, aqueous controlled radical polymerization (CRP) conditions are a prerequisite for preparing homopolymer- and block copolymer-protein bioconjugates, and recent advances in this area have allowed access to new conjugates that involve polymers with complex macromolecular architectures, many of which offer considerable promise for in vivo applications. We have employed both the grafting-to and grafting-from strategies to access these materials. Grafting-to was accomplished by conjugation of RAFT-generated polymers by copper(I)-catalyzed azide-alkyne cycloaddition, thiol-ene Michael addition, or amidation of activated esters. Each conjugation method was highly efficient and led to polymer-protein conjugates in good yield. While the first two methods allowed site-specific functionalization of thiols in cysteine residues in either bovine serum albumin (BSA) or ovalbumin, the latter approach targeted free amine groups contained in either lysine residues or the amine terminus of lysozyme or osteoprotegerin. Conjugation of RAFT polymers to proteins was also accomplished by first immobilizing the R-group of a RAFT agent to a protein and subsequently conducting the polymerization of a vinyl monomer in the presence of the protein macro-chain transfer agent. These grafting-from polymerizations can be initiated by conventional thermal initiation, irradiation of a conventional photoinitiator, or via direct photolysis of thiocarbonylthio compounds. Moreover, polymerization-induced self-assembly (PISA) in the presence of proteins has been shown to be an excellent strategy for incorporating proteins within vesicles.



POLY 122: Functional polymer nanostructures

Rachel K. O'Reilly, r.oreilly@bham.ac.uk. University of Birmingham, Birmingham, United Kingdom

The development of novel routes towards the preparation of hybrid nanomaterials is of great interest as it allows access to materials with novel properties. Of particular interest is the exploration of synthetic polymers with biomolecules and biomaterials. This presentation will describe recent work in the synthetic development and characterisation of such hybrid materials and their application.

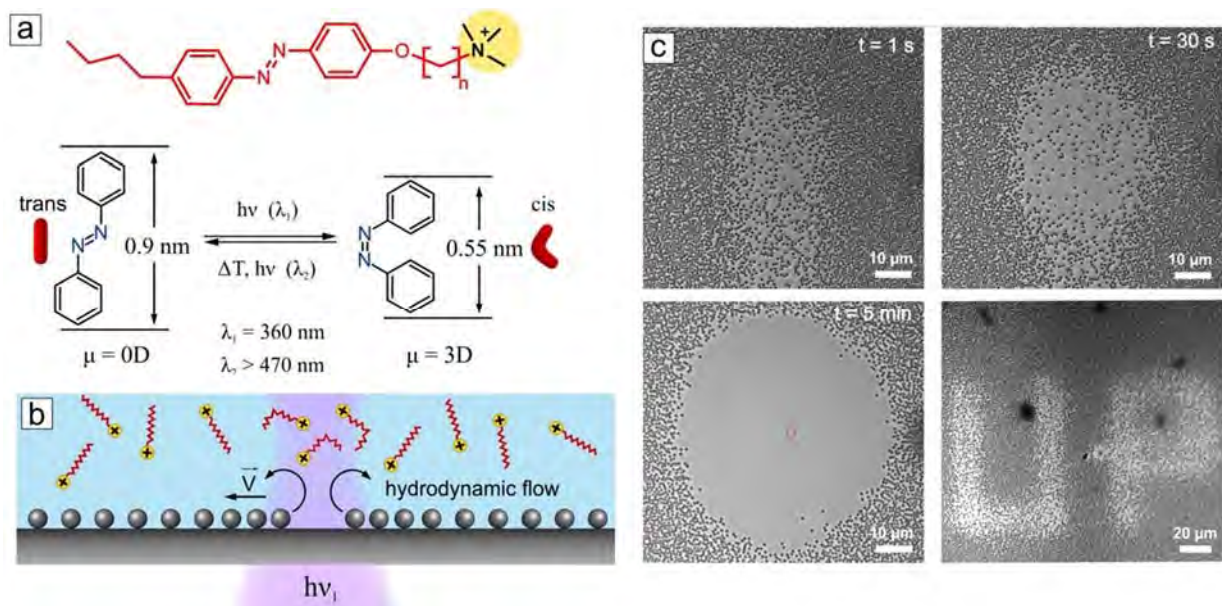


POLY 123: Light responsive soft nano-objects

Svetlana A. Santer, santer@uni-potsdam.de. Institute of Physics and Astronomy, University of Potsdam Faculty of Science, Potsdam-Golm, Germany

We discuss a novel mechanism to induce self-propulsion and to manipulate ensembles of micron-sized particles (artificial and biological) trapped at solid-liquid interfaces. The physical origin of our approach is related to so-called light driven diffusi-osmosis [1]. During irradiation of a solution of azobenzene containing surfactants with focused light, there is a formation of local hydrodynamic flow at a solid/liquid interface. The corresponding hydrodynamic forces are sufficient to swiftly clean the illuminated area from particles trapped at the interface. When the colloids are turned into Janus particles, their self-propulsion can be initiated in the solution of azobenzene containing surfactant under global/homogeneous illumination with UV light.

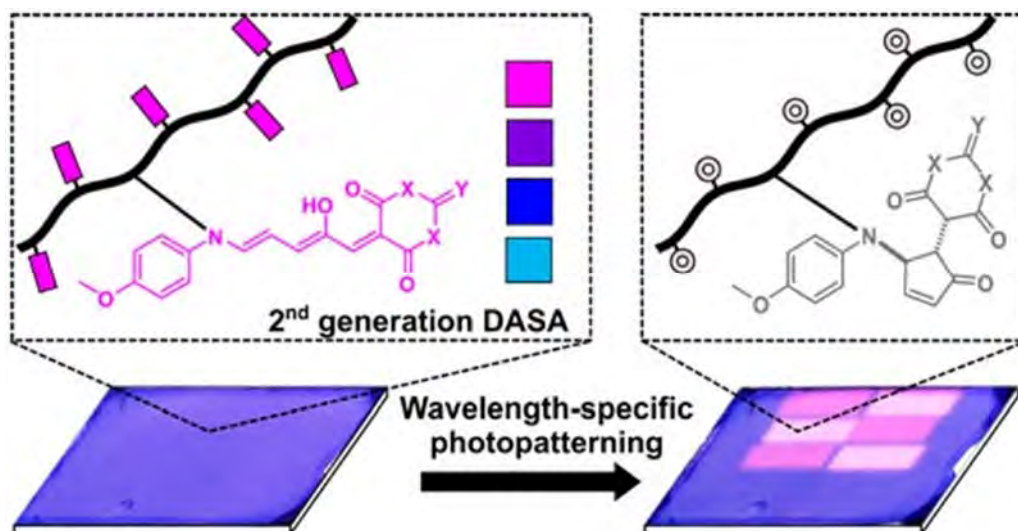
In the second part of my talk we discuss how soft nano-objects such as polymer brushes, microgels and DNA molecule can be turned to be photosensitive using azobenzene containing surfactant. We show that light sensitive microgel particles can change their volume in up to 8 times reversibly in response to illumination with light of different wavelengths [2]. Photosensitive polymer brushes can be structured during irradiation reversible or permanently on the nanometer scale [3]. DNA molecules can be compacted and decompacted by light in the presence of light sensitive surfactants [4].



POLY 124: Negative photochromic polymer conjugates

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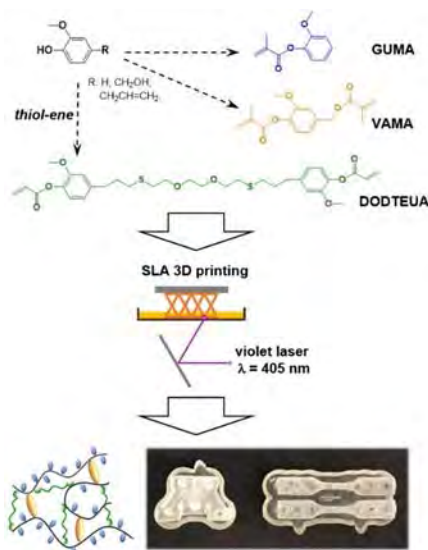
Photoswitchable systems that respond to low-energy visible light are highly desirable for applications in actuation, sensing, drug delivery, and data storage. Traditional photoswitches transition from one colored state to another, thus limiting the light penetration into bulk materials. This limitation can be overcome by utilizing negative photochromic compounds, which are naturally colored and become optically transparent upon exposure to light. Here we present the synthesis, polymer conjugation, and resulting structure-property relationships of an emerging class of negative photochromes termed Donor-Acceptor Stenhouse Adducts (DASAs).



POLY 125: Sustainable, photocurable acrylates based on natural phenolics for stereolithography 3D printing

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3D printable photopolymers have recently gained tremendous interest for a wide range of applications, such as industrial prototyping/manufacturing, electronics, medical/dental, and tissue engineering. However, current development of photoinitiated thermosetting formulations is mostly centered on commercial monomers/oligomers that are petroleum-derived and not environmentally friendly. This work aims to develop natural phenolic-based (meth)acrylates to expand the use of sustainable and mechanically robust 3D printable formulations. Utilizing thiol-ene chemistry, bifunctional 3,6-dioxa-1,8-octanedithiol eugenol acrylate (DODTEUA) was synthesized through a highly efficient, scalable approach. Real-time Infrared spectra and photorheology studies showed that DODTEUA exhibits competitive photocuring kinetics and that the viscosity and thermomechanical properties of this material can be tuned by adding a sustainable reactive diluent, guaiacyl methacrylate (GUMA). The effect of adding a crosslinker to GUMA-DODTEUA was further investigated by adding a third component, vanillyl alcohol dimethacrylate (VAMA) or trimethylolpropane trimethacrylate (TMPTMA). At 20 mol%, VAMA showed a moderate improvement in curing rate and a lower degree of cross-linking than TMPTMA due to VAMA's bifunctionality. However, the aromaticity of VAMA provided more resistance to chain deformation and breakage within the network, demonstrating storage moduli and tensile strengths up to 3.4 GPa and 56 MPa, respectively. Formulations GUMA 60-DODTEUA 20-crosslinker 20 by mol% with 2 wt% photoinitiator were successfully printed using a commercial desktop stereolithographic 3D printer. Our work informed a versatile, sustainable, and scalable synthetic strategy to design a class of natural phenolic acrylates for sustainable, high performance 3D printing.



POLY 126: Stereoselective photoredox ring-opening polymerization to prepare functional polyesters

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Polyesters with various microstructures have been synthesized by means of stereoselective ring-opening polymerization (ROP) of racemic lactide and β -lactones. However, stereoselective synthesis of polyesters with pendant side-chain functional groups remains challenging, owing in part to the lack of side-chain functionality in the lactone monomers. We recently reported the controlled photoredox ROP of enantiomerically pure OCAs that affords isotactic polyesters with expected MWs (>140 kDa) and narrow D s (< 1.1). Nevertheless, only low-MW (<20 kDa) syndiotactic polyesters synthesized from racemic OCAs has been achieved very recently. Here we report a new photoredox ROP protocol to accomplish stereoselective ROP of OCAs. We first examined various NNO ligand substituents. All of the complexes were tested in the photoredox ROP of **l-1** at -15°C at a $[\text{l-1}]/[\text{Zn}]$ ratio of 500 under irradiation with blue LEDs (400–500 nm) in the presence of a combination of (bpy)Ni(COD) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (**Ir-1**) with BnOH as the initiator ($[\text{l-1}]/[\text{Ni}]/[\text{Zn}]/[\text{BnOH}]/[\text{Ir-1}] = 500/1/1/1/0.1$). Reactions carried out with the complexes bearing electron-donating ligands, e.g., **NNO-1**, afforded polymers with M_n values close to the expected value (74.1 kDa) and with narrow D of 1.05, and monomer conversions were quantitative. We then investigated Zn complexes with the **NNO-1** ligand in the photoredox polymerization of *rac-1* by mixing **l-1** and **d-1** at a 1/1 ratio. We discovered that the photoredox ROP mediated by (**NNO-1**)ZnEt ($[\text{l-1}]/[\text{d-1}]/[\text{Zn}]/[\text{Ni}]/[\text{BnOH}]/[\text{Ir-1}] = 150/150/1/1/1/0.1$) resulted in a product with a M_n of 45.7 kDa, which was close to the expected MW (44.5 kDa), and a narrow D (1.06). Homonuclear decoupled ^1H NMR analysis of the microstructure of the formed polymer revealed a high degree of isotacticity, as evidenced by the large *mmm* tetrad peak ($\delta \sim 5.2$ ppm) with a P_m of 0.97. The obtained stereoblock copolymer, poly(*sb-1*), had a T_m of 172°C and a T_g of 50°C ; whereas both poly(**l-1**) and poly(*rac-1*) only had T_g s around 50°C and no observable T_m s, which was also the case for poly(**l-1-b-d-1**).

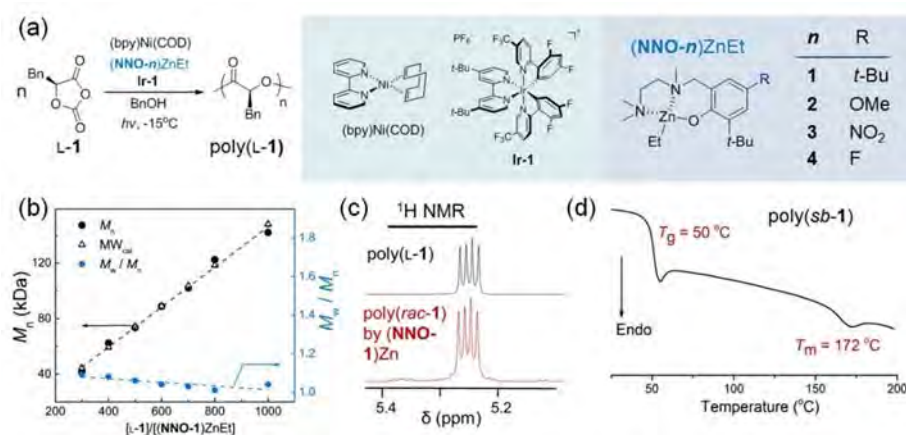
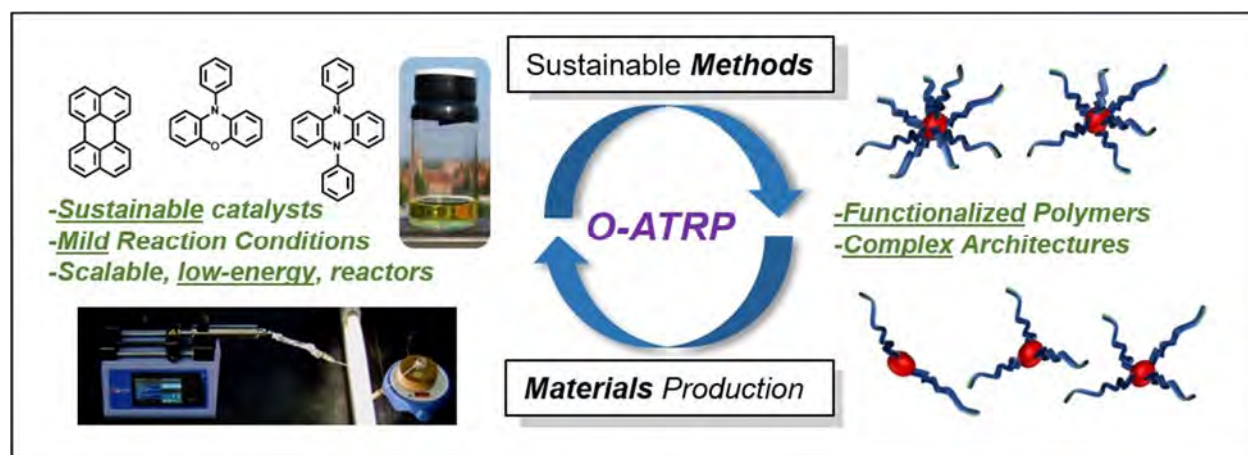


Fig 1. (a) Polymerization scheme. (b) MWs versus M/I. (c) ^1H NMR of poly(*sb-1*) and (d) its DSC.

POLY 127: Organocatalyzed atom transfer radical polymerization for functional polymer design and production

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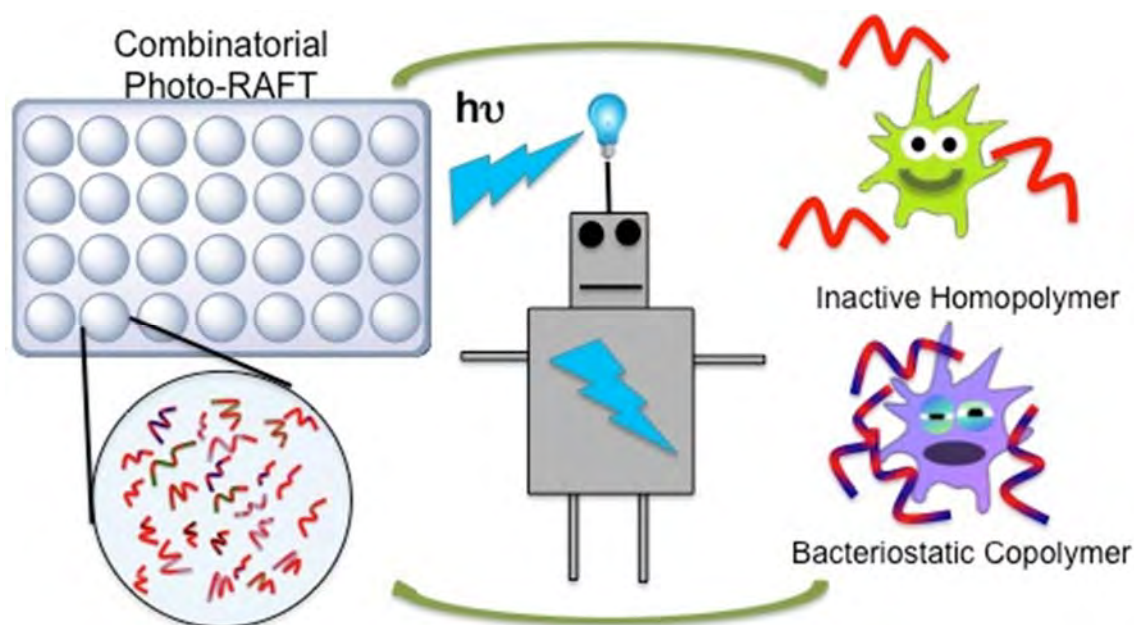
Organocatalyzed atom transfer radical polymerization (O-ATRP) has arisen as a metal-free variant of atom transfer radical polymerization, exploiting the benefits of photoredox catalysis to allow for the use of visible-light and mild reaction conditions to synthesize advanced materials. The success of this method centers on the ability of an organocatalyst to mediate an oxidative quenching photoredox catalytic cycle, which has been a central focus in the development of this technique. This presentation will discuss the progression of the catalytic abilities of this system to a scalable, low energy, continuous flow reactor system as well as the application of O-ATRP to enable the synthesis of functional complex architectures, along with recent developments on the design of new organocatalysts.



POLY 128: Combinatorial discovery of antimicrobial copolymers using 'in-air' photochemical RAFT polymerization

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The emergence and spread of antimicrobial resistance is a rapidly growing, global, healthcare threat. To counter this, new and innovative approaches to drug design are required. Synthetic cationic polymers and nanoparticles are particularly appealing as their composition and architecture can be finely tuned. In small molecule drug discovery, libraries with 1000's of unique structures are standard, this is not the case yet in polymer chemistry, due to the need for exclusion of air and sealed vials creating a bottleneck in the discovery process. Considering the huge design space of polymers, there is clearly an urgent need to develop methods that explore this potential for new biomaterial discovery. For this to be possible, a high-throughput, robust, air-tolerant polymerization technique, with easy purification and facile transfer to screening platforms is required. To achieve this we employ a photochemical 'in-air' RAFT polymerization method in 96-well microtiter plates, using liquid handling robots to assemble large libraries of cationic polymers, without the need for degassing or purification steps, facilitating simple transfer to antimicrobial and cytotoxicity screening. This enables a >100-member copolymer library to be assembled with excellent reproducibility and control over molecular weight. Several lead copolymers have been identified with up to 8-fold enhanced antimicrobial activity, and increased therapeutic window over the homopolymer. Mechanistic studies show this polymer is bacteriostatic and surprisingly does not lyse the cell membrane, implying an alternative mode of action to the homopolymer.

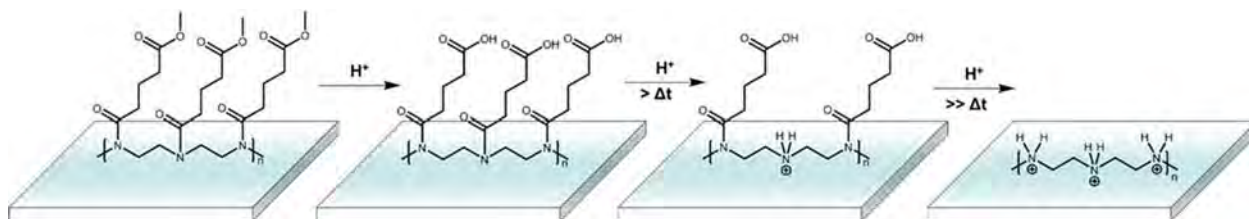


Robot-assisted synthesis and screening of polymer antimicrobials

POLY 129: Adjusted surfaces: Tailoring the isoelectric point via modification of ester-functionalized poly(2-oxazoline)s

Robin Hofmann, robin.hofmann@pccl.at, Inge Mühlbacher, Frank Wiesbrock. Polymer Competence Center Leoben, Leoben, Austria

2-Oxazolines can be (co-)polymerized in a single step via the cationic ring-opening polymerization (CROP). The hydrolysis of ester-functionalized poly(2-oxazoline)s (pEstOx) such as poly[methyl-3-(4,5-dihydrooxazol-2-yl)propanoate]s paves the way to carboxy-functionalized copolymers; extended reaction times (eventually including microwave-assisted reactions) in acidic media cleaves the amide bonds (as well), yielding polyamines. Hence, alkaline hydrolysis is used to selectively cleave the ester bond. Thiol-ene click-reactions involving side-chains double-bonds like in poly(2-dec-9'-enyl-2-oxazoline) (pDec⁺Ox) enable the introduction of a variety of functionalized groups into poly(2-oxazoline)s comprising alcohol functions. For the preparation of functionalized surfaces, polyolefins were blended with poly(2-oxazoline)s. In this study, polypropylene was blended with 5 wt.-% of the copolymer pEstOx₂₀-stat-pDec⁺Ox₈₀ as well as with its derivatives derived from hydrolysis in 1 M NaOH and/or thiol-ene click reactions with mercaptoethanol. For the characterization of the surfaces of the blends, zeta-potential measurements were used (among others), correlating the surfaces' isoelectric points with the degree of hydrolysis (content of carboxylic acid groups) and/or the content of hydroxy groups (introduced by thiol-ene reactions). The surfaces' isoelectric points could be adjusted in the pH range between 4-6. For subsequent surface functionalization, the carboxylic acid groups as well as the hydroxy groups were treated with, e.g., acyl chlorides.



Acidic hydrolysis of ester-functionalized poly(2-oxazoline)s yielding carboxyl functionalities; continued acidic hydrolysis leads to cleavage of the amide bonds.

POLY 130: Reactivity-property relationships in photocontrolled polymer networks

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The macroscopic properties of polymers emerge from a combination of molecular (covalent and noncovalent associations, van der Waals forces) and macromolecular (entanglement, reptation) interactions. Light uniquely offers precise, tunable, and external spatiotemporal control over molecular interactions, which can be translated into macroscopic responses. Photochemical crosslinking and cleavage allow precise tailoring of the *structure* of elastic polymer networks.

Recently, researchers have developed strategies to tune the *temporal* properties of viscoelastic networks that rely on changes in the composition and structure of the crosslinks, accessing multiple timescales for stress relaxation. I will describe my group's design of photoswitchable dynamic covalent crosslinks that enable *external*, *spatiotemporal*, and *reversible* control of viscoelasticity in hydrogels and vitrimers. I will discuss our efforts to elucidate the molecular mechanism underlying these macroscopic changes, as well as rational optimization of the structures to enable applications in 3D cell cultures and recyclable elastomers.

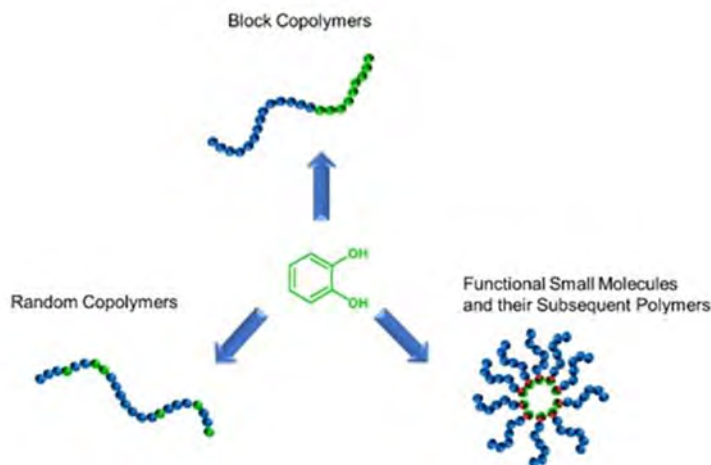


POLY 131: Utilizing the chemical toolbox for the synthesis of catechol-based polymers for the assembly of functional metal phenolic networks

Samantha L. Kristufek¹, samantha.kristufek@unimelb.edu.au, **Joseph J. Richardson**¹, **Kate Reidy**¹, **John Quinn**², **Thomas Davis**², **Frank Caruso**¹. (1) Department of Chemical Engineering, University of Melbourne, Melbourne, Victoria, Australia (2) Monash Institute of Pharmaceutical Sciences, Monash University, Parkville Campus, Melbourne, Victoria, Australia

Metal phenolic networks (MPNs) are a useful tool employed in the rapid assembly of coatings through which a coordination driven assembly process can be used on a variety of templates. In an effort to expand the library of suitable molecules and polymers for MPN systems, a series of catechol-based polymers and initiators have been synthesized. The assembly of these synthetic compounds will produce functional MPN materials whereby functional is defined as the introduction of chemical functional handles that can be used for the attachment of molecules of interest (e.g. drugs, dyes, targeting agents, etc.). Utilizing the diverse chemical toolbox will allow for the evolution of complexity in MPN systems which will further facilitate our understanding of both the fundamental properties and applications of these materials.

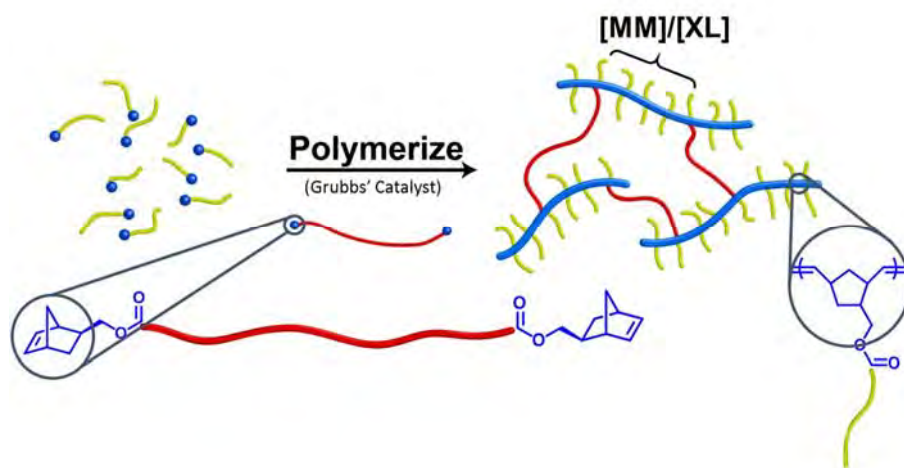
An initial system began with the synthesis of block copolymers *via* reversible addition-fragmentation chain-transfer polymerization with a water-soluble block and a block containing an activated ester. The final polymers were achieved through the post-polymerization modification of the activated ester block with a catechol-containing small molecule. The block copolymers were then assembled on a template to form MPN particles and characterized by various microscopy and spectroscopy techniques. Concurrently, random copolymers of dopamine-based acrylates were copolymerized with functional monomers which were fluorescent and/or conductive, among other properties. Upon the formation of MPNs, the effects of these added properties were studied for various applications. Collectively, these projects have begun to create a library of molecules for incorporation into MPN systems with various interesting properties to further the desired application. This talk will detail the design, synthesis, and properties of these catechol-based polymers and the subsequently formed metal phenolic networks.



POLY 132: Mechanics, structure, and fracture of super-soft tunable bottlebrush polymer networks prepared by ROMP

Joel M. Sarapas, *jmsarapas@gmail.com*, Edwin Chan, Kathryn Beers. *Materials Science and Engineering Division, NIST, Bethesda, Maryland, United States*

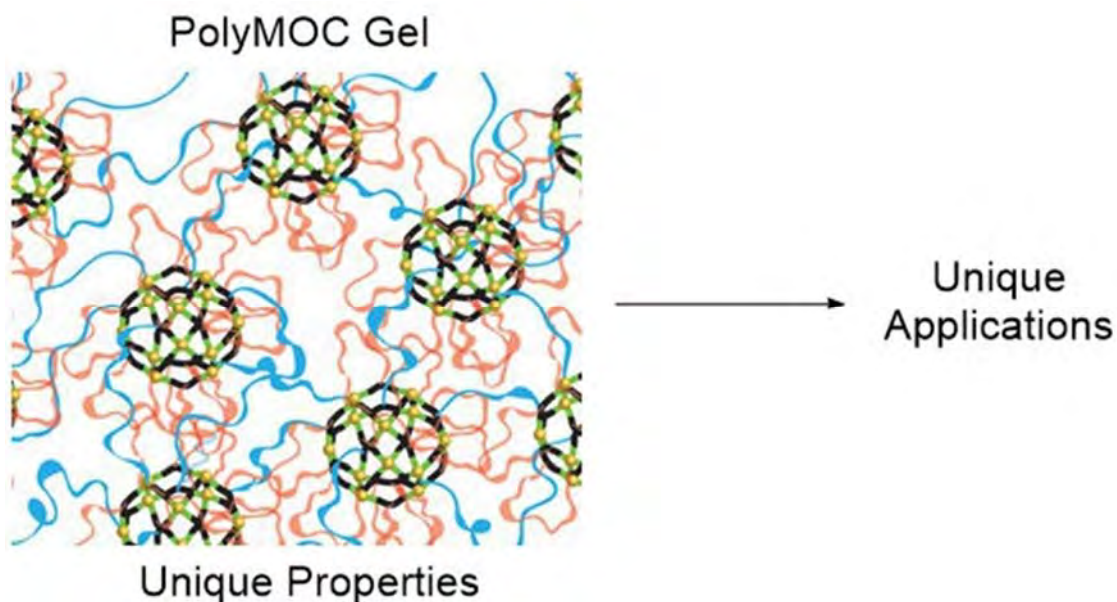
Polymer networks are a universal class of materials applicable across many disciplines, functioning as soft solids with a variety of tunable properties including porosity, biocompatibility, and elasticity, among countless others. Extremely soft networks have been of particular interest for biomedical applications, but generally require the dilution of entanglements through swelling to access such low moduli. In doing so, a myriad of complications can arise, including lowered elasticity, inhomogeneity from solvent loss, and potential inflammatory response if implemented biologically. By employing a network with a bottlebrush architecture, entanglements can altogether be avoided, and extremely soft, solvent free networks can be realized. Here, we demonstrate the successful synthesis of bottlebrush networks by grafting-through poly(*n*-butyl acrylate) (PnBA) macromonomers and crosslinker macromolecules using ROMP, yielding high gel fraction (>90%) networks with highly tunable moduli in the 1 – 20 kPa range. We present a family of networks, modulated by varying crosslinking chain and macromonomer molar mass, as well as chemical composition including co-networks. These materials are investigated through neutron scattering, swelling, and contact adhesion testing to give information about structure, and further characterized by razor cutting to begin to understand bottlebrush network fracture mechanics. The versatility of this ROMP-based platform allows for the rapid generation of chemically and mechanically diverse materials critical to better understanding and implementing bottlebrush network systems.



POLY 133: Novel polymer metal organic cage networks for applications in synthesis and drug delivery

Nathan J. Oldenhuis, *nateoldenhuis@gmail.com*, Jeremiah A. Johnson. Chemistry, MIT, Cambridge, Massachusetts, United States

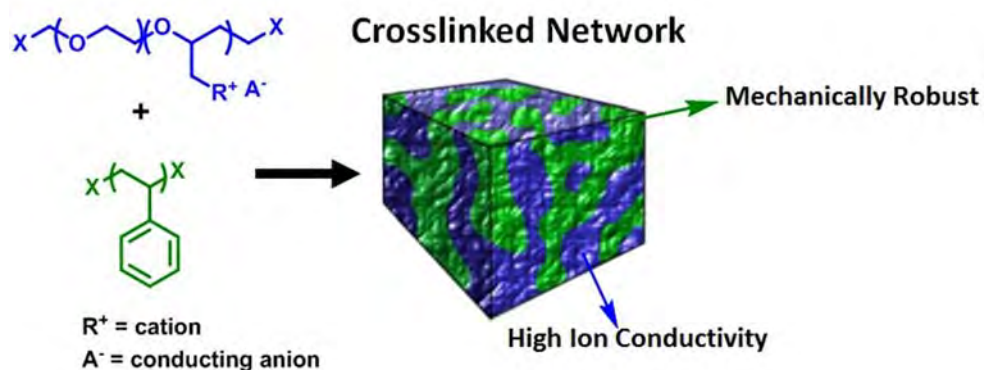
Polymer metal organic cage (PolyMOC) networks are a relatively new class of supramolecular gels. The polymer chains attached to the embedded MOCs allows for a high degree of branch functionality (f) resulting in exemplary mechanical properties at low concentrations. While these gels are interesting in their own right, the novel properties of MOCs embedded in a polymer network give rise to new applications. In this talk, the PolyMOCs gels created will be used towards drug delivery and synthesis applications.



POLY 134: Optimizing anion exchange membrane properties using networks made from telechelic polymers

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Anion exchange membranes (AEMs), for use in fuel cell applications, have recently garnered significant attention as the need for developing alternative forms of energy continues to grow. The field of AEMs has advanced significantly in recent years with the development of both highly conductive and chemically stable membranes. Despite those advancements, the trade-off between membrane mechanical properties and ion conductivity is still a major challenge. Typically, in order to obtain high conductivity, a significant amount of membrane hydration is required, to enhance ion mobility, however this increased water content inevitably results in poor mechanical integrity. Previous work in our group has demonstrated that crosslinking telechelic polymers, such as poly(ethylene oxide) (PEO) and polystyrene (PS), results in the formation of networks with a bicontinuous morphology over a much larger compositional range than typically observed, allowing for the simultaneous optimization of both mechanical properties and ion conductivity. Utilizing this approach in an AEM would also allow for simultaneous optimization, something that is notoriously difficult in the AEM field. Here, a series of crosslinked networks was synthesized by crosslinking telechelic, functional PEO with telechelic PS, where the PEO was functionalized with cationic, ion conducting side chains. The networks were synthesized using a wide range of PEO compositions, in an effort to capture the effect of changing the composition of these functional polymers on network morphology and performance. This range of compositions was chosen to understand what compositions result in both polymer phases being percolated throughout the crosslinked network. This percolation of both phases would simultaneously enhance both the mechanical properties and ion conduction, as both phases become interconnected. Overall, a facile method towards producing AEMs with both high mechanical robustness and ion conductivity, which is an elusive combination, is presented.



POLY 135: Thermal and mechanical properties of new high-sulfur-content copolymers of Bisphenol A

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Clemson University, Clemson, South Carolina, United States*

Elemental sulfur is an abundant byproduct of the petroleum refining process. In 2015, approximately 70 million metric tons of sulfur was produced globally by this process. All current industrial consumption underutilize the readily available elemental sulfur waste stream, to the extent that 7 million tons of excess sulfur remains annually. In terms of materials production, only a small fraction of this plentiful, affordable sulfur is used for vulcanization of rubber and its use as an additive in asphalt. The current contribution highlights our efforts to modify bisphenol A (BPA) to facilitate its cross-linking with sulfur-rich compounds to afford new synthetic polymers and network materials. The sulfur content was varied over a wide range, and the extent to which composition influenced thermal and mechanical properties was quantified. We report on analyses of thermal and mechanical properties for a series of BPS composites by TGA , DSC and DMA.

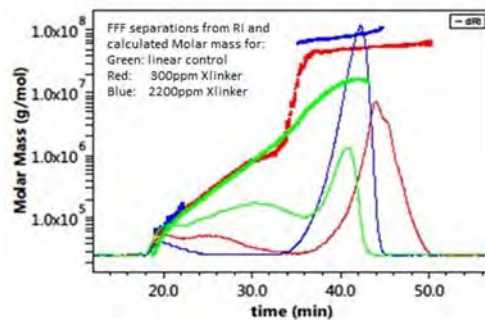


POLY 136: Characterization of crosslinked alkali-swellaable terpolymers by FFF-MALS

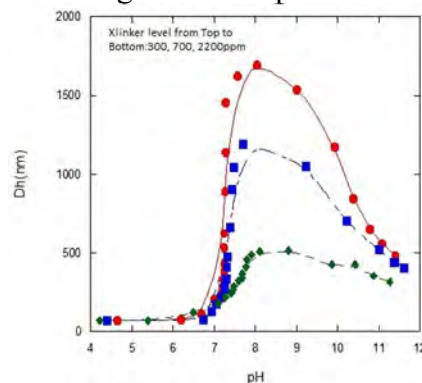
Zheng Li, lizheng319@gmail.com. Ashland Inc., Bridgewater, New Jersey, United States

Crosslinked terpolymers of Ethyl acrylate/Butyl acrylate/Methacrylic acid were synthesized using emulsion polymerization for the development of a new liquid acrylic rheology modifier for personal care applications. However, some most fundamental characteristics of the lightly crosslinked polymers could not be analyzed using SEC due to insufficient separation limits and unfavorable interactions between the polymers and the packing materials of the SEC columns. Field-Flow Fractionation (FFF) has been used widely in investigating protein aggregates since it's been introduced while much less have been reported for its use in analyzing crosslinking polymer materials.

In this study, crosslinked terpolymers of EA/BA/MAA with varying levels of crosslinking were thoroughly studied by FFF. Baseline-resolved separations of crosslinked/non-crosslinked fractions were achieved and the crosslinked % was calculated. With multi-angle light scattering detector (MALS), the molecular weight, size and chain conformation are easily characterized, all those results showed expected trend as with more crosslinker addition, polymers had higher crosslinked %, higher molecular weights and more compact structures. Close correlations of such fundamental characteristics with the final product properties, such as visual appearance, yield value or swelling efficiency, were established. This method has provided some the key guidance for both the R&D and manufacturing process.



FFF chromatograms and Molecular weights for samples with different crosslinker levels



Swelling behaviors of samples with different crosslinker levels by DLS

POLY 137: Combined characterization of polymers and polymer formulations using multi-detector GPC and rheology

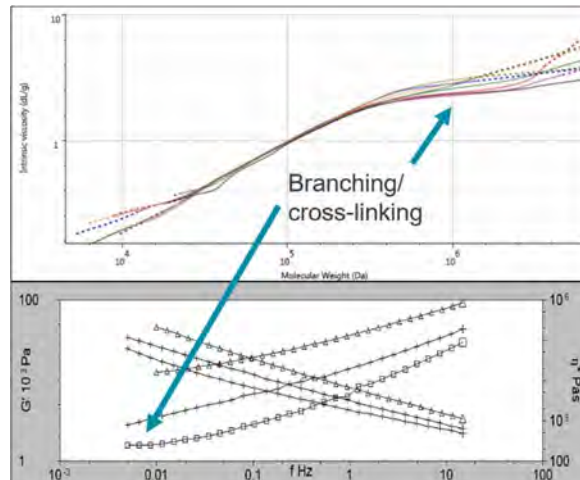
Vivek Shahi, *vivek.shahi@malvern.com*, Mark Potheary, John Casola, Chuck Rohn. Malvern Panalytical, Houston, Texas, United States

The flow properties of polymers and polymer formulations are strongly determined by their underlying molecular parameters. In any such application, fully understanding polymer behavior requires a thorough understanding of its underlying material properties that define such behavior. For example, low shear viscosity is known to be strongly correlated with molecular weight, while formulation viscosity is dependent upon intrinsic viscosity, and chain overlap. These relationships appear in applications from surface finish in PVC, to toughness and clearance rates in hyaluronic acid formulations used in the pharmaceutical industry. For example (see figure), cross-linking increases molecular weight and reduces surface finish quality in PVC.

Gel-permeation chromatography (GPC) is widely used for measuring the molecular weight (distribution) of polymers. With technological advances, multi-detector GPC offers *absolute* molecular weight and branching analysis through intrinsic viscosity (IV) or R_g .

Rotational rheology is routinely used to measure the flow properties of polymers and polymer formulations at different shear rates. Optical microrheology uses probe particles and dynamic light scattering (DLS) instruments to passively measure the rheological properties of solutions at high frequencies potentially opening up new application areas.

In this presentation, we will briefly discuss multi-detector GPC, rotational and optical rheology. A series of application of synthetic and natural polymers will demonstrate how this combination of molecular and bulk characterization techniques can be used to more strongly characterize material changes that can significantly affect the performance of products based on these materials.

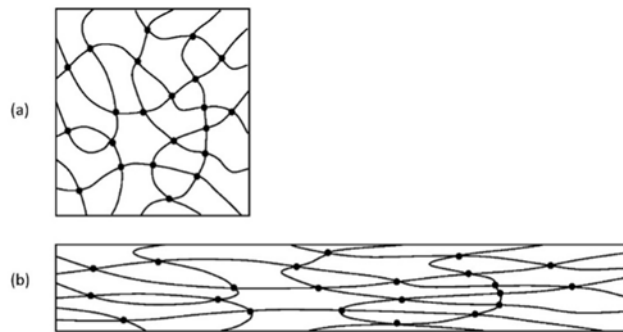


Mark-Houwink plot from GPC showing increased polymer branching/cross-linking at high molecular weights; (bottom) frequency plot from rotational rheology showing plateauing at low frequency ranges also indicating cross-linking.

POLY 138: Polymer microstructures and material properties: Relevant relations

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We demonstrate that it is possible to connect the behaviors of polymer materials directly to their detailed microstructures. Rigorous treatment of individual polymer chain conformational preferences is possible with development of Rotational Isomeric State (RIS) conformational models for chemically distinct polymers. Matrix multiplication methods enable these RIS models to be used to estimate a variety of conformationally sensitive properties of individual single polymer chains. These include conformational populations, expected ^{13}C -NMR resonance frequencies used for evaluating their microstructures and solid-state conformations, thermodynamic variables (E_{conf} , S_{conf} , F_{conf} , etc.), dimensions ($\langle r^2 \rangle_0$ and $\langle s^2 \rangle_0$), dipole moments, as well as others. Each is the result of rigorously averaging over all of their virtually innumerable conformations. These conformationally sensitive average single chain properties may be used to understand a variety of their microstructurally sensitive material behaviors. These include their dimensions in solutions and melts, entanglement molecular weights, crystalline conformations, melting temperatures, comonomer sequence dependent glass-transition temperatures, inherent conformational flexibilities governing their solid state permeabilities and impact strengths, and polymer network topologies and moduli. In other words, microstructure dependent realistic RIS conformational models of polymers can significantly contribute to our understanding of **Polymer Chemistry** and provide a means to establish relevant structure-property relations for their materials.



Cross-linked network (a) in unstrained at rest and (b) in strained states.

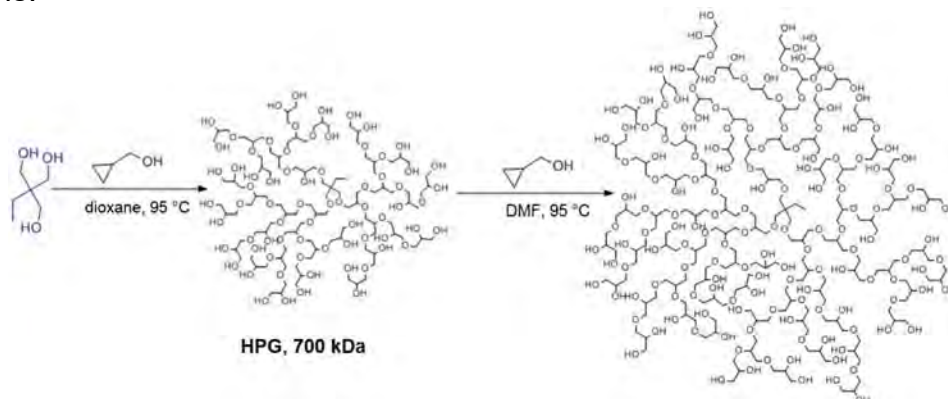


Illustration of the reduction in the end-to-end separation of polymer chain ends achieved by altering the conformation about a single backbone bond.

POLY 139: Synthesis and characterization of ultra-high molecular weight hyperbranched polyglycerols

Srinivas Abbina¹, srini.abbina@gmail.com, **Anilkumar Parambath**¹, **Lily Takeuchi**¹, **Jayachandran N. Kizhakkedathu**². (1) Department of Pathology and Laboratory Medicine, University of British Columbia, Vancouver, British Columbia, Canada (2) Univ of British Columbia CBR, Vancouver, British Columbia, Canada

Hyperbranched polyglycerols (HPGs) have been well known for their biocompatibility and utilization in diverse biomedical applications. However, the generation of high molecular weight HPGs is challenging but offer wide opportunities in nanomedicine. High molecular weight HPGs have long circulation time, high functionality, and compactness in addition to excellent biocompatibility in comparison to linear polymers. We report, for the first time, the synthesis of ultra-high molecular weight hyperbranched polyglycerols (uHPG) (M_w -1.5 to 9.5 MDa) by solution based anionic ring opening multibranching polymerization of glycidol with good control over polydispersity. The molecular weight of the uHPGs are controlled by the amount of glycidol added. The uHPGs have been well characterized for molecular weight (gel permeation chromatography with light scattering), branching, viscosity, solubility, and size (dynamic light scattering and atomic force microscopy (AFM)). The polymers are found to be highly compact with low intrinsic viscosity and are highly water soluble with degree of branching around 0.58-0.60. The hydrodynamic size of the polymers are in the range of 21-44 nm which increased with increase in molecular weight. AFM imaging showed discrete particles with increase in size with molecular weight. The uHPGs are highly biocompatible in comparison to commercially available water soluble linear polymers (polyethylene oxide, polyvinyl alcohol, and dextran) of similar molecular weight based on the analyses of cell compatibility and blood compatibility. The uHPGs did not activate platelets, blood coagulation, and complement. In addition, uHPG showed reduced red cell aggregation when compared to commercially available linear polymers with similar molecular weights demonstrating their superior hemocompatibility. Further, uHPG demonstrated excellent cell viability against fibroblast and chondrocyte cell lines compared to saline control. Overall, the current studies demonstrated that uHPGs are highly biocompatible and is currently being investigated in different biomedical applications.

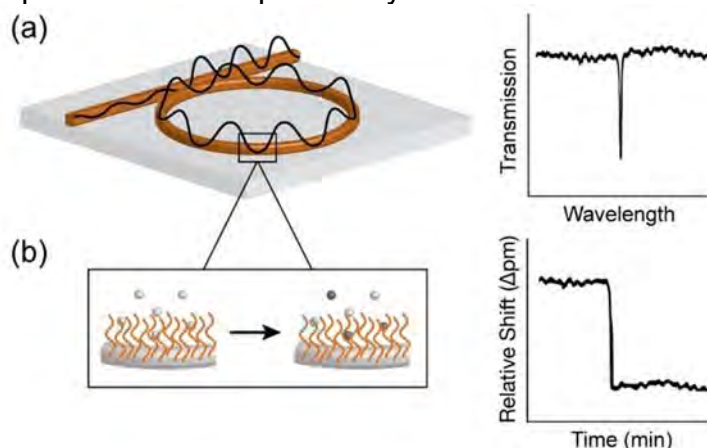


A schematic representation of synthesis of ultra-high molecular weight hyperbranched polyglycerols

POLY 140: Simultaneous real-time measurement of analyte partitioning and polymer brush conformation using whispering gallery mode sensors

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Polymer thin films are commonly used to tailor material properties, transforming surfaces with sub-micron coating thicknesses. In particular, brushes grown from the surface can drastically change the properties of that surface with just a few nanometers. The unique nature of these ultrathin polymer coatings stems from the dense and extended conformations that are possible at high grafting densities. With applications in wettability, adhesion, biocompatibility, actuation, gating, and detection, many robust techniques have been used to characterize properties such as stimuli-responsive changes in thickness. However, accessible characterization of other polymer properties remains lacking. Herein, we present a new technique for simultaneous measurement of analyte partitioning and polymer brush conformation using whispering gallery mode sensors. Silicon photonic microring resonators were functionalized with several different polymers and their response to changing conditions was monitored in real time. This technique is applied to investigate the kinetics of small molecule partitioning into hydrophobic poly(methyl methacrylate) and hydrophilic poly(2-hydroxethyl methacrylate) brushes as a function of solvent type and concentration. We also studied the behavior of poly(2-dimethylaminoethyl methacrylate) as a function of pH, investigating pKa values as a function of brush thickness. Thus, we demonstrate that our technique allows for accessible characterization of hydrophobic, hydrophilic, and stimuli-responsive polymer films in the presence of complex analyte-solvent interactions.

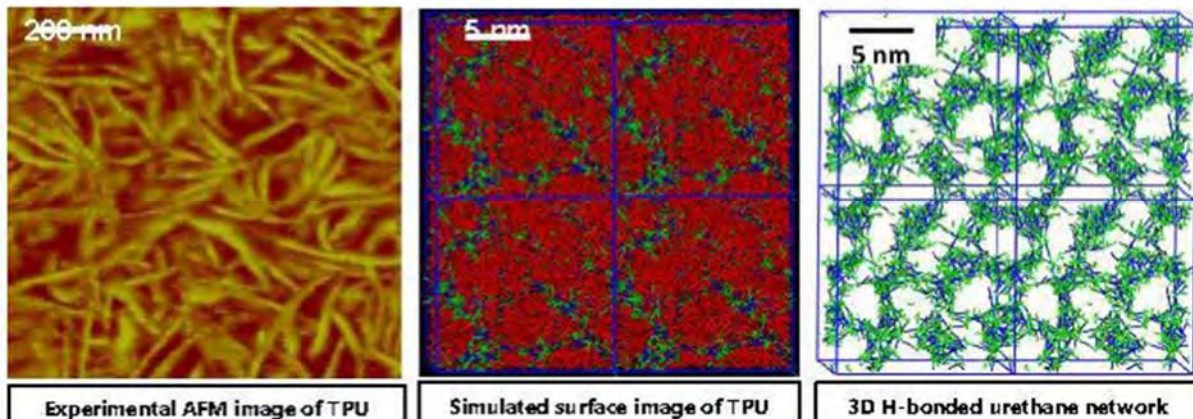


Brush-modified microring resonators are used to interrogate polymer response to complex analyte-solvent interactions. (a) A silicon photonic microring resonator couples light from the waveguide and resonant optical modes are visualized by a dip in transmission intensity. (b) Changes in the resonant mode can be used to visualize small molecule partitioning and brush conformational changes in real-time.

POLY 141: Temperature-dependent changes in the hydrogen bonded hard segment network and microphase morphology in a model polyurethane: Experimental and simulation studies

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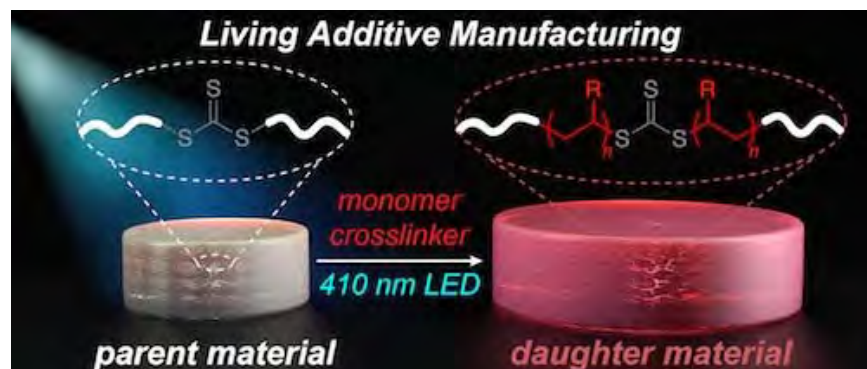
Hydrogen bonding between hard segments (HS) has a critical effect on the morphology and properties of segmented polyurethanes and polyureas (TPU). 3 Dimensional structure of the hydrogen bonded HS network in TPU strongly depends on temperature. Influence of temperature on the nature and extent of hydrogen bonded urethane HS network and microphase morphology of a model TPU based on p-phenylene diisocyanate (PPDI) and PTMO-1000 was investigated by experiments and simulations. Simulations were performed using dissipative particle dynamics (DPD) and molecular dynamics (MD) approaches. Melting behavior of the semi-crystalline PPDI-PTMO-1000 based TPU investigated by AFM, FTIR and WAXS was compared with simulations. DPD simulations showed a room temperature microphase morphology consisting of a 3-dimensional hydrogen bonded urethane hard segment network in a continuous and amorphous PTMO matrix. The first order melting transitions of crystalline urethane HS observed during the continuous isobaric heating in DPD and MD simulations (340 – 360 K) were in reasonably good agreement with those observed experimentally by; AFM (320 – 340 K), WAXS (330 – 360 K) and FTIR (320 – 350 K) studies. Quantitative verification of the melting of urethane hard segments was demonstrated by sharp discontinuities in energy versus temperature plots obtained by MD simulations due to substantial decrease in the number of hydrogen bonds above 340 K.



POLY 142: Living additive manufacturing: Transformation of parent gels into diversely functionalized daughter gels made possible by visible light photoredox catalysis

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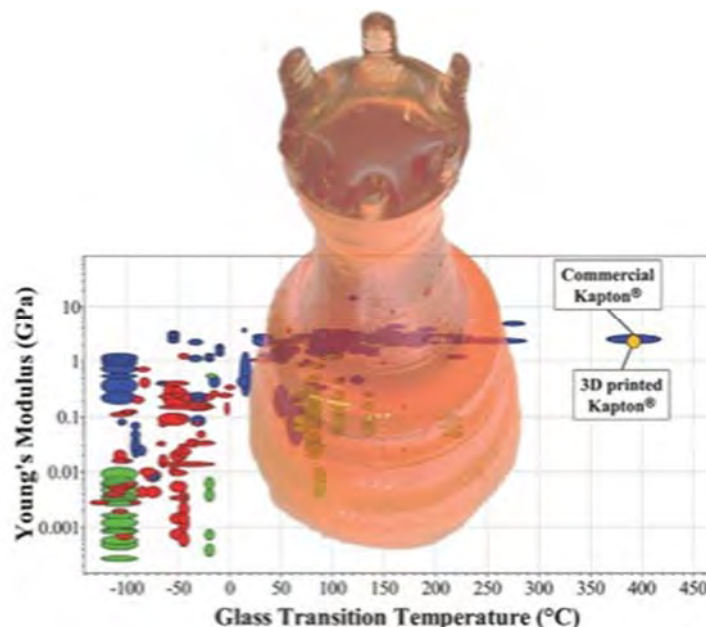
Light-initiated additive manufacturing techniques typically rely on layer-by-layer addition or continuous extraction of polymers formed via nonliving, free radical polymerization methods that render the final materials “dead” toward further monomer insertion; the polymer chains within the materials cannot be reactivated to induce chain extension. An alternative “living additive manufacturing” strategy would involve the use of photocontrolled living radical polymerization to spatiotemporally insert monomers into dormant “parent” materials to generate more complex and diversely functionalized “daughter” materials. Here, we demonstrate a proof-of-concept study of living additive manufacturing using end-linked polymer gels embedded with trithiocarbonate iniferters that can be activated by photoinduced single-electron transfer from an organic photoredox catalyst in solution. This system enables the synthesis of a wide range of chemically and mechanically differentiated daughter gels from a single type of parent gel via light-controlled modification of the parent’s average composition, strand length, and/or cross-linking density. Daughter gels that are softer than their parent, stiffer than their parent, larger but with the same modulus as their parent, thermally responsive, polarity responsive, healable, and weldable are all realized.



POLY 143: Designing polymers to tune interfaces in 3D printing: From all-aromatic polyimides to poly(dimethyl siloxane) elastomers

Jana Herzberger, Philip Scott, Justin Serrine, Nicholas Chartrain, Viswanath Meenakshisundaram, Christopher B. Williams, **Timothy E. Long**, telong@vt.edu.
Virginia Tech, Blacksburg, Virginia, United States

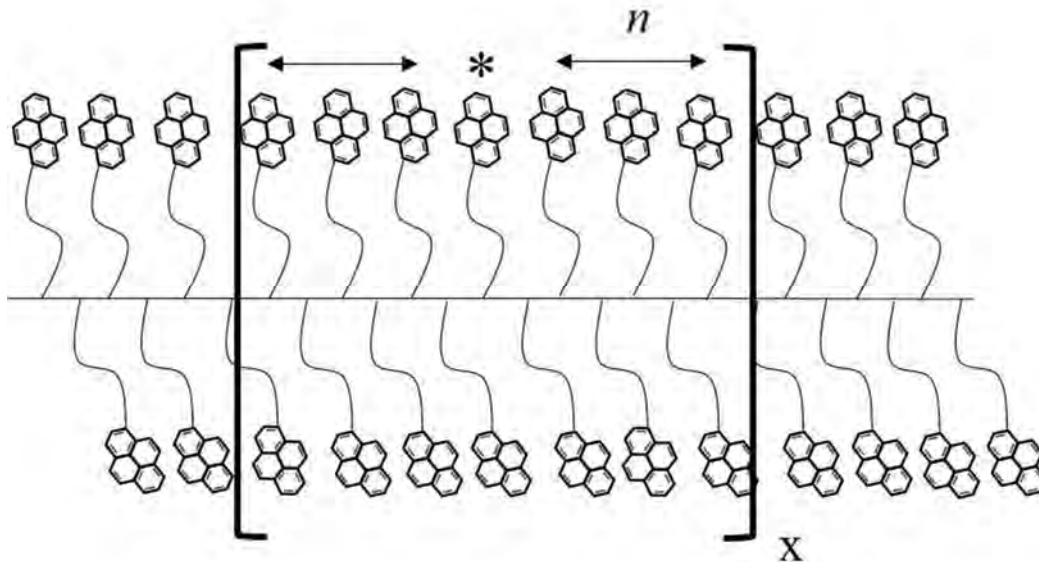
Additive manufacturing (AM) of multifunctional polymers enables the formation of tailored and well-defined 3D objects for aerospace, electronics, and structural applications. Mask projection stereolithography (MPSL), an established and versatile AM technology, constructs objects with features as low as 10 μm by projecting masked ultraviolet (UV) light onto a photopolymer surface in a layer-by-layer, iterative fashion. In one example, AM of a phosphonium-containing ionic liquid is demonstrated. This 3D-printed polymerized ionic liquid (PIL) demonstrated high thermal stability, optical clarity, ionic conductivity, and tunable thermal properties based on ionic liquid incorporation into the poly(ethylene glycol) dimethacrylate matrix. In another example, MPSL enabled 3D printed polyimide precursors based on pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), otherwise known as Kapton®. Post-printing thermal imidization converted the poly(amic acid) precursors into polyimides while retaining shape and resolution. This application of MPSL enables generation of well-defined 3D objects with exceptional thermal and structural adhesive properties, effectively processing the unprocessable. In a final example, AM of elastomers is examined. Production of elastomeric objects requires high molecular weight precursors, which are typically possess a viscosity too high for processing with standard vat photopolymerization techniques. A variety of methods for reducing photopolymer viscosity are explored, including the use of heat, reactive & unreactive diluents, and systems with simultaneous chain extension and crosslinking. These examples demonstrate that the combination of novel synthetic strategies with tailored geometries from additive manufacturing can displace what is attainable with traditional materials and manufacturing processes.



POLY 144: Pyrene excimer fluorescence yields the same structural and dynamic information on macromolecules as FRET but in a mathematically much simpler manner

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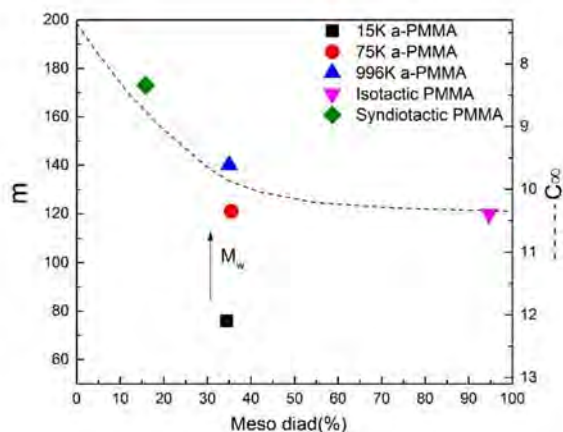
Fluorescence resonance energy transfer (FRET) is widely recognized as being the main fluorescence tool to obtain quantitative information about the dynamics and structure of macromolecules. Yet, because FRET depends on both the distance (dDA) between a pair of donor and acceptor and the internal dynamics of the macromolecules that control the displacement of the dyes, it is rarely applied to macromolecules labeled with more than a single energy donor and acceptor separated by a single contour length. Indeed, beside end-labeled linear oligomers, FRET is hardly ever used for quantitative studies on large macromolecules with more complex architectures due to intractable mathematical complications associated with the difficulty of tracking an a priori unknown dDA distribution that varies as a function of time. This presentation will demonstrate that these mathematical complications vanish when dealing with pyrene excimer formation/fluorescence (PEF) since PEF occurs on contact which removes the FRET requirement of dealing with a time-dependent dDA distribution. The effectiveness of PEF for the characterization of pyrene-labeled macromolecules will be illustrated with a series of pyrene-labeled dendrimers and a series of pyrene-labeled polymeric bottle brushes.



POLY 145: Connecting polymer chemical structures and their glass transition temperatures and dynamic fragilities: a conformational approach

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(1) North Carolina State University, Raleigh, North Carolina, United States (2) Campus Box 8301, North Carolina State University, Raleigh, North Carolina, United States (3) TECS, North Carolina State University, Raleigh, North Carolina, United States

The nature of the glass transition is widely accepted as one of the most complex and interesting unsolved problems in condensed matter physics. Both glass transition temperature (T_g) and dynamic fragility, m , play a vital role in the selection and use of amorphous polymers. Relationships between chemical structures and their resultant T_g s and m s, remain a topic of open discussion. Unlike small molecules whose dynamics are dominated by intermolecular interaction, polymers generally have large m which conceivably has an intra-chain origin; i.e., rotational barriers and chain connectivity. It is well-known that different tactic forms of PMMA have different T_g s; isotactic (i) PMMA's T_g is the most peculiar at 60-70K lower than that of the chemically identical syndiotactic (s) and atactic (a) PMMAs. A similar trend was reported for their fragilities in a recent study. Therefore, three PMMAs with different tacticities offer the possibility to evaluate any conformational contributions to their glass transition temperatures, T_g s, and dynamic fragilities. Because of the wide range of the reported values, due most likely to the differences in materials and instrumentation, new dynamic fragility measurements were conducted using DSC to provide reliable comparisons of the dynamic fragilities of two stereoregular PMMAs and three a-PMMAs with different molecular weights. The m s determined for a-PMMAs showed a prominent molecular weight dependence and the comparison of s- and i-PMMAs was consistent with previous studies. Backbone bond rotational probabilities and conformational entropies obtained from Rotational Isomeric State conformational Model were used to explain the conformational origin of the low and high T_g and fragility of i-PMMA and s-PMMA, respectively. In the future, we plan to extend this conformational approach to connect microstructure sensitive local conformations or geometries to dynamic fragilities of many other polymers.

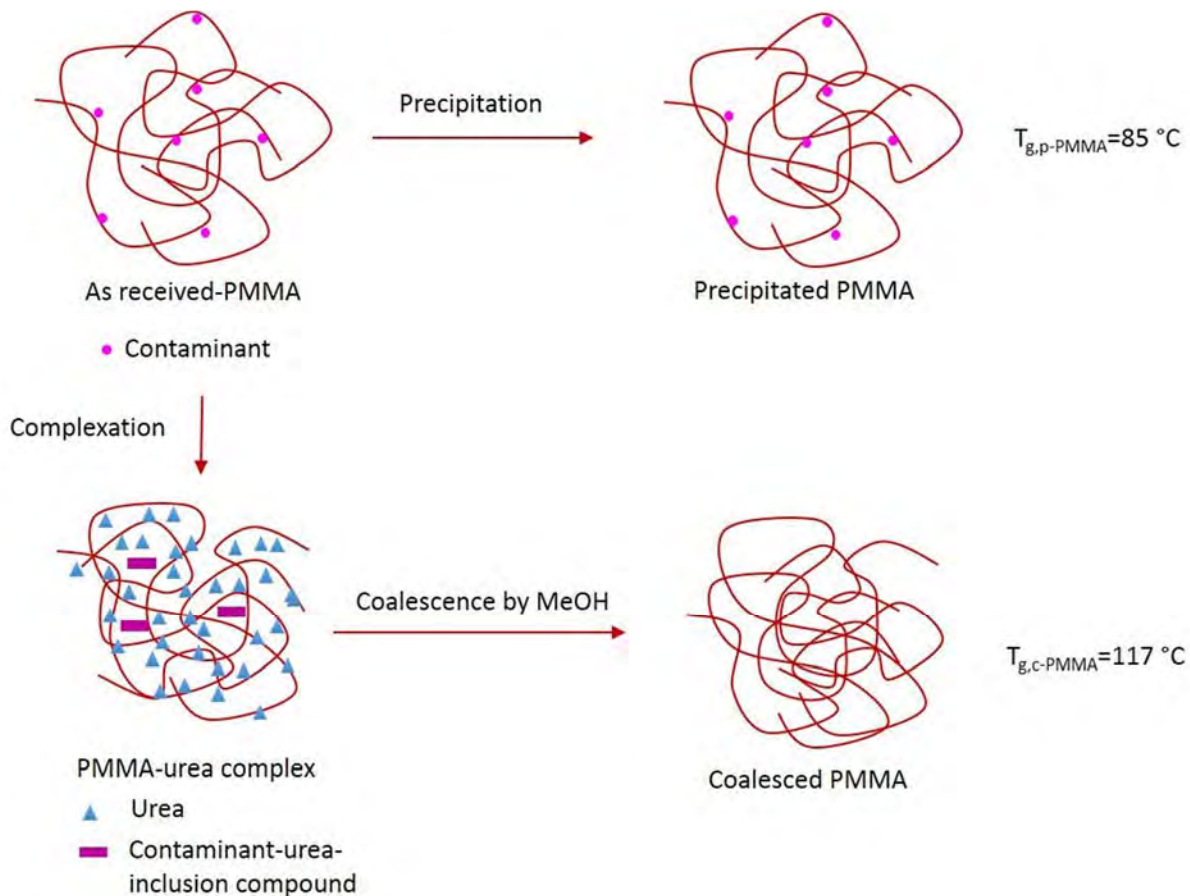


Relationship between dynamic fragility and meso diad content for all PMMA samples.

POLY 146: Introduction of a new purification method for the removal of a contaminant in commercial PMMA by using urea and N,N'-dimethylurea

Shanshan Li, *sli31@ncsu.edu*, Jialong Shen, Alan Tonelli. *TECS, North Carolina State University, Raleigh, North Carolina, United States*

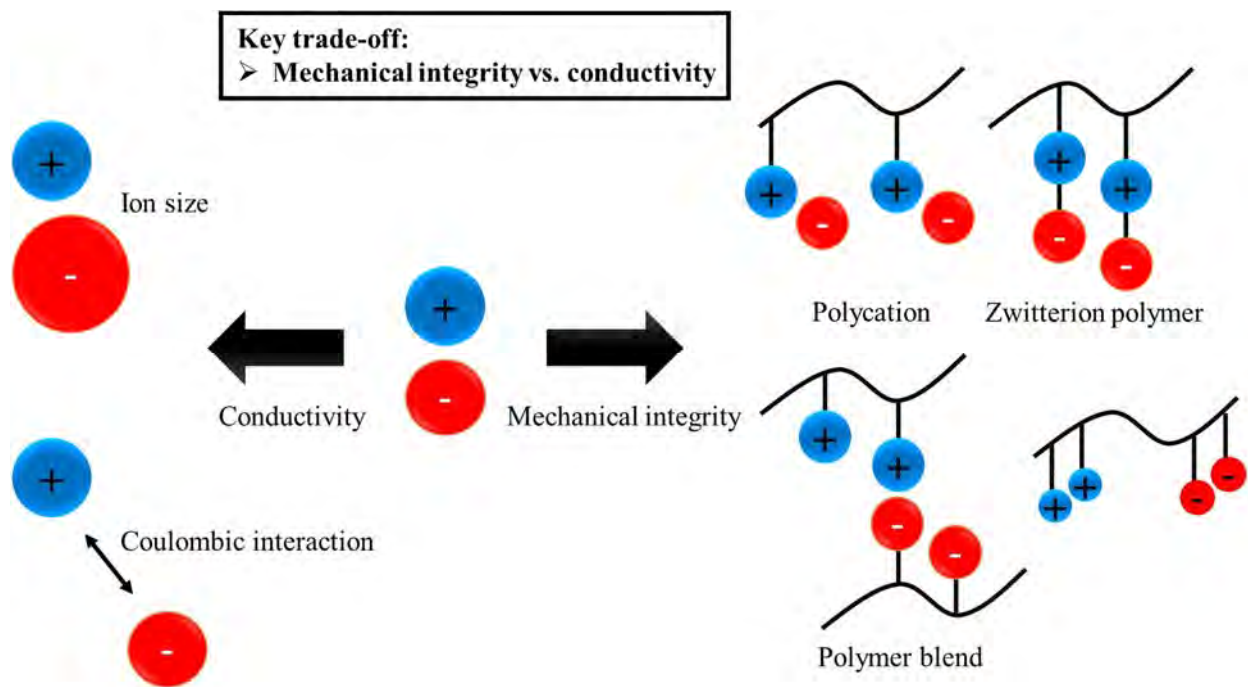
A contaminant in commercial poly(methyl methacrylate) (PMMA), likely a surfactant used in its emulsion polymerization, significantly reduces the glass transition temperature of as-received PMMA (asr-PMMA) by acting as a plasticizer. Precipitation, the common purification method used in most PMMA research, may not be able to remove the contaminant efficiently, since it is highly dependent on the solvents and non-solvents used. In this research, we introduce a new purification method for the removal of the contaminant in asr-PMMA by first complexing asr-PMMA with urea or N,N'-dimethylurea and then removing both the small molecule and contaminant in the system by using methanol. Urea and N,N'-dimethylurea can separately form noncrystalline complexes with asr-PMMA. They each penetrate and reside between PMMA chains in the non-crystalline complexes and may accelerate transportation of methanol in and among PMMA chains, thus helping with the purification process. Our PMMA sample purified by the new purification method showed a 30° C higher T_g than the asr-PMMA plasticized by the contaminant.



POLY 147: Ionic liquids inspiring next generation ion-containing polymers

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Poly(ionic liquid)s (PILs) have emerged as powerful materials in gas separation, ion conduction electrolytes and adhesive and anti-fouling coating. The incorporation of ionic groups into the polymer introduces electrostatic interactions that result in intriguing mesoscale structures and macroscopic responses. Using controlled polymerization methods, we highlight (1) low T_g , imidazolium-containing AB diblock copolymers with deuterium labelling to study *in situ* meso-scale morphological changes during an actuation process, (2) doubly charged ABA triblock copolymers to investigate ion aggregation within microphase-separated morphologies and their influence on macroscopic thermomechanical properties, and (3) the application of phosphonium-containing crosslinked materials in additive manufacturing to achieve conductive 3D objects with access to high resolution structural hierarchy controls. Rational design of ionic liquids in polymers introduces unprecedented microscopic phenomena and macroscopic properties, representing new directions in ion-containing polymers.



Integration of mechanical integrity to ionic liquids

POLY 148: Porous ionic liquids: Challenges and opportunities

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Functional materials using or in the presence of ionic liquids represents a burgeoning direction in materials chemistry. Ionic liquids are a family of non-conventional molten salts that can act as both functional materials and solvents. They offer many advantages, such as negligible vapor pressures, wide liquidus ranges, good thermal stability, tunable solubility of both organic and inorganic molecules, and ion conductivity. The unique solvation environment of these ionic liquids provides new reaction and separation media for controlling many energy-related processes. We have recently developed a class of ionic liquids with intrinsic porosities based on nanoscopic building blocks (Figure 1). Challenges and opportunities in synthesizing and using these porous ionic liquids in energy-related applications will be discussed.

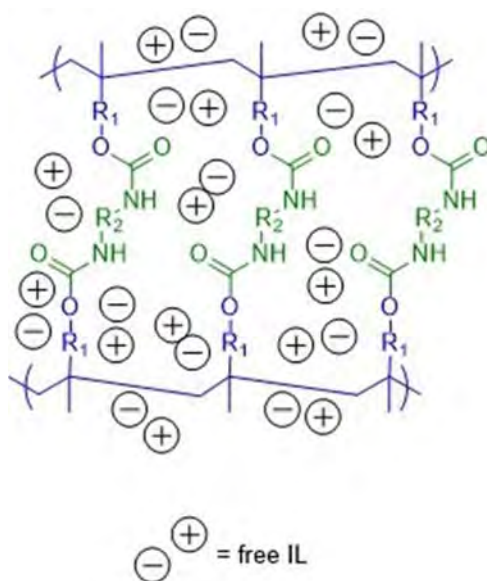


Figure 1. A porous ionic liquids composed of functionalized hollow silica nanospheres.

POLY 149: Poly(ionic liquid)/ionic liquid composites based on curable ionic liquid prepolymers for organic toxic industrial chemical hazard mitigation

Douglas L. Gin^{1,2}, gin@spot.colorado.edu, Dylan I. Mori¹, Richard D. Noble². (1) Dept. of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado, United States (2) Dept. of Chemical & Biological Engineering, University of Colorado, Boulder, Colorado, United States

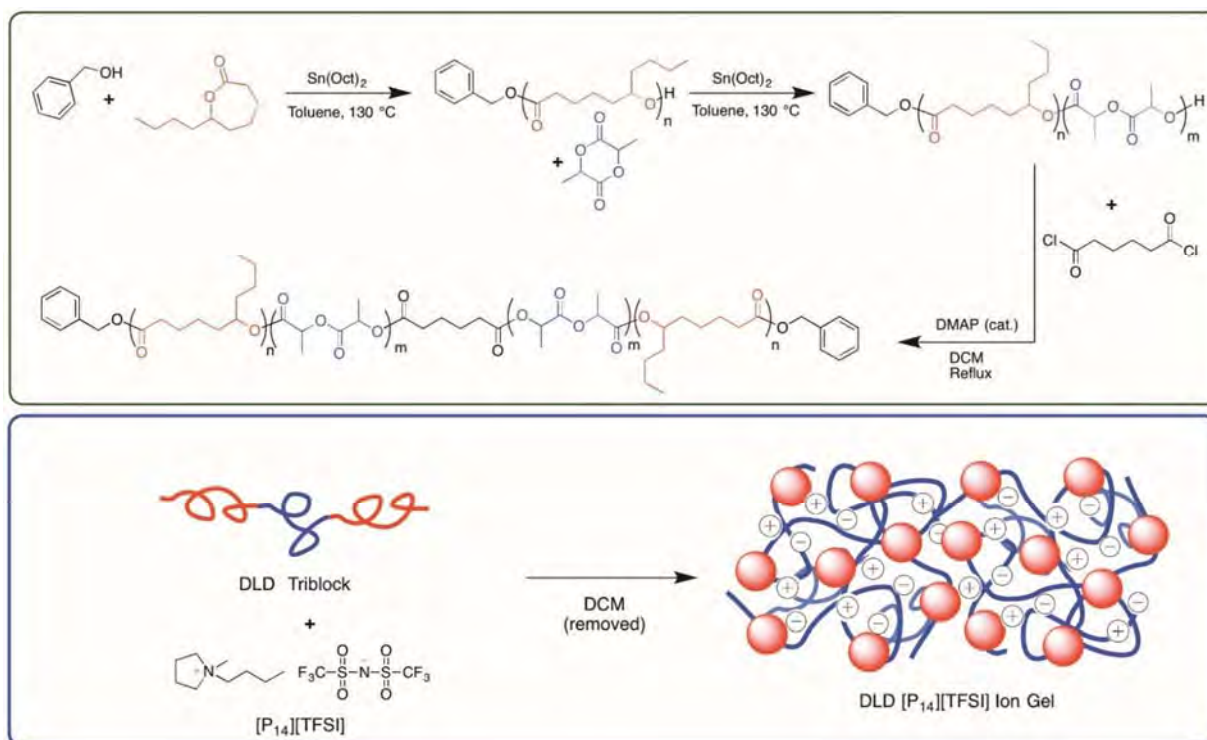
Poly(ionic liquid)/ionic liquid (PIL/IL) composite materials have solid-like mechanical properties that arise from the presence of a PIL matrix and a high degree of internal fluidity/diffusivity that arises from the presence of incorporated free IL. PIL/IL-based composite materials have traditionally been prepared via in situ polymerization or cross-linking of small-molecule IL monomers in the presence of added free IL and other additives. Although this approach works well in many situations, the low-viscosity nature of these initial (small-molecule IL monomer/IL/additive) mixtures allows them to rapidly soak/penetrate into porous substrate materials, thus making it very difficult to form integral thin films of PIL/IL on top of highly porous materials for applied coatings applications. We have found that instead of using small-molecule IL monomers to prepare PIL/IL composites, the use of controlled-molecular-weight, reactive IL oligomers (i.e., prepolymers) prepared by RAFT polymerization can generate curable fluid mixtures with higher viscosities and faster curing times that minimize initial solution penetration into porous substrates. This presentation will show how we have applied this (reactive IL prepolymer / IL / additive) approach to prepare new curable and peelable IL-based coatings for mitigating toxic industrial chemical (TIC) vapor release and absorbing soaked-in liquid TIC from organic-TIC-contaminated porous substrates such as wood and ceramic. The synthesis of these new curable, controlled-molecular-weight IL prepolymers and their benefits over traditional small-molecule IL monomers for PIL/IL composite preparation will be presented.



POLY 150: Functional ion gels

Timothy P. Lodge, lodge@umn.edu. Dept Chem Koltoff Smith Halls, University of Minnesota, Minneapolis, Minnesota, United States

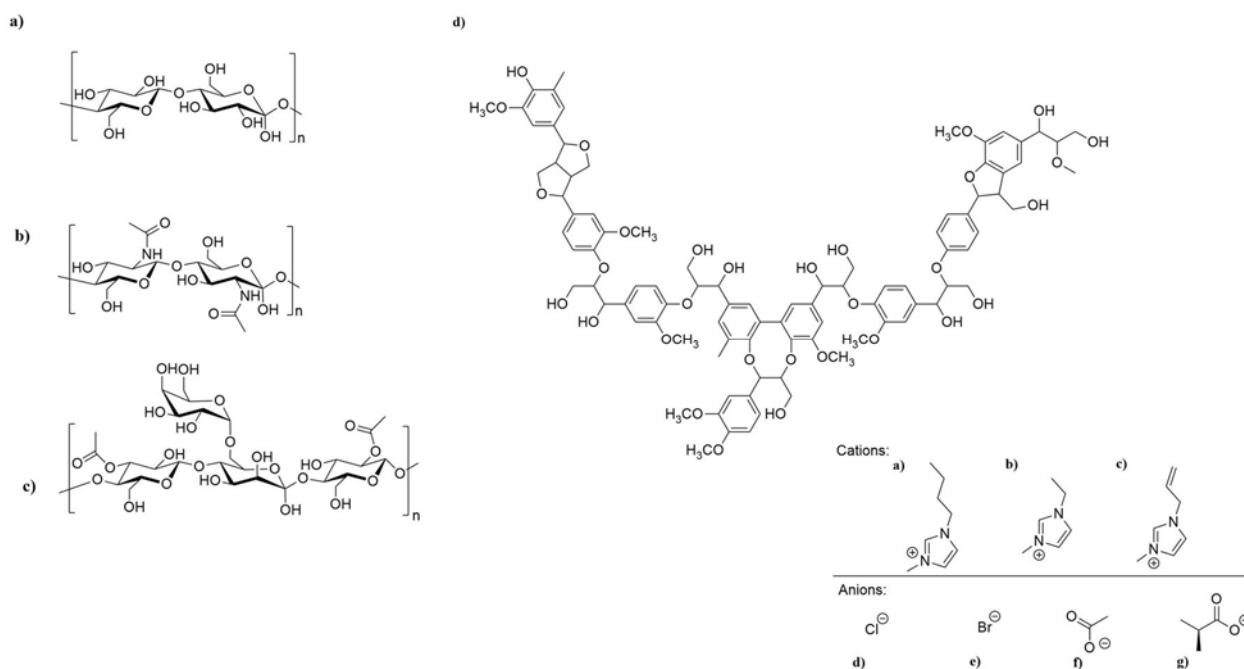
Ionic liquids are an emerging class of solvents with an appealing set of physical attributes. These include negligible vapor pressure, impressive chemical and thermal stability, tunable solvation properties, high ionic conductivity, and wide electrochemical windows. The non-volatile nature of ionic liquids renders them practical components of devices, but they require structure-directing agents to become functional materials. Block polymers provide a convenient platform for achieving desirable nanostructures by self-assembly, with lengthscales varying from a few nanometers up to several hundred nanometers. In particular, appropriate strategies enable independent tuning of mechanical strength and ionic conductivity. By combining block polymers and ionic liquids we have demonstrated materials with superior performance for a remarkably diverse set of applications, including gate dielectrics in organic transistors, electrochromic and electroluminescent gels, and membranes for gas separation, lithium ion batteries, and fuel cells.



POLY 151: Ionic liquid platform for electrospinning biopolymers

Robin D. Rogers^{1,2}, rdrogers@ua.edu. (1) 525 Solutions, Inc., Tuscaloosa, Alabama, United States (2) The University of Alabama, Tuscaloosa, Alabama, United States

Polymers constitute the largest group of chemicals that are currently used for manufacturing of nanofibers *via* electrospinning. Among those, use of synthetic polymers is nearly exclusive, mainly because of ease of their handling either through solution or melt processing. In recent years, there has been a growing shift toward the use of biopolymers including cellulose, chitin, chitosan, *etc.* because of many attractive properties of biopolymers (*e.g.*, tissue biocompatibility and biodegradability) which inspired multiple big industry players in using them for the development of materials of the future. Yet, traditional electrospinning methods from common solvents (such as volatile organic solvents, VOCs) are not suitable for biopolymers due to their insolubility in those. This presentation focuses on recent advances in the electrospinning of biopolymers which led to the development of an enabling technology based on ionic liquids that allow electrospinning of virtually any biopolymer directly from its natural source.

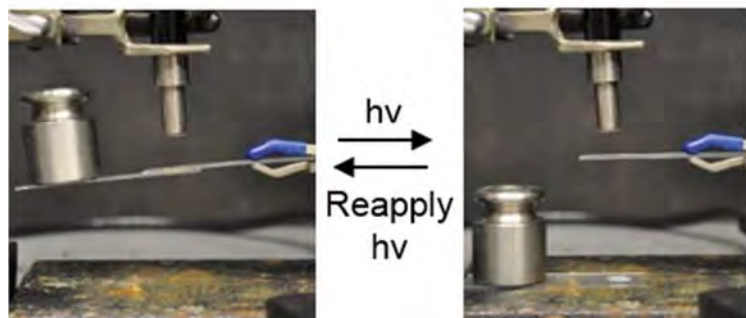


POLY 152: Design and synthesis of adaptive dynamic covalent polymers

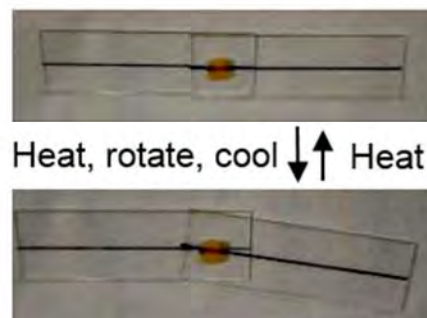
Stuart J. Rowan^{1,2}, stuartrowan@uchicago.edu. (1) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States (2) Department of Chemistry, University of Chemistry, Chicago, Illinois, United States

The dynamic bond can be defined as any class of bond that selectively undergoes reversible breaking and reformation, usually under equilibrium conditions. The incorporation of dynamic bonds (which can be either covalent or non-covalent) allows access to structurally dynamic polymers and composites. Such materials can exhibit macroscopic responses upon exposure to an environmental stimulus, on account of a rearrangement of the polymeric architecture. In such systems, the nature of the dynamic bond not only dictates which stimulus the material will be responsive to but also plays a role in the response itself. Thus, such a design concept represents a molecular level approach to the development of new stimuli-responsive/adaptive materials. We have been interested in the potential of such systems to access new material platforms and have developed a range of new mechanically stable, structurally dynamic polymer and nanocomposite films that change their properties in response to a given stimulus, such as temperature, light or specific chemicals. Such adaptive materials have been targeted toward applications that include healable plastics, responsive liquid crystalline polymers, adhesives, chemical sensors, and shape memory materials. Our latest results in these areas will be discussed.

Reversible Bonding/Debonding



Shape Memory

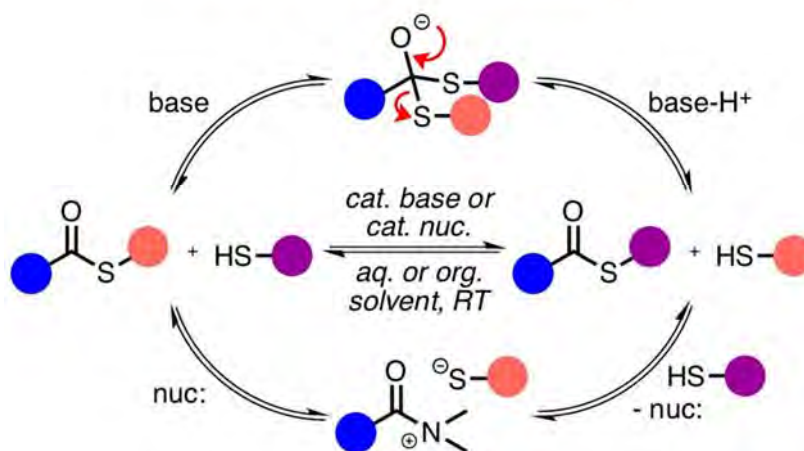


POLY 153: Photoinitiated thioester-containing polymer networks: Bistable, photoinduced (de)activation of dynamic covalent chemistry and fluid-solid transitions

Christopher Bowman, *christopher.bowman@colorado.edu*. Department of Chemical and Biological Engineering, Materials Science and Engineering Program, University of Colorado, Boulder, Colorado, United States

Covalently cross-linked polymer networks, once formed, cannot generally be reshaped, remolded, or deformed, which is attractive for creating robust materials but severely limits recyclability and repurposing, which is becoming evermore important with the advent of customized materials and devices as well as additive manufacturing. Recently, approaches incorporating dynamic covalent chemistries, particularly reversible exchange reactions, into the cross-links of these polymers challenged this paradigm. A thioester containing cross-link capable of dynamic exchange is reported here which is seamlessly incorporated into nearly any type of network forming polymerization. The thiol-thioester exchange gives rise to rapid bond rearrangement and plastic-like flow observable at ambient temperature in otherwise elastic networks. Based on this exchange reaction's response to reagents released using photoinduced processes, light-induced switching of material plasticity from OFF to ON and vice versa was achieved. This system was utilized to spatially and temporally control network rearrangement, stress relaxation, and shape changes on scales ranging from 100's of nm to 10 cm.

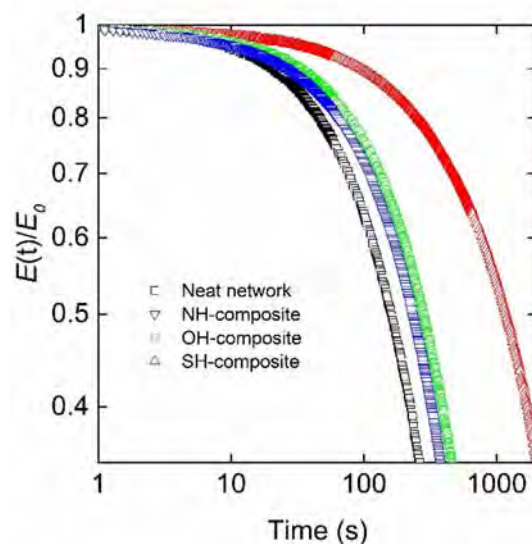
Thiol-Thioester Exchange



POLY 154: Reprocessable polyhydroxyurethane network composites: Effect of filler surface functionality on reprocessability and stress relaxation behavior

Xi Chen, *xichen2017@u.northwestern.edu*, *Lingqiao Li*, *John M. Torkelson*.
Northwestern University, Evanston, Illinois, United States

We discovered that polyhydroxyurethane (PHU) networks synthesized in the presence of catalyst (4-dimethylaminopyridine) from five-membered cyclic carbonates are intrinsically reprocessable with full property recovery via transcarbamoylation exchange reactions and reversible cyclic carbonate aminolysis. Recently, we investigated the effect of nanofiller surface functionality on the reprocessability and the rearrangement process of PHU network composites. Silica nanoparticles (diameter ~80 nm) with superhydrophobic (SH-composite), hydroxyl group (OH-composite), or amine group (NH-composite) functionality were incorporated into the PHU network at 4 wt% loading. Depending on the surface functionality, the nanoparticles can participate in transcarbamoylation exchange reactions (in the OH-composite) or reversible cyclic carbonate aminolysis (in the NH-composite) or exhibit behavior like a dormant species (in the SH-composite). The SH-composite was reprocessed (at 140 °C with ~10 MPa pressure for 2 hr) with full property recovery associated with cross-link density as determined from the rubbery plateau modulus. In contrast, the OH-composite and NH-composite showed losses of ~10% and ~20%, respectively, in cross-link density after reprocessing. Stress relaxation experiments were performed on the PHU network composites to determine the effect of different nanoparticles on the rate and the apparent Arrhenius activation energy of stress relaxation. Compared with the neat network, the network composites showed slower stress relaxation, with the SH-composite being the slowest, followed by the OH-composite and the NH-composite. In contrast, there was no significant impact of the nanoparticle surface functionality on the apparent activation energy of stress relaxation.

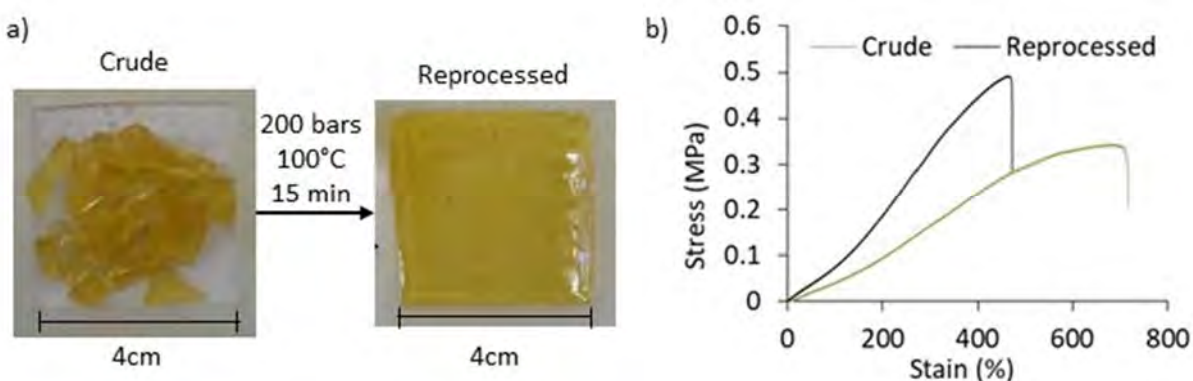


Stress relaxation of PHU network and network composites at 140 °C (5% strain)

POLY 155: Healing properties in hybrid polymers: impact of the metal-ligand bonds' strength

Aude Duhamel¹, *aude.duhamel1@gmail.com*, **Guillaume Penvern**¹, **Nathalie Donnat**², **Pierre-Antoine Bonnardel**³, **Jean-Christophe Joseph**³, **Lionel Nicole**¹, **Laurence Rozes**¹.
(1) *Chimie de la Matière Condensée de Paris, Paris, France* (2) *Expiris, Marignane, France* (3) *PCAS, Porcheville, France*

Organic-inorganic hybrid materials offer a wide range of interesting properties, especially due to the iono-covalent nature of the organic-inorganic bonds that leads to polymers with healing properties. In polymers, the inorganic component can play two main roles: network modifier or network former. The hybrid materials presented here are modified polyacrylates permanently cross-linked via metal-ligand bonds. Thanks to the exchangeability of these bonds within the networks, these particular materials show thermally induced healing properties. Furthermore, the inorganic part reinforces the polymers and improves the thermal stability of the whole material. Moreover, the hybrid organic-inorganic approach allows by tuning the strength of the metal-ligand bonds to have healing properties at different temperatures from room temperature to 150°C. Hereby, we have investigated the healing properties of polyacrylates dynamically cross-linked with different organic ligands able to complex metallic oxides. The adaptability of the networks has been highlighted by creep test and the efficiency of healing properties has been investigated by mechanical tests (tensile tests and DMTA) on both crude and repaired materials. Thereby, each system exhibits a critical temperature for healing properties that differs from the others and this temperature strongly depends on the strength of the metal-ligand bond at the hybrid interface.

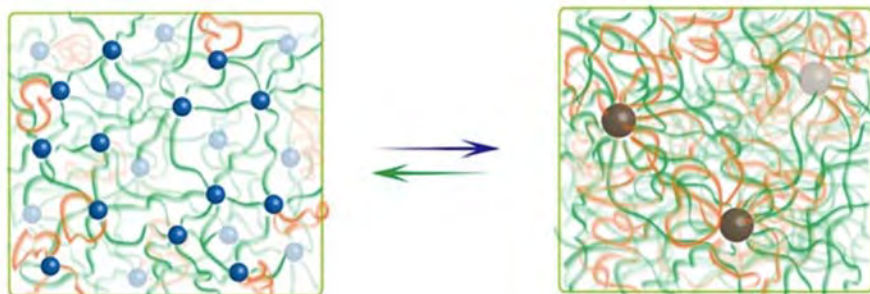


- a) Damaged material and reprocessed material at 200 bars, 100°C for 15 min
b) Tensile tests on crude and reprocessed material

POLY 156: Switching polymer network topology with light

Yuwei Gu¹, Eric A. Alt¹, Heng Wang², Xiaopeng Li², Adam Willard¹, **Jeremiah A. Johnson¹**, jaj2109@mit.edu. (1) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Department of Chemistry, University of South Florida, Tampa, Florida, United States

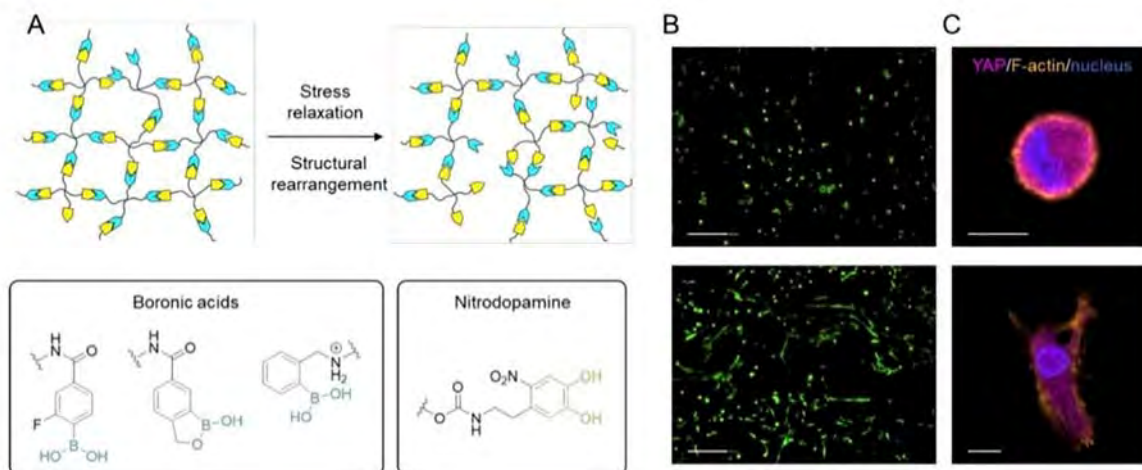
We have developed supramolecular polymer metal-organic cage/polyhedra (polyMOC) gels that feature MOC junctions that can be switched between two different metal-ligand stoichiometries in response to green and ultraviolet (UV) light, respectively, to produce reversible changes in the network topology. These polyMOCs display vastly different static and dynamic properties depending on their topological state.



POLY 157: Viscoelastic hydrogels based on boronate esters for understanding cell-matrix signaling

Shengchang Tang¹, Hao Ma¹, Po-Chiao Lin², **Kristi S. Anseth**¹,
kristi.anseth@colorado.edu. (1) University of Colorado, Boulder, Colorado, United States (2) Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan

New biomaterials that can faithfully recapitulate viscoelastic properties of tissues has been an area of growing interest in cell mechanobiology. While cumulative evidence suggests that the stiffness of synthetic extracellular matrices can influence cell function and fate, more recently, the importance of viscoelastic properties has been revealed and appreciated. However, it is still challenging to thoroughly understand the cell-niche interactions in viscoelastic materials, in part due to the complex coupling between time-dependent material mechanical properties and various cellular processes that span a wide range of timescales from seconds to weeks. Here, we use reversible boronate esters to prepare hydrogels that exhibit very fast relaxation on the order of seconds and tune the viscoelasticity of gels by changing small molecule properties. Using human mesenchymal stem cells (hMSCs) as a model system, we show that stress relaxation better maintains cell viability post-encapsulation and promotes the spreading of hMSCs. By examining YAP/TAZ subcellular localization at different time points, we show that cells respond to their surrounding 3D environments at different rates and that stress relaxation eventually induces nuclear localization of YAP/TAZ. We also investigated expression levels and spatial distribution of various proteins in focal adhesion complexes and observe significant $\beta 1$ integrin clustering in the stress-relaxing hydrogels. Given the relevance of fast relaxation dynamics in many biological processes, we expect that this material platform will find use as versatile platform to probe many fundamental aspects of cell-matrix interactions and signaling.

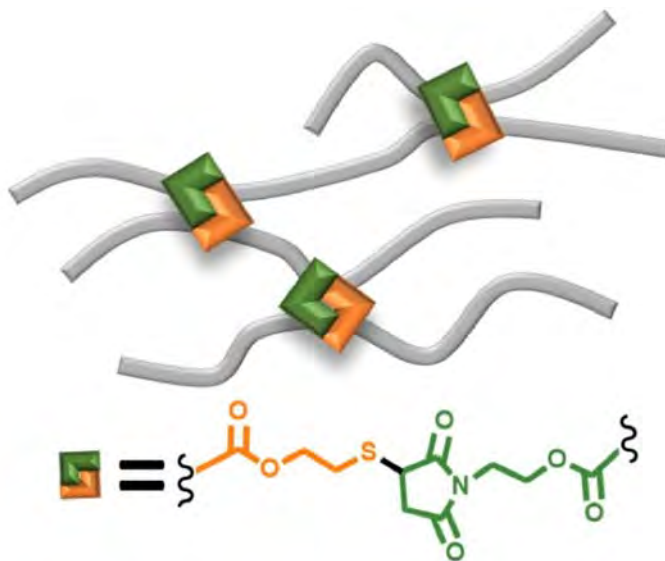


A. Chemical structures of boronic acids and nitrodopamine forming boronate esters (bottom) and viscoelastic networks (top). B. Live/dead assay of hMSCs in elastic (top) and stress-relaxing (bottom) gels showing high cell viability post-encapsulation and spreading of hMSCs in relaxing gels by Day 7. Scale bar 200 μ m. C. IF images of cells in elastic (top) and stress-relaxing (bottom) gels showing distinct YAP/TAZ subcellular localization. Scale bar 10 μ m.

POLY 158: Externally activated thiol-Michael chemistry for stable yet adaptable networks

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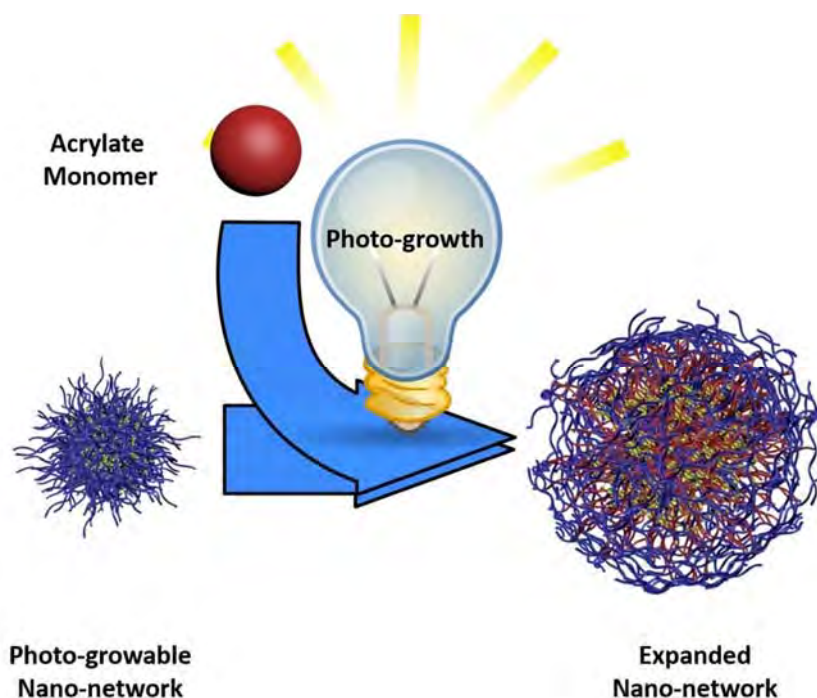
The thiol-Michael reaction is a highly efficient reaction with applications ranging from protein modification to polymer crosslinking. Although known for over 50 years, the thiol-Michael reaction has seen a significant resurgence in recent years due to its “click” like nature. However, despite the highly efficient nature of the thiol-Michael reaction upon appropriate external stimulus such as high temperature or high pH, the thiol-Michael reaction can be activated and made dynamic. In this abstract, thiol-Michael adducts are introduced into polymer materials as crosslinkers. Initially, the dynamic exchange properties of the thiol-Michael adducts are explored in solution phase model systems, to evaluate the kinetics of dynamic exchange. Subsequently the mechanical properties of dynamic thiol-Michael materials are evaluated.



POLY 159: Photo-controlled growth of crosslinked nano-networks

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Polymer networks are structural components of hydrogels, nanoparticles, surface coatings, organic frameworks, and vitrimers. Their versatility and range of properties has seen to their increased importance in polymer science with far-reaching potentials in biomedical science, in environmental science, and in advanced functional materials. Recently, light induced polymerizations, specifically RAFT polymerization techniques, have opened the possibility to reach a higher degree of control in polymer network architectures. Photo-controlled growth of polymer networks post-formation can precisely introduce higher levels of complexity within a network. This work seeks to prepare a diverse set of light responsive nanomaterials through the formation of nano-networks crosslinked with trithiocarbonate RAFT initiators.

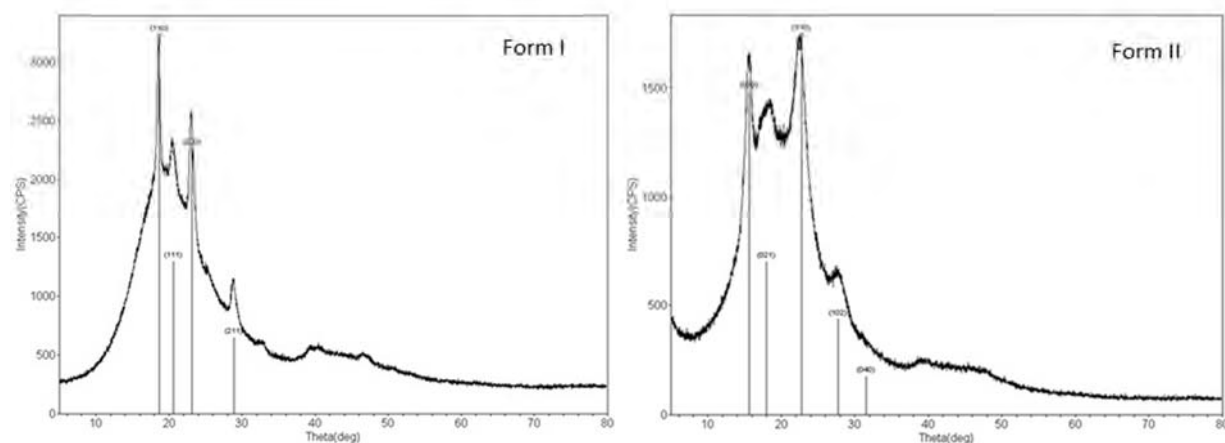


POLY 160: Understanding structure and property of PAEK polymers and their application in Additive Manufacturing processes

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Additive Manufacturing (AM), otherwise known as three-dimensional (3D) printing, is a growing technology area comprised of a spectrum of processes that allow production of solid objects of virtually any shape from information obtained from a digital object. These days, AM processes drive major innovations in engineering, manufacturing, art, education and medicine. However, most AM processes are not necessarily new. Introduced commercially in the 90's mainly through prototyping efforts for the manufacture of complex metal parts, AM processes have almost a 30-year history for plastics, and have driven the development of multiple commercial products through manufacturing techniques ranging from stereo-lithography to laser-based powder based fusion processes.

A growing number of polymeric resins intended for AM have become available in recent times due to developments of new processes and technological advancements. Of these, high-performance thermoplastics such as the poly(aryletherketone)s (PAEKs) are perhaps the most promising material candidates for demanding engineering applications. Among these, PEEK, PEKK, and PEKEKK, could revolutionize and enable the use of additively manufactured polymer parts in critical environments. However, despite their similarity in terms of chemistry and composition, commercially available PAEK resins show varying physical properties due to their molecular size-dependent structural differences. This talk will describe an in depth study of the structure and property relationships of commercially available PAEKs, as well as the morphological changes observed in these resins when subjected to conditions typically found in common AM processes. We conclude that the fundamental understanding of the resulting structure of these polymers in critical environments is crucial and necessary for the development of new technologies and future complex processing techniques.



WAXD patterns for PEKK crystalline polymorphs (Form I and Form II).

POLY 161: High throughput screening and design of experiments: How to obtain predictive models for thermoplastic blends and compounds

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Thermoplastic compounds for commercial use are usually complex mixtures, including components such as antioxidants, heat stabilizers, processing aids, fillers, fibers, flame retardants and synergists, colorants and others. Optimizing properties or even just improving one property such as toughness is no simple task, because changing one component usually affects all properties simultaneously, and not always towards the desired direction.

Complex systems are best handled using mathematical methods (DoE) to design the experimental plan. However, for a complex system consisting of many components (e.g. Polymer, glass fibers, flame retardant, synergist, dispersant, impact toughener), still hundreds of compounds need to be produced and tested, if the system is to be covered satisfactorily. The combination of experimental plans by DoE with high throughput screening methods (HTS) is the best way to handle this.

As an example to show the power of the combination of DoE and HTS, we have mapped the landscape of blends of PLA with petrochemical polymers with the target to meet the properties of petrochemical plastics as near as possible while keeping the content of PLA as a polymer from renewable resources as high as possible. This includes mechanical properties, softening temperature, crystallinity, rate of crystallization, and stabilization against hydrolytic degradation. Approximately 1500 compositions were screened by producing injection molded samples and measuring them on our X-Plorator® High Throughput Screening System, grouped into 10 DoE plans for different targets. 15 Different thermoplastics, 13 different nucleating agents and synergists, 11 softeners and compatibilizers, and 6 different reinforcing fibers were included into the screening. Predictive models could be constructed from the results, and were used to match the PLA blends against selected thermoplastics. Figure 1a shows a comparison of properties of selected PLA blends vs. a commercial ABS grade. Figure 1b shows the stability of selected PLA blends vs. hydrolytic degradation (600h, 50°C, 96%rh).

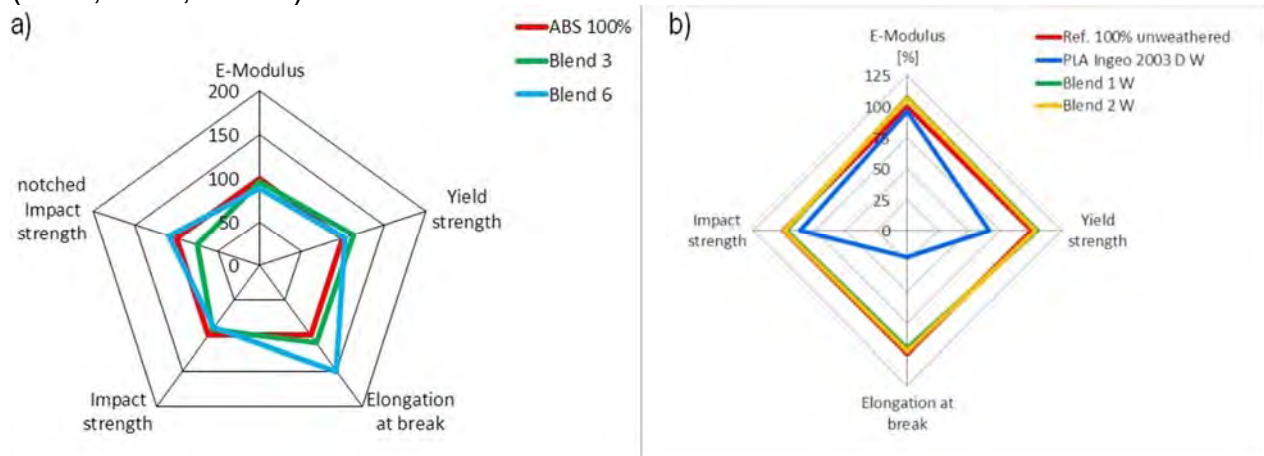
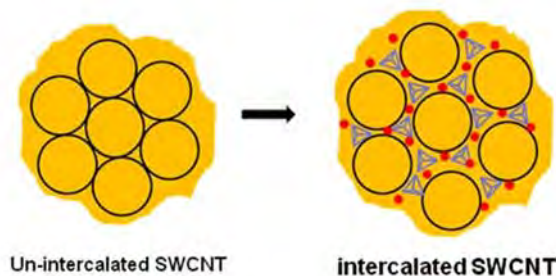


Figure 1: a) Comparison of PLA blends with a commercial ABS grade; b) degradation stability of PLA blends in comparison to a commercial PLA grade

POLY 162: Polymeric hands at work: Design tools in the synthesis of multifunctional nanomaterials

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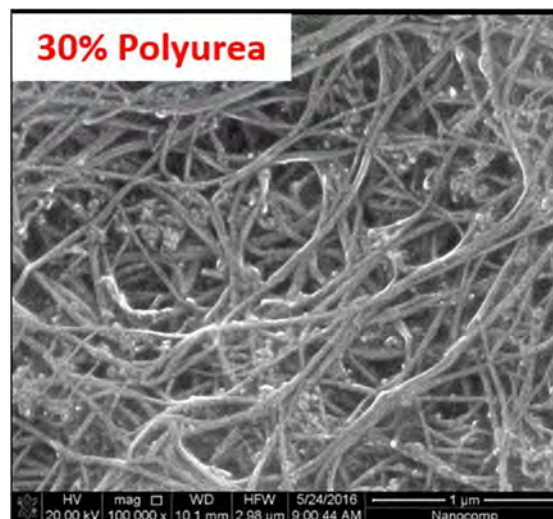
A significant number of advancements in the synthesis and application of multifunctional nanosystems often invoke a molecular level design principle enabled by a specific polymer delivering the key design requirement. Such principles in general, aim to control the organization of large molecules, nanoparticles, nanoscale rigid rods or lamellar nanoparticles at heterogeneous interfaces, enabling one or more of an optical, electrical, magnetic, mechanical or a chemical functionality. The multiple length scales involved in the final material, ranging from molecular sizes to mesoscale lengths to several micron-sized domains add further complexity to the process of selecting the right players. This presentation will cover various case studies drawn from the speaker's own work spanning twenty years. Historic examples will include designer dielectrics for integrated thin film capacitors that require controlled interfacial polarization loss at a polymer-inorganic interface and alignment of single-walled carbon nanotubes enabled by the directing effects of either a self-organizing di-block copolymer or nematic phases formed due to the rigid rod polymer-like behavior of carbon nanotubes. Most recent examples showing immense commercial potential will include nanohybrid films enabled by a polyelectrolyte which allow the reinforcement of a brittle indium-tin oxide film, tailored charge transport pathways at the polymer-ceramic interface in a bulk-heterojunction photovoltaic cell and proton reservoir membranes for PEM fuel cells and supramolecular polymers that help the separation of semiconducting carbon nanotubes for printed electronics applications.



POLY 163: Understanding CNT-polymer composites on a molecular level

Ashley E. Hart, ahart@nanocomptech.com. Product Development, Nanocomp technologies, Merrimack, New Hampshire, United States

As the need for ultra-high strength, light weight composites has increased, carbon nanotube (CNT) composites have become more attractive due to their potential to exhibit far superior properties compared to traditional carbon fiber (CF) composites. To realize that potential, the interaction between a resin matrix and CNT surface needs to be optimized. Currently there is a lack in understanding of how polymers interact with CNTs on a molecular level. Nanocomp Technologies INC (NTI) manufactures a CNT hybrid material called Miralon® which is a non-woven, semi-isotropic mat comprised of long-range interconnections of branched CNT bundles surround by non-CNT carbon creating a unique macrostructure that can serve as scaffolding for an ultra-strong composite. NTI has conducted resin compatibility studies on Miralon® sheets to identify resin system that will be compatible and provide load transfer between the CNT bundles and polymer matrix. Resins were dissolved in solvent and spray coated onto the Miralon sheets for a 30 wt% target resin loading. Spray coating the polymers is necessary due to the small pore size of Miralon and previous attempts at resin film lamination proved ineffective at complete and uniform resin loading. The mechanical properties of resin loaded Miralon sheets were investigated, and the panels were analyzed with scanning electron microscopy and thermogravimetric analysis in order to determine compatibility. The studies showed that resin compounds containing zwitterionic, specifically nitrogen and doubled bonded oxygen, and aromatic functional groups are the most compatible with Miralon®. Polyurea, a polymer which contains all of the above mentioned functional groups has found to be the most compatible resin to Miralon to date.



POLY 164: Polymeric material considerations for electrocaloric-based thermal management

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Dielectric fluoropolymer are useful class of materials for a number of advanced engineering applications. These materials can also possess intriguing morphological, mechanical, and phase change behavior that in many applications such as capacitors result in distinct application challenges, however if harnessed in new ways can reveal other unique application opportunities. This presentation specifically focuses on a review and empirical analysis of PVDF-TrFE-CTFE terpolymers and their electrocaloric response when subjected to an electric field. It is well known that the composition of this specific terpolymer can be tailored to adjust the curie transition. If adjusted such that the transition approaches room temperature and the enthalpy of transition is great enough, these materials can be considered for solid state cooling applications. This presentation will also outline the calorimetry setup under field demonstrating material level cooling capability and outline the industrial impact that these and future electrocaloric materials may have on HVAC and other industries which desire high efficiency thermal management.

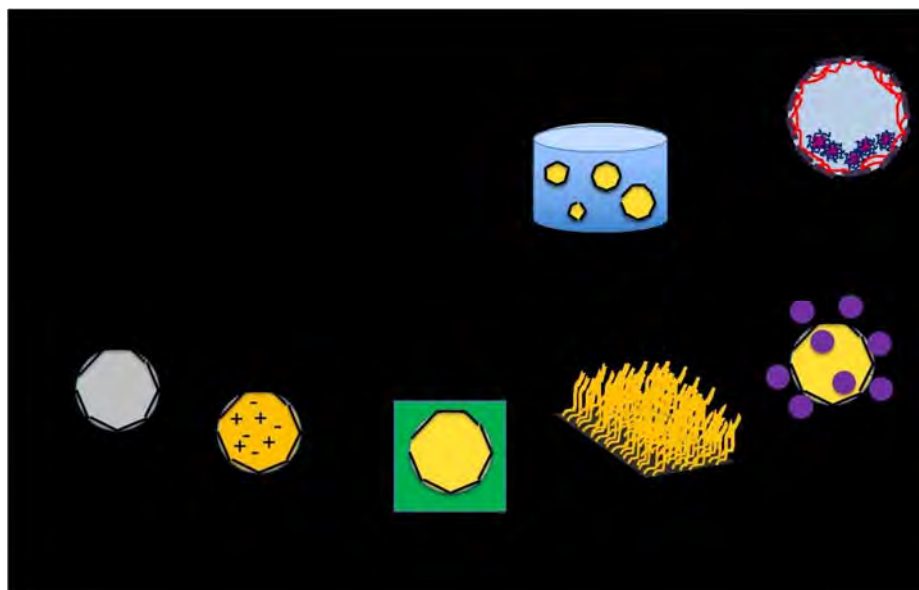


**United Technologies
Research Center**

POLY 165: Using the assembly of 2D particles at fluid-fluid interfaces to architect composite materials

Qinmo Luo³, Peiran We², **Emily Pentzer**¹, ebp24@case.edu. (1) Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (3) Case Western Reserve University, Cleveland, Ohio, United States

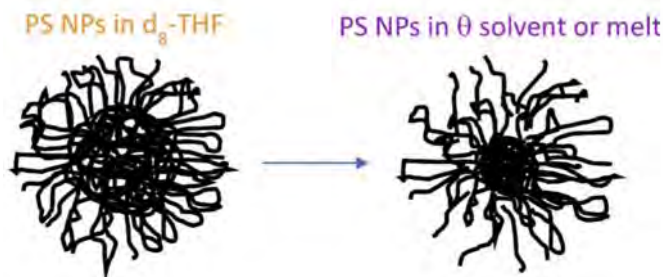
The interface between two fluids is not only important for defining reactivity of dislike materials, but is also applicable for the preparation of stable higher order structures. Recently, the Pentzer lab developed 2D carbon-based nanosheets that assemble at different fluid-fluid interfaces including oil-water, oil-oil, and ionic liquid-water and demonstrated the use of these Pickering emulsions as templates for the preparation of higher order hybrid structures. Graphene oxide (GO) and its functionalized analogues are used as the 2D particle surfactant, and are especially attractive given they have properties distinct and complimentary to the more commonly studied spherical and rod-like counterparts, and because these nanosheets are multifunctional (e.g., antimicrobial, good gas barriers, precursor to electrically conductive nanosheets, etc.). Recent advances from the Pentzer lab will be reported, including preparation of Janus nanosheets, water-sensitive reactions in oil-in-oil emulsions, GO capsules filled with ionic liquid for supercapacitor electrodes, GO capsules for compartmentalization of phase change materials, and GO coatings for 3D printable polymers to prepare conductive structures. This work makes use of fundamental organic chemistry reactions and thus gives access to unique structures and assemblies of interest for a broad range of applications in a scalable fashion.



POLY 166: Structure of soft nanoparticles in solvents and melts: Correlation of nanoparticle structure to nanocomposite dynamics

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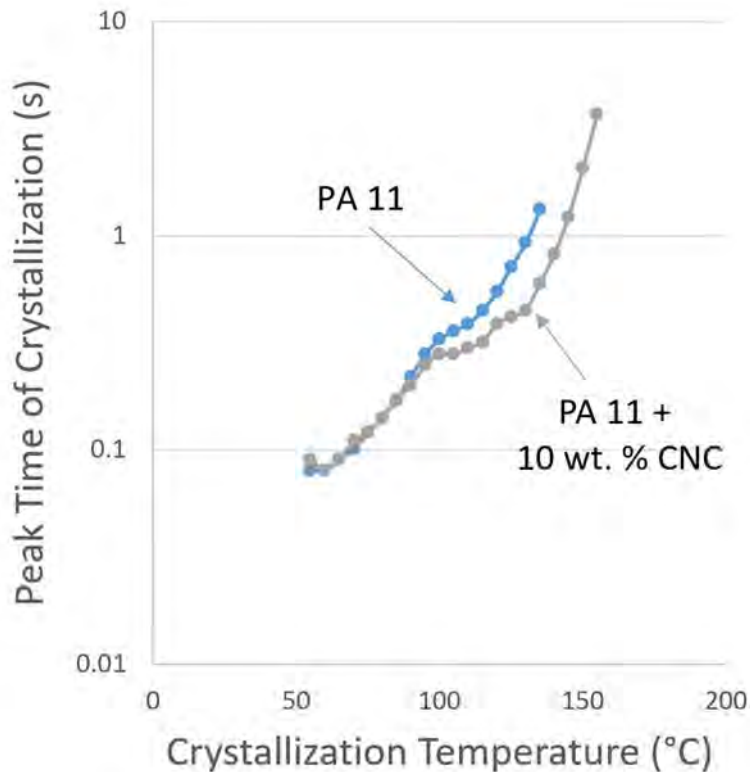
Single chain, soft nanoparticles are interesting as models for self-assembling macromolecules, and as novel additives in polymer nanocomposite. Our recent results have shown that the addition of a soft nanoparticle can significantly alter the diffusion of surrounding polymer chains[i] and that the soft nanoparticle is not stationary in the melt, but its motion is consistent with the cooperative motion of polymer chains and soft nanoparticles.[ii] Our recent small angle neutron scattering results also show that synthetic conditions correlate well to internal morphology of the soft nanoparticle, providing tunable control of the nanoparticle internal structure and size.[iii] In this talk we will present results that document the structure of polystyrene soft nanoparticles in a good solvent, in a theta solvent and in a polystyrene melt and how their structure correlates to the diffusive motion of the neighboring polymer chains. These results provide crucial insight into the importance of the structure of the penetrable interface between the nanoparticle and the linear polymer chain and its impact on their interaction and motion.



POLY 167: Crystallization of polyamide 11 / cellulose nanocrystalline composites across a broad range of supercooling

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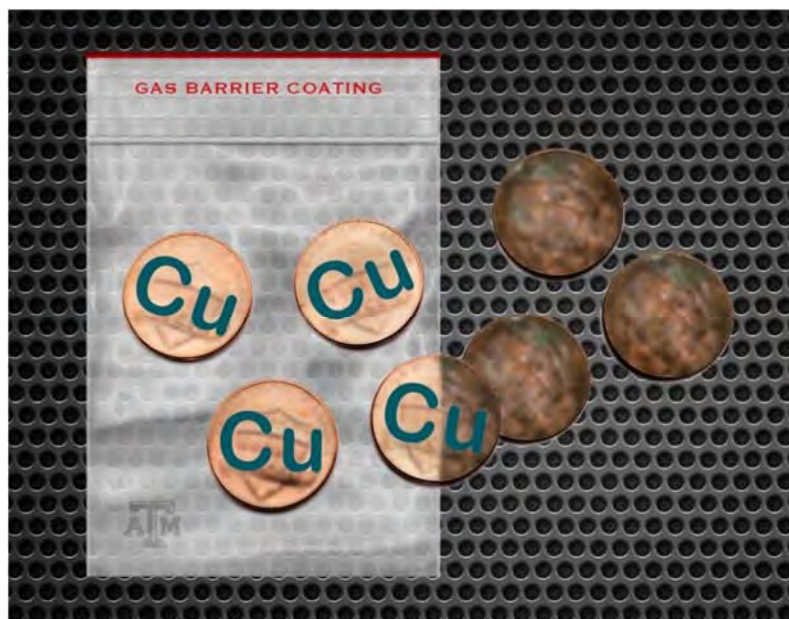
Crystallization in polyamide 11 (PA11) / cellulose nanocrystals (CNC) composites is characterized using fast scanning chip calorimetry and differential scanning calorimetry. The CNC nanocrystals nucleate and enhance crystallization in the heterogeneous regime, between 95 and 155 °C. The nanocrystals had no effect on isothermal crystallization below 95 °C, confirming that the bimodal isothermal halftime curve for PA11 is attributed to the prominence of homogeneous nucleation at high supercooling. Cooling studies indicate the CNC influence the non-isothermal crystallization behavior, particularly at higher cooling rates. Results are discussed in light of CNC particle dispersion as observed in environmental scanning electron microscopy (ESEM) and related mechanical properties.



POLY 168: Nanobrick wall nanocomposites with super gas barrier properties

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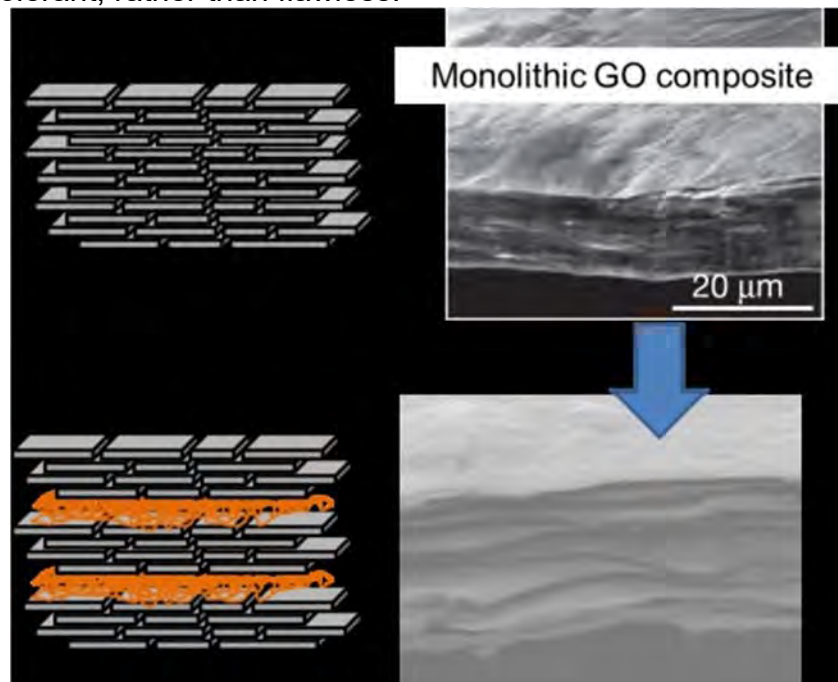
Polyethylene terephthalate (PET) and oriented polypropylene (OPP) are widely used in various packaging applications. Vapor deposited SiO_x and Al_xO_y and polymer-clay nanocomposites coatings have been used to improve the gas barrier of these films, but these approaches often reduce flexibility and transparency. Layer-by-layer (LbL) assembly provides a cost-effective alternative. OPP film was coated with a polymer-clay LbL gas barrier nanocoating that improved oxygen and water vapor transmission rate (WVTR). A 30 bilayer polyethylenimine (PEI)/vermiculite (VMT) coating improved the oxygen transmission rate by more than 160X, rivaling most inorganic coatings. WVTR was simultaneously reduced by 42.5% relative to uncoated OPP. This water-based technology is both effective and scalable. Hydrogen-bonded multilayer thin films are very stretchable, but their gas barrier properties are modest compared to more traditional ionically-bonded assemblies like PEI/VMT. In an effort to improve the gas barrier of poly(ethylene oxide) (PEO) – poly(acrylic acid) (PAA) multilayer films, without sacrificing stretchability, montmorillonite (MMT) clay platelets were combined with PAA and alternately deposited with PEO. A ten bilayer PEO/PAA+MMT film (432 nm thick), deposited on a 1 mm polyurethane substrate, resulted in a 54X reduction in oxygen transmission rate and was not damaged after being strained 20%. This nanocoating system is currently the best combination of stretchability and gas barrier ever reported. It is also possible to deposit a high oxygen barrier coating in a single step using a polyelectrolyte complex of polyethylenimine and poly(acrylic acid). A two micron coating reduces the OTR of 175 micron PET by two orders of magnitude. These types of multilayer coatings are an effective and environmentally benign option for high barrier food, pharmaceutical and electronics packaging.



POLY 169: Thin-film structures based on graphene oxide—models for the ideal polymer-graphene oxide nanocomposites

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Synthetic nanostructures such as carbon nanotubes and graphene oxide have stiffness, strength, and toughness that exceed those of any commercial structural material (e.g., steel, concrete, polymers) by several orders of magnitude. However, their applications have been limited, as currently available techniques for assembling these nanoscopic building blocks into macroscopic nanocomposite materials fail to extend their impressive nanoscale properties to the macroscale. In contrast, nanostructures of brittle minerals such as CaCO_3 can be assembled into strong macroscopic natural materials like nacre or bone in the presence of a small amount of proteins. Nature achieves this through a synergistic combination of atomic-scale control of chemical interactions and nanometer- to micrometer-scale control of component organization. Taking inspirations from these natural examples, we have been able to design lightweight, mechanically strong nanocomposites, either by mechanical fabrication and chemical crosslinking, or by interfacing nanofillers such as carbon nanotubes and graphene oxide sheets with polymers. This presentation will chronicle our findings in the fabrication of composite thin films of polymers and carbon-based nanofillers by: 1) elucidating the mechanical properties of the interfaces between graphene oxide monolayers and polymers through nanomechanical studies and 2) fabricating polymer-graphene oxide nanocomposites that are flaw-tolerant, rather than flawless.

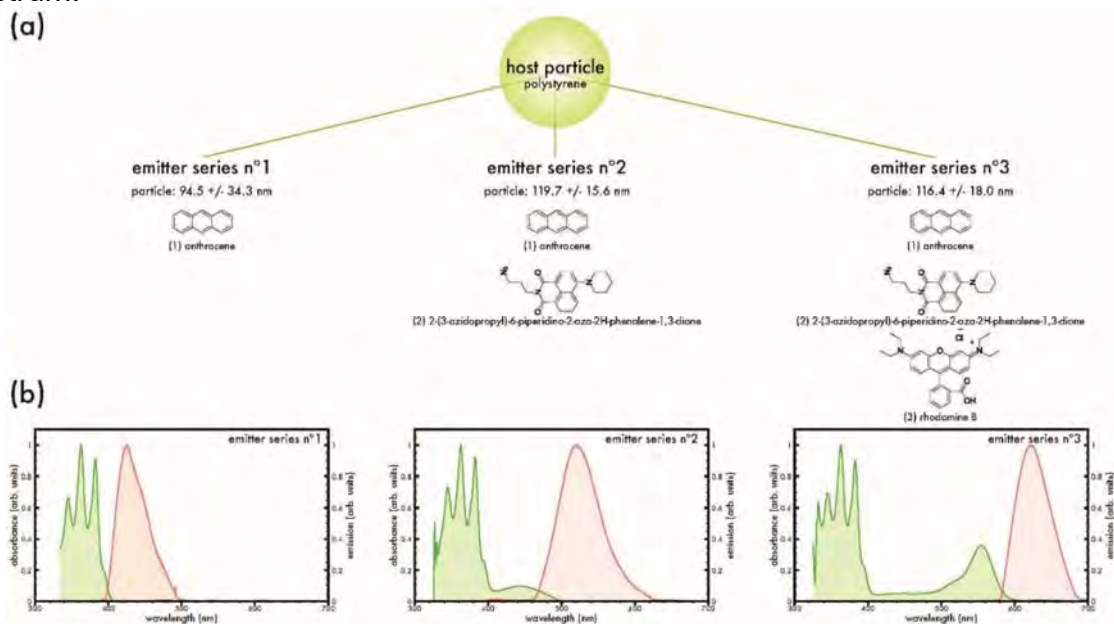


Top: A pure-graphene-oxide films showing clean fracture surfaces consistent with crack initiation and propagation perpendicular to the applied tensile load. Bottom: A multilayer nanocomposite films of graphene oxide-poly(methyl methacrylate) (GOPMMA) showing terracing that consistent with crack stopping and deflection mechanisms.

POLY 170: Dynamic emission tuning of X-ray radioluminescent dye-doped crystalline colloidal arrays

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Sub-100 nm polystyrene nanoparticles were doped with an x-ray radioluminescent organic molecule and two different fluorophores, resulting in three groupings of particles. The three groupings included particles doped with (1) anthracene (Anth); (2) Anth and 2-(3-Azidopropyl)-6-piperidino-2-aza-2H-phenalene-1,3-dione (Naph), and (3) Anth, Naph, and Rhodamine B (RhB). In these particles, the Anth served as the x-ray radioluminescent emitter that transferred energy over to the subsequent dye(s) in the particles. Particles doped only with Anth exhibited a fluorescence peak spanning from 394 nm to 500 nm and a maximum at 424 nm when excited by an x-ray source. Particles that encapsulated both the Anth and Naph emitters exhibited an emission peak centered at 520 nm that was primarily attributed to the Naph fluorophore. Particles doped with all three of the dyes (Anth, Naph, and RhB) resulted in the radioluminescence spectrum exhibiting a peak located at 622 nm that was solely attributed to the RhB dye. In this latter series of particles, Forster resonance energy transfer (FRET) was cascaded between the three dyes for a total wavelength shift in emission, relative to the Anth, of 198 nm. Utilizing self-assembly of the particles into crystalline colloidal arrays allowed for a modulating of the FRET efficiencies between the fluorophores with a dynamic tuning of the rejection wavelength within the emission spectrum.

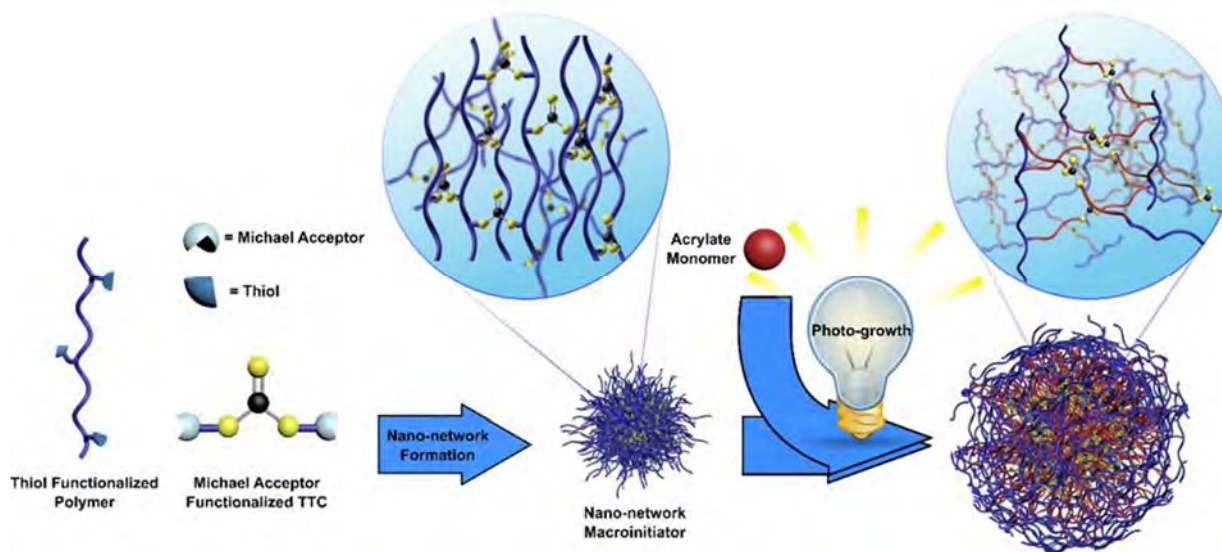


(a) X-ray radioluminescent polystyrene particles were doped with anthracene (Anth)(emitter series n1), Anth and 2-(3-Azidopropyl)-6-piperidino-2-aza-2H-phenalene-1,3-dione (Naph) (emitter series n2), or Anth, Naph, and rhodamine B dye (RhB) (emitter series n3). (b) Optical absorbance (green curve) and x-ray radioluminescence (red curve) for emitter series n1 - n3.

POLY 171: Network expansion and the effect on the macromolecular structure

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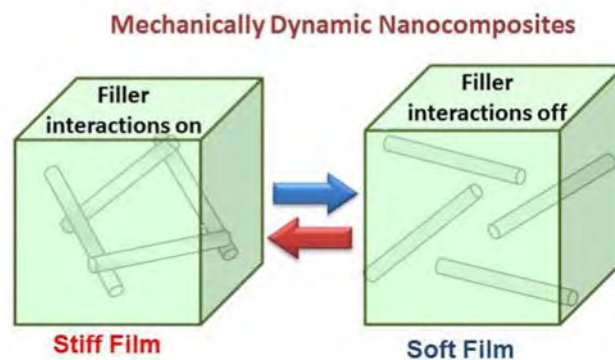
The lecture will present recent results preparing spherical and controlled polymeric structures in the nano- and microscale with the option to decide at later stages of the material development about the desired size and function from one parent nanoparticle structure. The synthetic understanding of how to manipulate nanoscale networks to control their composition and size leads to the development of functional nanomaterials that perform unique chemistry in a tailored environment. The presented method will allow to form unique particle structures that go far beyond what is possible with current methods for particle design. In particular, nanoscopic polymer networks containing symmetrical trithiocarbonates reversible addition-fragmentation chain transfer agents have shown to experience photo-growth with a variety of monomers starting from nanoparticles of different composition and size. The lecture will elucidate on the characterization methods of these expanded networks and degraded particles.



POLY 172: Bio-inspired nanocomposites

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Nature uses nanocomposites for a wide range of applications. Inspired by this we have been interested in how cellulose nanocrystal (CNC) composites can be used to access a range of nanocomposites that mimic the basic architecture and function of natural biosystems. For example, we have been investigating the use of CNCs to access mechanically-dynamic nanocomposites that have been inspired by the inner dermis of the sea cucumber and the squid beak. A key aspect of these materials are the interactions between the CNC and matrix polymer and as well as between the CNCs themselves. We have shown that CNCs (from a range of different biosources such as tunicates, cotton and microcrystalline cellulose) embedded within a variety of polymer matrices show mechanical switching (stiff to soft) upon exposure to water. It is proposed that in the dry state hydrogen bonding interactions between adjacent CNCs play a role in this reinforcing network, transferring mechanical stresses across the sample, and resulting in stiff materials. Once the water diffuses into the nanocomposite, it competitively hydrogen bonds to the CNC surfaces disrupting the stress-bearing CNC scaffold and softening the nanocomposite. More recently, we have shown that it is possible to reprogram this response by grafting lower critical solution polymers on the CNCs to yield composites that start soft and become stiff upon insertion to water at body temperature. Our latest results on using CNCs to access bioinspired nanocomposites will be discussed.



POLY 173: Polymer science for an overall study of micro and nanoplastic hazards: Sources, fate and effects

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Novel samplers have been developed to sequester and concentrate organic pollutant and contaminants. They differ from classic samplers by their unique geometry as a result of the manufacturing technique. A droplet-flow millifluidic process allowed precise control of the size and the geometry and the sensors have been called Diffusive Milligel Beads (DMG)¹. DMG opens a lot of perspectives and opportunities in environmental monitoring. Developed in a first approach to detect heavy metal in soils, they are now dedicated to better understand the dynamic and the fate of nanoplastics (NPs)² in freshwater and seawater. Not only is the toxicity of NPs of major concern, but also NPs associated-toxicants. DMG are designed to give a comprehensive approach of the Trojan horse effect of nanoplastics (NPs). This term was recently used to warn the community about the notion of microplastic and a fortiori NPs concentrating pollutants acquired from the surrounding environment and potentially releasing them into tissues or cells of the ingesting organism as bioavailable contaminants. The study includes an overall approach to address several issues: the elaboration of representative NPs in terms of size, size distribution, morphology and chemical composition, the NPs characterization via hyphenated methods³, and to the evaluation of the pollution level, the evaluation of the biodisponibility and the toxicity of metals mediated by NPs.

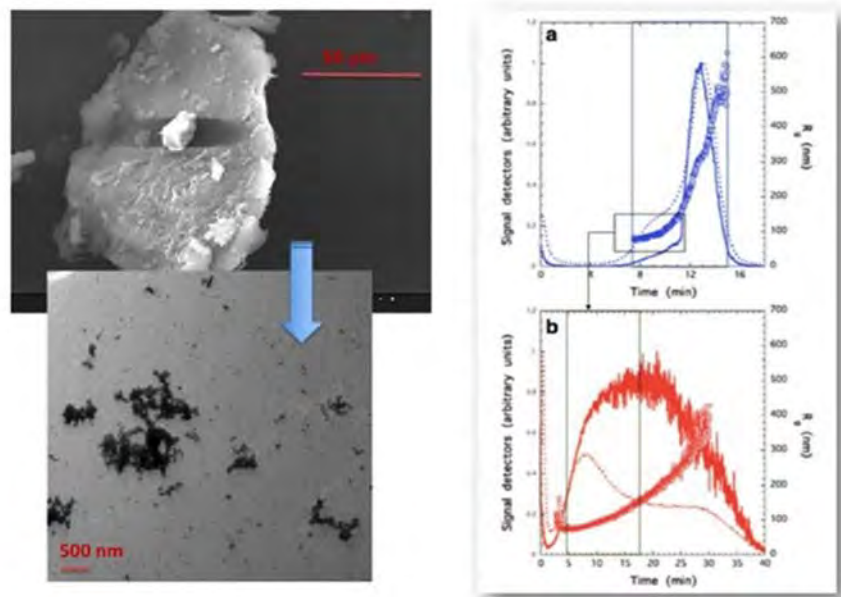
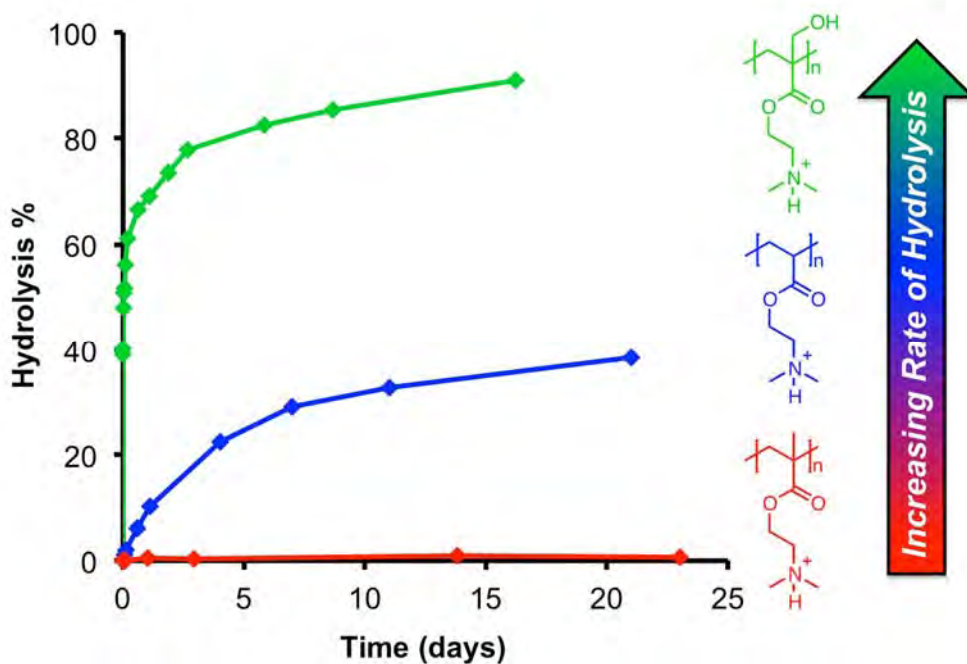


Figure 1. Nanoplastic model based of mechanical fragmentation of manufactured polystyrene (left) and size analysis by A4F (right)

POLY 174: Charge-shifting polycations with tunable rates of hydrolysis

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While polycations based on 2-(dimethylamino)ethyl (meth)acrylate are used in applications ranging from biomaterials to wastewater treatment, their remarkable difference in hydrolytic stability of the ester group remains little explored. This presentation will discuss how the nature of the α -substituent affects the ester hydrolysis of such polymers, with emphasis on the resulting shift of net polymer charge from cationic towards anionic. 2-(Dimethylamino)ethyl 2-hydroxymethyl acrylate (DHMA) will be introduced as a new, very hydrolytically labile, cationic acrylate monomer that can be used in a homopolymer and to tune copolymer hydrolyses. DHMA synthesis and free radical polymerization are described, including reactivity ratios for protected derivatives of DHMA with 2-(dimethylamino)ethyl acrylate (DMAEA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA). Hydrolyses of PDHMA, PDMAEA, PDMAEMA, and PDHMA containing copolymers in pH 5 and 7 buffer will be presented. Results from hydrolysis studies showed that the presence of the hydroxymethyl α -substituent in PDHMA led to rates of hydrolysis two to three orders of magnitude faster than the already rapid hydrolysis of PDMAEA. As well, copolymers of DHMA showed an increase in rates of hydrolyses with increased mol fractions of DHMA, which provides a new route to adjusting acrylate ester reactivity of such copolymers in aqueous media.



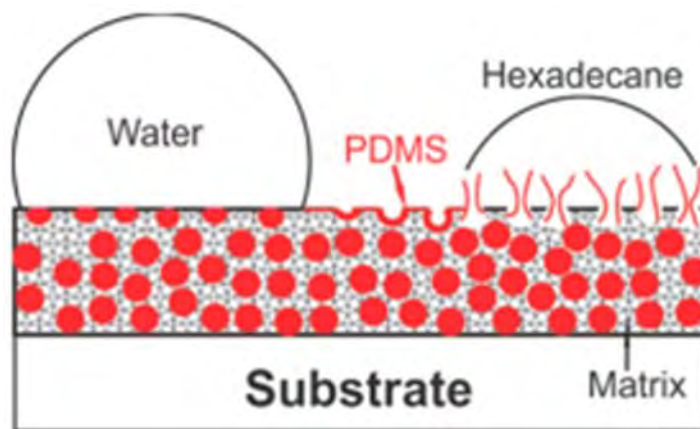
Effect of polymer backbone: Hydrolysis of PDMAEMA, PDMAEA, and PDHMA at pH 7 showing increasing rates, respectively.

POLY 175: Relationship between PDMS architecture and anti-smudge properties in a polyurethane coating

Brandon Becher Nienhaus, *Onblb@queensu.ca*, Heng Hu, Guojun Liu. Dept Chemistry, Queens Univ, Kingston, Ontario, Canada

Coatings that repel both oil and water have a number of potential applications, ranging from keeping surfaces clean to reducing drag in piping. While such coatings have been developed, they often rely on low surface tension fluorinated groups and/or surface roughness; which pose environmental concerns and reduce the transparency of the coated surface, respectively. The Liu group has developed coatings that use liquid-like poly(dimethylsiloxane) (PDMS) to form a slippery surface which readily slides a variety of liquids and possesses excellent transparency. However, when kept in water for long periods of time, PDMS chains on the surface of the coating undergo surface reorganization and enter the coating matrix, leading to a loss of slippery properties.

In an effort to minimize surface reorganization, we are examining how the degree of branching in PDMS alters both surface reorganization in water and its impact on overall liquid sliding ability. We hypothesize that using branched PDMS should reduce the rate of surface reorganization when in contact with water due to increased steric bulk, improving the water repellency properties of the coating. We will prepare slippery polyurethane-based coatings containing linear, single-branched, or multi-branched PDMS units and the changes in the surface properties will be investigated.

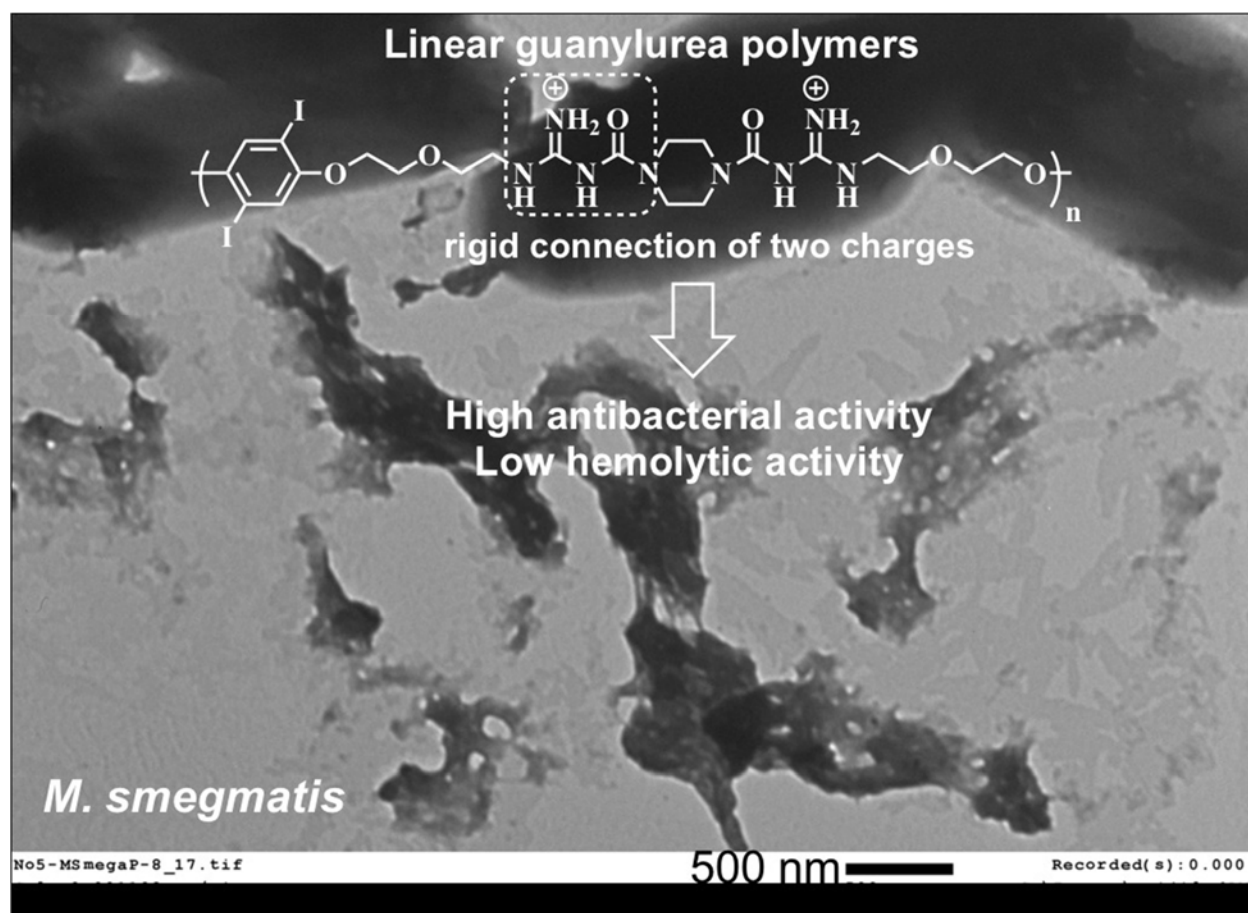


Surface reorganization of PDMS chains in water, air, and hexadecane.

POLY 176: Synthesis of antimicrobial poly(guanylurea)s

Joong Ho Moon, *jmoon@fiu.edu*, Md Salauddin Ahmed. *Chemistry Biochemistry Cp338a, Florida International University, Miami, Florida, United States*

Bacterial infections are serious health threats. Emerging drug resistance in bacteria further poses serious challenges to the treatment options involving traditional antibiotics. Antimicrobial polymers disrupt the physical cell membrane integrity of bacteria to address the drug resistance problems. Here, we introduce a conceptually new class of antimicrobial polymers containing positively charged guanylurea backbones for enhanced antimicrobial effects. The initial structure-activity relationship studies demonstrate that poly(guanylurea piperazine)s (PGU-*Ps*) exhibit excellent antimicrobial activity against different types of bacteria with high selectivity. The new design concept of using a positively charged guanylurea backbone will contribute to the development of future biocompatible, specific, and selective antimicrobial polymers.

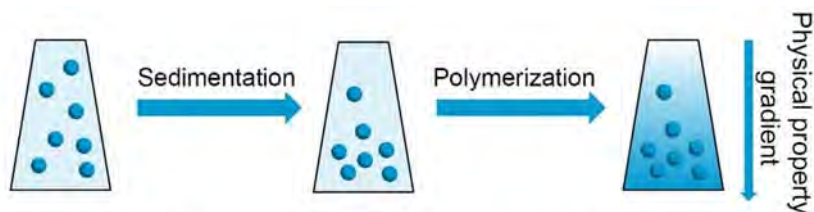


Transmission microscopic image of *M. smegmatis* treated with PGUs.

POLY 177: Synthesis of polymer gradient Materials in ultracentrifugal fields

Andreas Spinnrock, andreas.spinnrock@uni-konstanz.de, Helmut Cölfen. Chemistry, University of Konstanz, Konstanz, Germany

Polymer gradient materials are a unique class of functional materials. Their continuous spatial gradient of composition or structure leads to diverse physical property profiles. Therefore, polymer gradient materials have a remarkable potential for applications in coatings, space science and the automotive industry. Polymer gradient materials are well known, but the established preparation methods lack the possibility of predicting and controlling the gradients in advance. In this work, this problem is solved by polymerization in ultracentrifugal fields. Analytical ultracentrifugation is used to form a concentration gradient of a high molecular component by centrifugal force. The concentration gradient can be simulated in advance and controlled by the implemented interference optics anytime. Subsequently the integrated Xe flash lamp is used to start a photopolymerization and produce the desired polymer gradient material. In addition, nanoparticle-polymer composite materials are produced when nanoparticles are used as the sedimenting species. For instance, optical property gradients are obtained with gold or semiconductor nanoparticles and gradients of magnetization are obtained with magnetite nanoparticles. Gradients of a macrophotoinitiator can be used to control molecular weight distributions and gradients of macromonomers with a small comonomer lead to gradients of composition. Different gradients and distributions are generated by applying different centrifugation experiments like sedimentation velocity (sigmoidal gradient) or sedimentation equilibrium (exponential gradient) runs. Therefore, the new technique of performing polymerization in ultracentrifugal fields has the potential to fabricate materials with gradients of various physical properties in a controlled way.

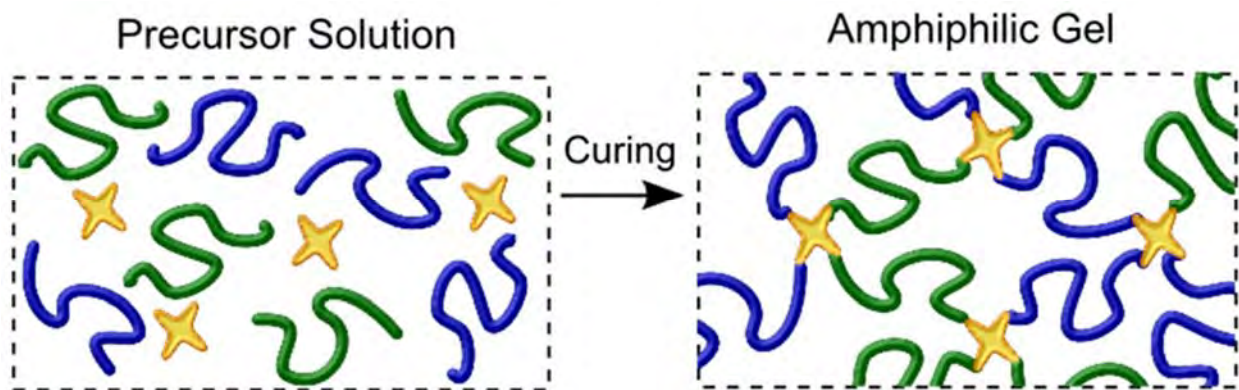


Schematic view of a bulk polymerization process in the AUC cell to synthesize composite polymer gradient materials; ● = nanoparticles

POLY 178: New approaches to amphiphilic polymer conetworks with broad cocontinuous phase compositions

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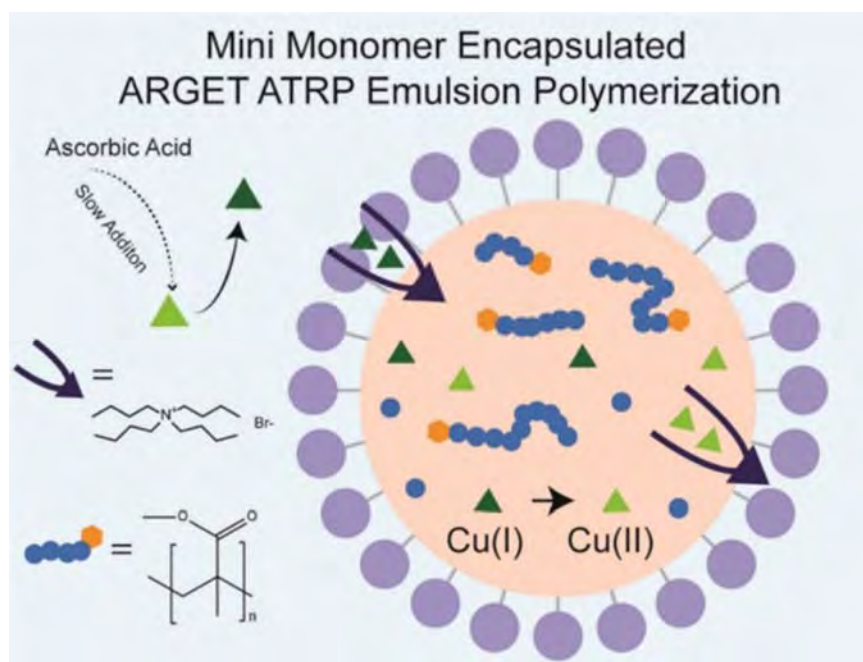
Phase-separated and self-assembled co-network materials offer a simple route to bicontinuous-like morphologies, which are expected to be highly beneficial for applications such as ion, charge, and oxygen transport. Here, a thiol-ene end-linking platform enables the systematic investigation of phase-separated poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) or polystyrene (PS) networks in terms of the molecular weight and relative volume fractions of precursor polymers. Small angle X-ray scattering (SAXS) shows that microphase separation of these co-networks yields disordered structures with d -spacings similar to the prediction by de Gennes of $d \sim M_n^{0.5}$. These findings demonstrate that this approach to thiol-ene co-networks is a versatile platform to create bicontinuous morphologies.



POLY 179: Mini monomer encapsulated emulsion polymerization of PMMA using ARGET ATRP

Christopher K. Ober¹, *cko3@cornell.edu*, **Roselynn Cordero**¹, **Ali Jawaid**², **Ming-Siao Hsiao**², **Zoe Lequeux**¹, **Richard A. Vaia**². (1) Cornell Univ, Ithaca, New York, United States (2) Air Force Research Lab, Dayton, Ohio, United States

In this work, a new emulsion polymerization based on Activators Regenerated by Electron Transport (ARGET ATRP) was developed to produce poly(methyl methacrylate) (PMMA). Mini monomer encapsulated (Mini ME) ARGET ATRP emulsion polymerization resulted in well-defined PMMA with a dispersity as low as 1.14. By localizing the propagation and controlling the availability of the monomer, we provide a foundation that addresses the challenges of traditional miniemulsion and emulsion polymerizations. In this method, monomer is isolated in a micelle by pre-emulsification through high-power stirring. Acetone is introduced to the polymerization to aid in reactant transport and tetrabutylammonium salts, for example, tetrabutylammonium bromide (TBAB) and tetrabutylammonium chloride (TBAC), are used as phase transfer agents. ATRP components such as ATRP catalyst, ligand, TBAB/TBAC, and initiator are dissolved in the aqueous phase, while slow addition of ascorbic acid reduces deactivator Cu(II)-Br₂/TPMA to activator Cu(I)-Br/TPMA. Oligomeric PMMA is produced in the aqueous phase and later absorbed into the micelle, while the ATRP activator, Cu(I)-Br/TPMA, is transported into the micelle by the phase transfer agent where polymerization occurs (Scheme 1). Polymerizations using TBAB were more controlled and demonstrated low dispersity (<1.17), where those using TBAC displayed higher dispersity (>1.50). First-order linear kinetics for MMA polymerizations at 100 mM TBAB was demonstrated, while reactions deviated from linearity at higher concentrations of TBAB and all concentrations of TBAC.

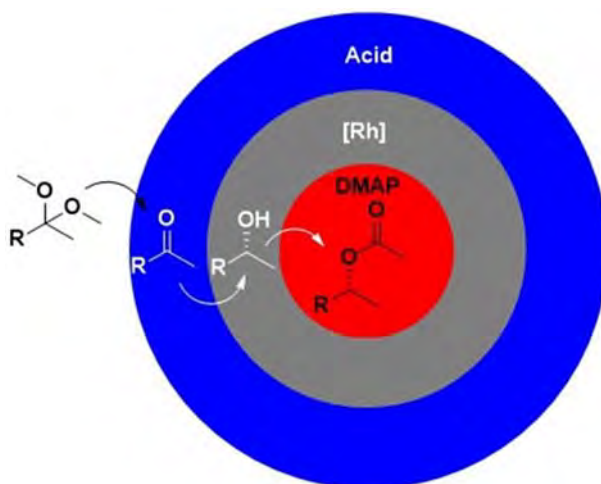


Depiction of proposed mechanism of mini ME ARGET ATRP emulsion polymerization.

POLY 180: Shell cross-linked micelles (SCM)s as nanoreactors for enantioselective three step tandem catalysis

Michael Kuepfert, michaelkuepfert@gmail.com, Marcus Weck. New York University, New York, New York, United States

The concept of compartmentalization allows the biological cell to perform otherwise incompatible chemical transformations simultaneously and in close proximity. Motivated by nature's design principles we describe an amphiphilic poly(2-oxazoline) tri-block copolymer with three covalently attached catalysts that are spatially separated from one another. This polymeric support structure assembles into spherical micelles with carboxylic acids in the hydrophilic corona, Rh-TsDPEN catalysts in the cross-linked shell, and 4-Dimethylaminopyridine (DMAP) inside the hydrophobic core. The spatial positioning of each catalyst in the shell cross-linked micelle (SCM) is designed to exploit the path of the substrate during each step of the non-orthogonal tandem reaction: Ketal hydrolysis to a prochiral ketone, asymmetric transfer hydrogenation (ATH) to an enantioenriched secondary alcohol, acylation to the final ester product.

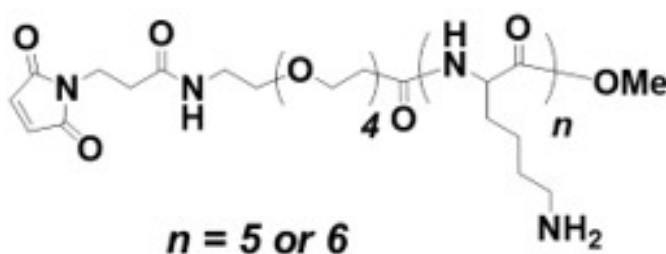


SCM support for orthogonal tandem catalysis

POLY 181: Polyion complex micelles functionalized with a cell penetrating peptide for plant gene delivery

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Enzyme Research Team, RIKEN Center for Sustainable Resource Science, Wako,
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Plant gene delivery is essential for various applications in agriculture, biorefinery and energy industry. However, the dual barriers of the cell wall and the cell membrane in plants hamper the introduction of exogenous genes into plant cells. To achieve efficient gene delivery in plants, new carrier systems are needed. In the present study, we synthesized a block copolymer, maleimide modified tetraethylene glycol-poly(L-lysine) (MAL-TEG-PLL), to use as a gene carrier in plants. We envisaged that MAL-TEG-PLL would condense plasmid DNA (pDNA) and form sufficiently small micelles to pass through the cell wall. We also anticipated that MAL-TEG-PLL/pDNA micelle would display maleimide groups on its surface, and therefore the micelle can be functionalized with cell-penetrating peptides by using thiol-maleimide coupling. DLS measurements showed that the diameters of MAL-TEG-PLL/pDNA micelles (at N/P ratios 4–7) were around 80–90 nm. We performed model reactions between MAL-TEG-PLL (60 μM) and a cell-penetrating peptide with a cysteine residue (BP100-Cys, 12–48 μM) in 3 mM HEPES buffer (pH 6.5). After incubation for 1 h at room temperature, the conversion rate of MAL-TEG-PLL (determined by HPLC) reached a plateau and varied from ~15 to ~55% depending on BP100-Cys concentration (12–48 μM). The micelle prepared at N/P 6 (MAL-TEG-PLL, 60 μM) was reacted with BP100-Cys (12–48 μM) in 3 mM HEPES buffer (pH 6.5) for 1 h. The successful conjugation of the micelles to BP100-Cys was confirmed by MALDI-TOF MS analysis. The micelle sizes were maintained less than 100 nm after the conjugation. We are now evaluating the gene delivery efficiency of BP100-Cys modified micelles in plants.



Chemical structure of MAL-TEG-PLL

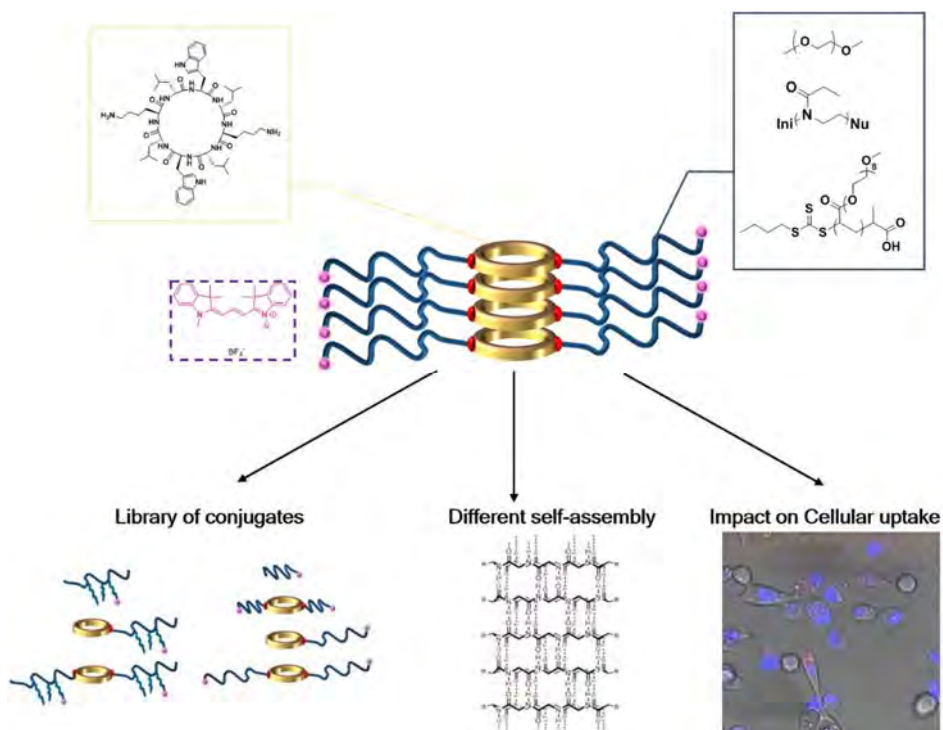
POLY 182: Understanding the interaction of cyclic peptide polymer nanotubes with mammalian cells

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The design of efficient drug delivery systems is an important challenge in pharmaceutical research, as it allows for a better control of pharmacokinetic parameters (bioavailability, potency of the drug...) and reduction in side effects. Particle shape has been described as a key factor in improving cell internalization and bio-distribution among the different properties investigated for drug delivery systems.¹ In particular, tubular structures, such as cyclic peptide (CP) polymer nanotubes, have been identified as a promising candidate for improving drug delivery.^{2,3}

The aim of this work is to investigate the influence of different design elements of CP-polymer conjugates on cellular uptake including; nature and length of the polymer, the cyclic peptide building block, and the cell line studied. The addition of polymer chains to the CP has previously been shown to improve the control over the length of the tubes, leading to high aspect ratio structures.⁴ A variety of fluorescently labelled CP-polymer conjugates have been synthesized to track their behaviour *in vitro* over time and in different conditions. In parallel, self-assembly of the different CP conjugates in water has been assessed, showing an interesting correlation between the formation of nanotubes and the results obtained from cell studies.

This work will provide a design rationale for the creation of further drug delivery systems based on CP-polymer conjugates for *in vivo* investigations.



POLY 183: Biodegradable polymeric nanoparticles for modulating lysosomal pH

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We have synthesized a new class of novel pH-activable, acidifying nanoparticles (acNPs) that modulate the pH of compromised lysosomes, and restore autophagy inhibition and cellular function in liver cells (HepG2) under lipotoxicity. Non-alcoholic fatty liver disease (NAFLD) is the most prevalent liver disease in developed countries today. Liver cells under chronic exposure to high levels of fatty acids (i.e., lipotoxicity) leads to compromised lysosomal acidity and inhibition of autophagy, exacerbating impairment of various cellular functions, and resulting in progressive disease. Clinically today, no specific pharmacological agent has been approved for the treatment of NAFLD. In this study, we have synthesized acNPs that contain caged acid that will be released when exposed to moderate pH changes (i.e., pH 6.0 in dysfunctional lysosomes). In order to control the degree of acidification, we prepared the acNPs from polyesters composed of varying ratios of tetrafluorosuccinic acid to succinic acid and confirmed their compositions using ¹H, ¹³C and ¹⁹F NMRs. The polyesters possess relatively high molecular weights (>10K g/mol) with narrow polydispersity indexes (PDIs) (1.3-1.5). Different formulation parameters such as polymer concentration and surfactant types were explored for the series of polyesters in order to form small and monodispersed nanoparticles, where their sizes were characterized by scanning electron microscopy and dynamic light scattering. A set of conditions were identified which formed non-toxic nanoparticles of 99.8 nanometers with a narrow PDI (0.1-0.2), and allowed efficient localization into the lysosomes of HepG2 cells. The degradation rates and the degree of acidification of the nanoparticles increase with greater amounts of tetrafluorosuccinic acid to succinic acid in the polymer composition. The acNPs with higher tetrafluorosuccinic acid to succinic acid ratio also significantly restore both lysosomal acidity and autophagic flux, indicating an overall restoration of autophagy and cellular function in the liver cells.

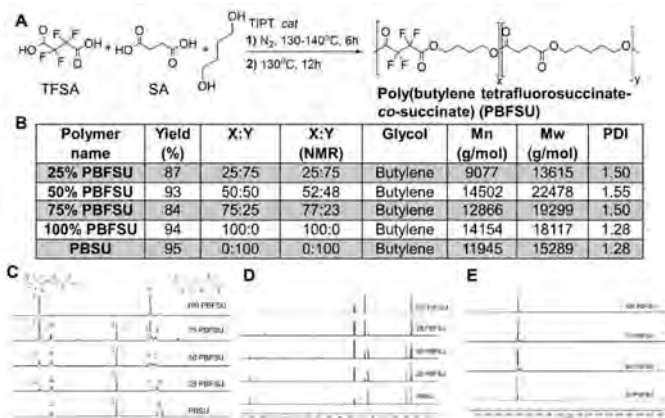
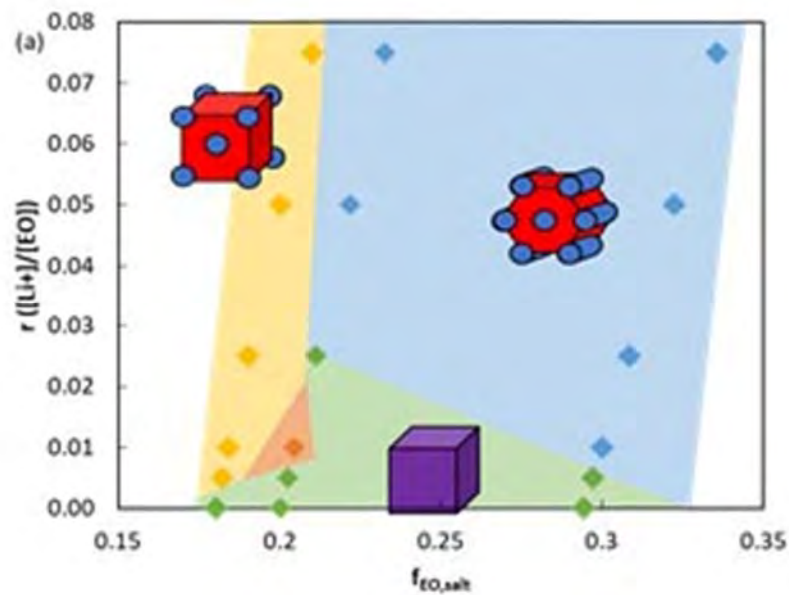


Figure. Synthetic scheme and polymer characterizations for butylene based polyesters. A) Synthetic scheme of butylene based polyesters via polycondensation, B) polymer properties characterizations. C – E) ¹H, ¹³C and ¹⁹F NMR spectra of the polyesters respectively.

POLY 184: Phase behavior of mixtures of block copolymers and a lithium salt

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Mixtures of block copolymers and lithium salts are of interest for lithium battery applications. We present a study of the morphology of these systems in the weak segregation limit. Our results are compared to the well-established phase diagram of pure block copolymers and prevailing theories on the thermodynamics of block-copolymer-salt mixtures.

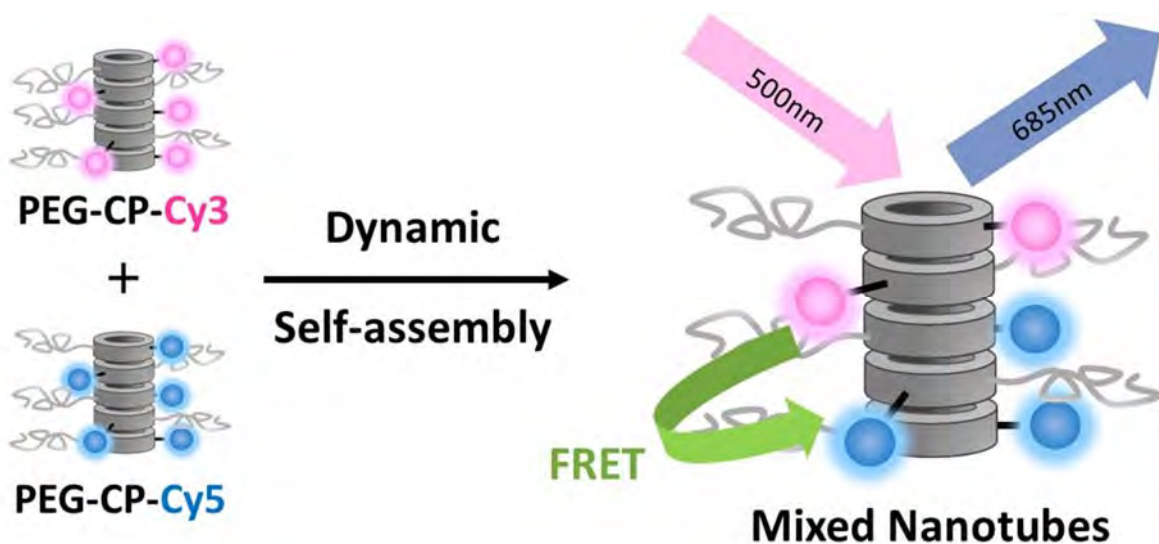


POLY 185: Controlling the dynamics of self-assembling cyclic peptide-polymer nanotubes

Julia Rho¹, J.rho@warwick.ac.uk, **Sebastien Perrier**². (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) University of Warwick, Coventry, United Kingdom

Cyclic peptide (CP)-polymer nanotubes have recently gained much attention thanks to their monodisperse diameters and ease of functionalisation as compared to other nanotubular systems. In particular, conjugation of polymers to the peptide periphery, resulting in an enhanced solubility of the nanotubes in aqueous solutions, make them attractive for a variety of biomedical applications such as drug delivery vectors, antimicrobials and biosensors.¹

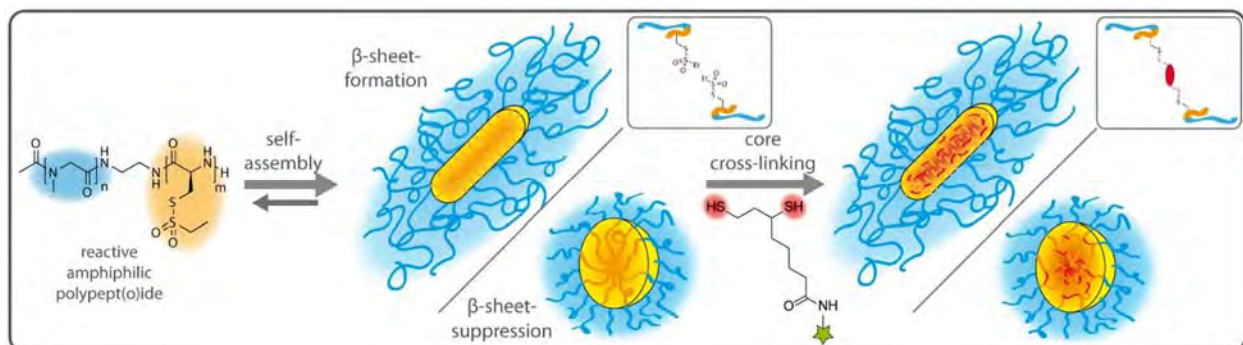
Using a 'bottom up' approach, we developed a new class of model conjugates to help understand the dynamics of these nanotubes. These model conjugates enabled us to demonstrate that their self-assembly is highly dynamic, as well as strongly influenced by both solvent and concentration.² Additionally, the dynamic exchange of unimeric dye conjugates between nanotubes was characterised in mammalian cells using confocal microscopy. To deepen our understanding of these supramolecular systems, current focus has turned to controlling the assembly of these structures using non-covalent hydrophobic interactions.



POLY 186: Secondary structure-driven self-assembly of reactive polypept(o)ides for cross-linked polymeric micelles with defined core polarity and function

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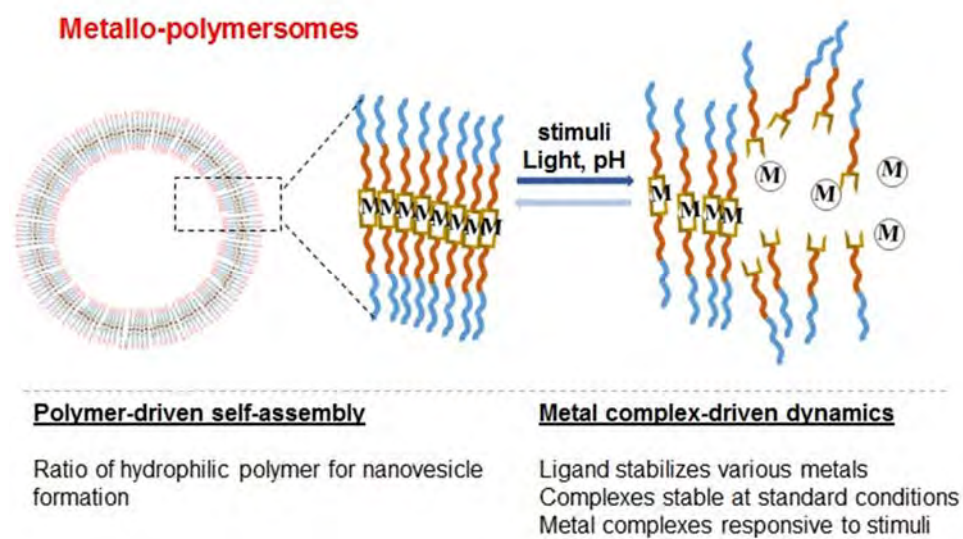
Polypept(o)ides represent a novel class of copolymers that combine the diverse functionality of polypeptides with the shielding properties of polypept(o)ids (e.g. polysarcosine). Polypept(o)ides can be conveniently synthesized by controlled sequential ring-opening polymerization of the respective α -amino acid *N*-carboxyanhydrides (NCAs) or *N*-substituted *N*-carboxyanhydrides (NNCAs), yielding polymers with narrow and symmetrical molecular weight distributions ($PDI < 1.2$). In addition to functionality and the formation of reactive poly(amino acids), the polypeptide block can be exploited for the tendency to grow secondary structures (e.g. α -helix, β -sheet) that provide an additional parameter for nanoscale self-assembly. Consequently, cylindrical or spherical polymeric micelles (D_h 30-100 nm) were prepared by secondary structure-directed self-assembly of identical poly(sarcosine)-*block*-poly(*S*-alkylsulfonyl-L-cysteine) copolymers, depending on the formation or suppression of anti-parallel β -sheets mediated by chaotropic thiourea. Independent from the previously adjusted morphology, these micelles were then converted into core cross-linked polymeric micelles by addressing the *S*-alkylsulfonyl groups with dithiols in a chemoselective manner. This technique not only stabilizes the micelle and prevents disintegration upon dilution, but also allows for a tailored core polarity, which can be specifically adjusted. For this reason, a library of liponamide-based cross-linkers ($\log P$ 7.30 (hydrophobic) to -2.87 (hydrophilic)) has been developed and employed to tune or even invert core polarity. In addition, complex pro-drugs of active pharmaceutical ingredients were synthesized and bio-reversibly attached to the micellar core. In summary, this platform uniquely enables to generate a library of functional core cross-linked carriers that can be customized to the desired application in a simple but controlled manner.



POLY 187: Stimuli-responsive nanoassemblies from metallo-supramolecular coordination polymers

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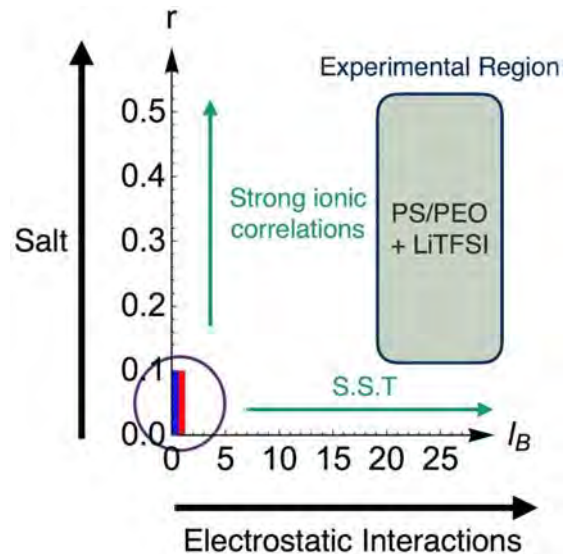
The design of functional (nano)materials has continuously grown in complexity. In practice, however, the underlying syntheses can be complicated and often involves laborious tasks relying on trial-and-error approaches to finely adjusting the ever-increasing multitude of desired properties for enhanced specificity and applicability. Particularly relevant here, development of functional polymer-based soft nanomaterials entails molecular engineering of the polymer chain itself which typically leads to materials for a specific use, and change in the target application may require a complete re-design in order to accommodate the new properties of interest. By combining metal complexes with amphiphilic polymers, here we present a new approach toward the design and development of functional (nano)materials as flexible platforms capable of structure-property tunability from facile substitution of metal-ligand moieties. We have examined this approach by assembling stimuli-responsive metallo-supramolecular polymer nanovesicles from the coordination of ligand-functionalized amphiphilic block co-polymers with a variety of metals. As a result, the physical and chemical properties of each polymer construct have been demonstrated to significantly change and respond to various stimuli in a controlled way upon simple complexation with different metal ions, showing the potential application of such assemblies as versatile polymeric platforms with a broad range of imparted metal-organic functionalities.



POLY 188: Solvation and dilution regimes in morphological behaviors of ion-doped block copolymers

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Ion-containing polymers have emerged as an important electrolyte materials found use in various energy applications. Successful engineering of the properties of these electrolyte relies on the fundamental understanding of the thermodynamics of their morphological behaviors. We focus on salt-doped block copolymers, and present a minimal model that captures the effects of solvation free energy and electrostatics in dielectrically heterogeneous medium. The typical assumption that ions are bound to the conductive species is discarded in our treatment. A symmetry-adapted solver for Poisson's equation is developed, enabling efficient exploration of parameter space and accurate resolution of all the classical self-assembly morphologies. We present a series of phase diagrams for varying salt concentrations and average dielectric permittivity. The results demonstrate the existence of two distinct types of morphological behaviors, one dominated by ionic solvation, and another by the translational entropy of ions. Because of the comparatively low dielectric permittivity, the canonical solid polymer electrolytes, such as PS-PEO/LiTFSI, is expected to be in the solvation regime.



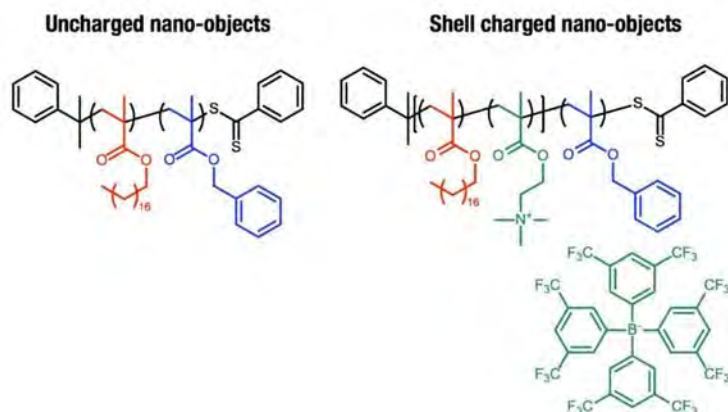
POLY 189: Ionic and non-spherical diblock copolymer nano-objects in non-polar solvents

Gregory Smith^{1,2}, gregoryneil@gmail.com, Sarah L. Canning², Steven P. Armes². (1) Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark (2) Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

Diblock copolymer nano-objects are promising materials in a variety of solvents (water, alcohols, and oils). The non-polar oil solvents, however, are perhaps the most challenging medium to generate stimuli responsive nano-objects in due to their low dielectric constant. Despite this, such charged species are essential for many technological applications, such as petrochemicals, printing, electrorheological fluids, electrophoretic displays, or polymerization catalysis, for example.

Through the incorporation of a polymerizable ionic monomer, we have introduced ionizable units into the stabilizer of otherwise nonionic poly(stearyl methacrylate)–poly(benzyl methacrylate) diblock copolymers synthesized in *n*-dodecane. The full range of expected pure morphologies (spheres, worms, and vesicles) has successfully been produced. The ionic groups interact at the surface, effectively increasing the projected area, and this shifts the critical degree of polymerization for morphology formation as compared to the nonionic case. The ionic nano-objects are also electric field responsive, undergoing counterion condensation, a characteristic of ionic species in low dielectric media. To investigate the importance of ionic groups on the self-assembly process, nano-objects were also prepared with a small fraction of ionic stabilizer chains, and these give morphology boundaries that are the same as the nonionic case but, surprisingly, have a greater electric field response than nano-objects with a fully ionic stabilizer.

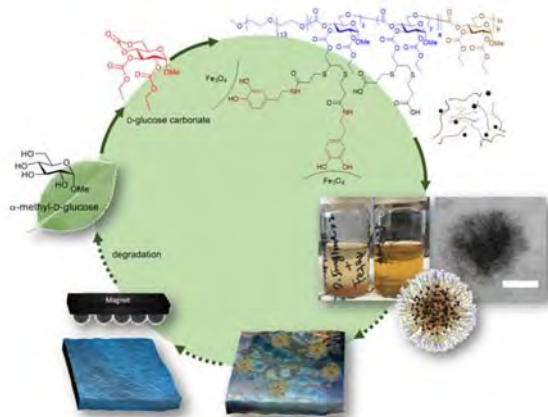
We anticipate that the extensive knowledge of how to synthesize non-spherical nano-objects by PISA in non-polar solvents using hydrocarbon and silicocarbon stabilizers can be directly applied to enable the production of electrophoretic nano-objects. Introducing ionic groups into non-polar solvents using diblock copolymer nano-objects offers the promise of generating interesting ionic functional nanomaterials in technologically relevant solvents.



POLY 190: Magnetic sugar-based nanocomposites for environmental remediation

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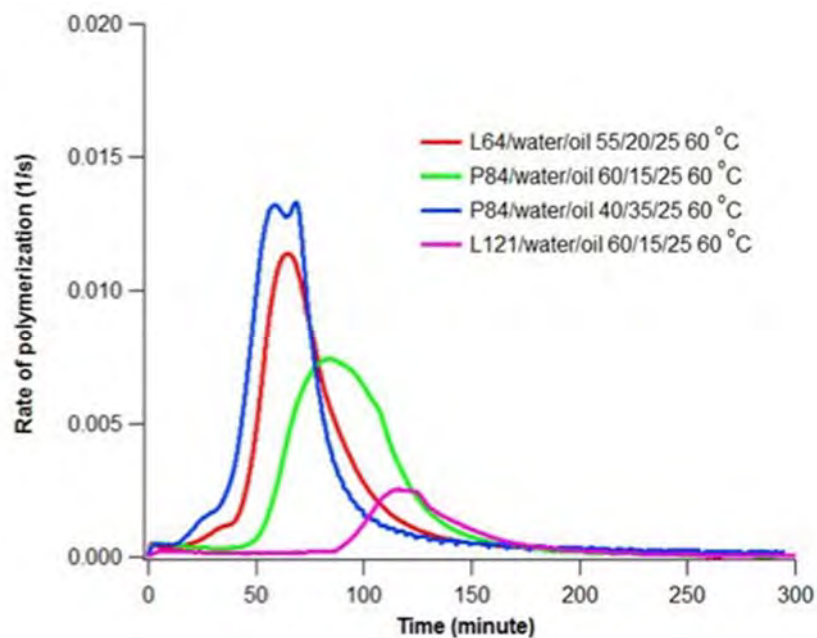
Petroleum-based oils pose severe contamination problems to the environment. Nanotechnology has been utilized to address those problems recently, since the large surface area leads to better contact between nanomaterials and pollutants. Magnetic/polymer hybrid nanoparticles were demonstrated with high oil sorption capacity, 10 times their initial dry weight, and magnetic activity in our previous research, in which well-defined magnetic shell cross-linked knedel-like nanoparticles (MSCKs) were constructed through co-assembly of amphiphilic poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS) block copolymers with magnetic iron oxide nanoparticles. Those organic and inorganic cross-linked micellar structures were generated as an amphiphilic block copolymer framework trapped with magnetic nanoparticles. However, PAA and PS are both nondegradable polymers that may remain in the ocean for decades. To tackle these concerns, a new scaffold consisting of degradable glucose-based polymers was strategically designed and synthesized to replace the PAA-*b*-PS. These glucose materials will eventually break down into natural byproducts even if not recovered. The linear triblock copolymer poly(ethylene glycol)-*b*-poly(ethyl propargyl glucose carbonate)-*b*-poly(ethyl glucose carbonate), PEG-*b*-PGC(EPC)-*b*-PGC(EC), was synthesized *via* sequential ring-opening polymerization (ROP) of two glucose carbonate monomers, initiated by hydroxyl-terminated PEG as macroinitiator. Carboxylate groups were introduced *via* well-demonstrated thiol-yne reaction, followed by the conjugation with dopamine anchoring groups *via* an amidation reaction. The resulting amphiphilic triblock copolymers and iron oxide particles were co-assembled to afford hybrid nanocomposites after a solvent exchange process. Crosslinking of the shell of MSCKs was performed after the establishment of the core-shell morphology, to stabilize the overall nanoscopic structure.



POLY 191: Chemorheology of polymerization in nano-confined structures of self-assembled block copolymers

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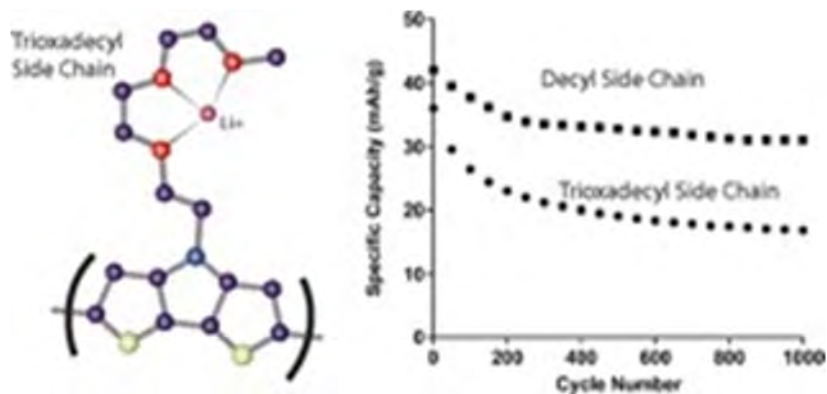
Block copolymers self-assemble in the presence of solvents and produce nano-scale structures such as lamellar, normal, and reverse hexagonal also known as lyotropic liquid crystals (LLCs). Mesoporous organic materials can be made through mesophase templating. This work describes the kinetics of thermal polymerization in nano-confined structures of mesophase templates using chemorheological studies. A set of isothermal time sweep tests at three different temperatures is performed on mesophases to discern the polymerization rate and reaction constants. We have fixed the concentration of monomeric phase in lamellar and hexagonal phases while retaining the structure during thermal polymerization at elevated temperatures. The obtained mesoporous structures have domain sizes comparable to that of mesophases before polymerization. We found that the type of mesostructure strongly influences the polymerization kinetics. The fastest polymerization rate occurs in reverse hexagonal mesophases due to high local monomer concentration and depression of termination rates. In lamellar nanoconfinement, the polymerization rate is higher than bulk polymerization, but lower than the reverse hexagonal confinement. Differential scanning calorimetry at elevated temperatures confirms the obtained results from chemorheology.



POLY 192: Electron- and ion-conducting block copolymers as binders for battery cathodes

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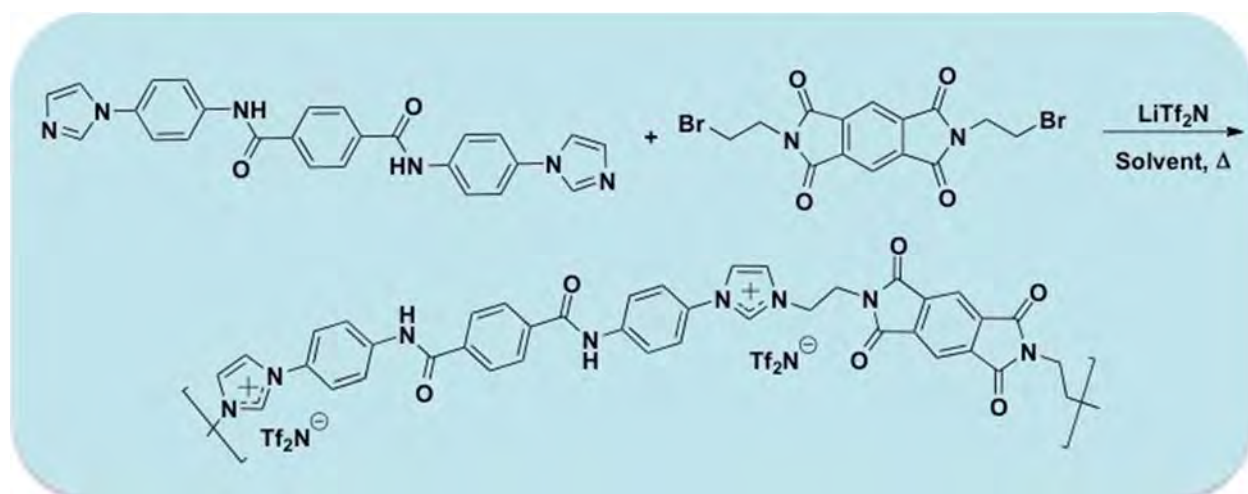
Simultaneous electron- and ion-conducting polymeric binders for battery electrodes offer a multifunctional alternative to commonly used poly(vinylidene fluoride). Besides mechanically binding and "gluing" the various electrode components together, the multifunctional polymeric binder also offers conductivity and redox activity. One example is P3HT-b-PEO, which conducts electrons and ions in the P3HT and PEO domains, respectively, and the P3HT stores charge by doping and dedoping. Here, the effect of the block copolymer loading and morphology on the redox activity of a V₂O₅ Li-ion battery cathode will be presented. The synergistic mechanism by which the binder improves the V₂O₅ performance is analyzed in two aspects: chemical and mechanical. In the first, it is quantitatively shown that the P3HT block contributes to the redox activity. In the second aspect, it is shown that the block copolymer prevents cracking and pulverization of the V₂O₅ electrode after prolonged cycling. Also, conjugated P3HT has been extensively studied for various solid state applications (e.g., photovoltaic cells, field-effect transistors, and light-emitting diodes), where the performance is strongly affected by regioregularity and molecular weight. However, in electrochemical systems such as in batteries, the effects of regioregularity and molecular weight on the charge storage performance are not understood for P3HT-b-PEO. Here, by comparing different P3HT-b-PEO block copolymers of varying P3HT regioregularity (86-97%) and molecular weight (8-19 kDa), a strong correlation between regioregularity and molecular weight with electrochemical properties (i.e., capacity, and redox potential) is demonstrated. It is shown that the charge storage capacity of P3HT-b-PEO significantly increases with increasing regioregularity. The redox potential increases with decreasing molecular weight. The changes in capacity and redox potential are attributed to P3HT's backbone conformation, planarity, and chain packing.



POLY 193: The design and synthesis of ultra-high performance ionenes and their interactions with ionic liquids

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Despite their seemingly disparate structures, the synthetic reactions which are used to create UHP/HP polymers and ionenes/poly(ILs) are entirely compatible. Careful analysis of UHP/HP polymer synthetic methods and requisite precursors reveals that hybrid, "ionic" UHP/HP polymers are much more readily accessible than they might seem. Our work does not append, tether or graft ionic components onto existing polymer backbones, but rather uses and controls the step-growth chemistries associated with UHP/HP polymers to build entirely new, unexplored polymer architectures in which ionic components are covalently bound and precisely integrated with rigid/aromatic structural elements within the polymer backbone. Furthermore, these ionene-UHP polymer hybrids can retain ILs within their structures as a means of modifying properties and structure. This presentation will detail our approach to the design and synthesis of UHP ionenes and present selected results associated with our work in gas separation membranes and additive manufacturing.

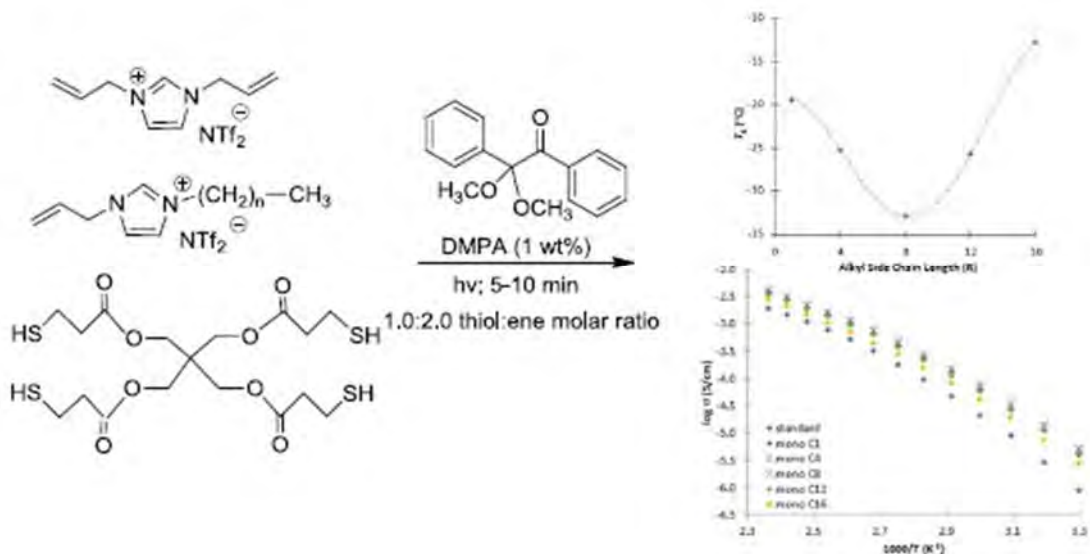


Example of an ionic polyamide-imide.

POLY 194: Influence of pendant alkyl chain on the conductive and gas permeability properties of thiol-ene poly(ionic liquid) networks

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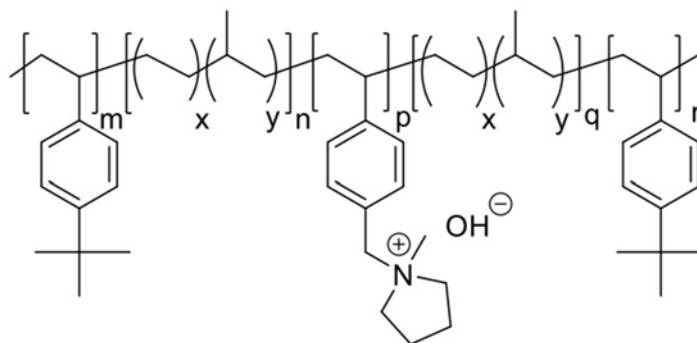
Poly(ionic liquid)s (PILs) are considered to be very promising materials for a variety of high-performance applications, including electrolytes for batteries and as membranes for flue gas separation. Here, thiol-ene 'click' photopolymerization has been utilized to prepare a variety of covalently crosslinked, PIL networks which contain an imidazolium functional group. In an effort to improve ionic conductivity and gas permeability of previously described thiol-ene PIL networks from our research group, mono-functional imidazolium 'ene' monomers with variable pendant alkyl chain length were incorporated into the PIL networks, maintaining an overall thiol:ene molar ratio of 1.0:2.0. As the alkyl spacer was increased from methyl (C4) to octyl (C8), a noticeable decrease in T_g was observed along with an increase in ionic conductivity (30 % RH). Upon further increasing the alkyl chain length to C16, the T_g was observed to increase, presumably due to side chain stacking within the network. This effect was coupled to a decrease in the ionic conductivity. Gas permeability (CO_2 , N_2), determined using a time-lag gas separation device, was found to increase as alkyl chain length increased (range of 6-28 Barrers), which correlated with % swelling of the networks.



POLY 195: Saturated *N*-heterocyclic cationic multiblock polymers as solid-state separators in alkaline fuel cells and lithium ion batteries

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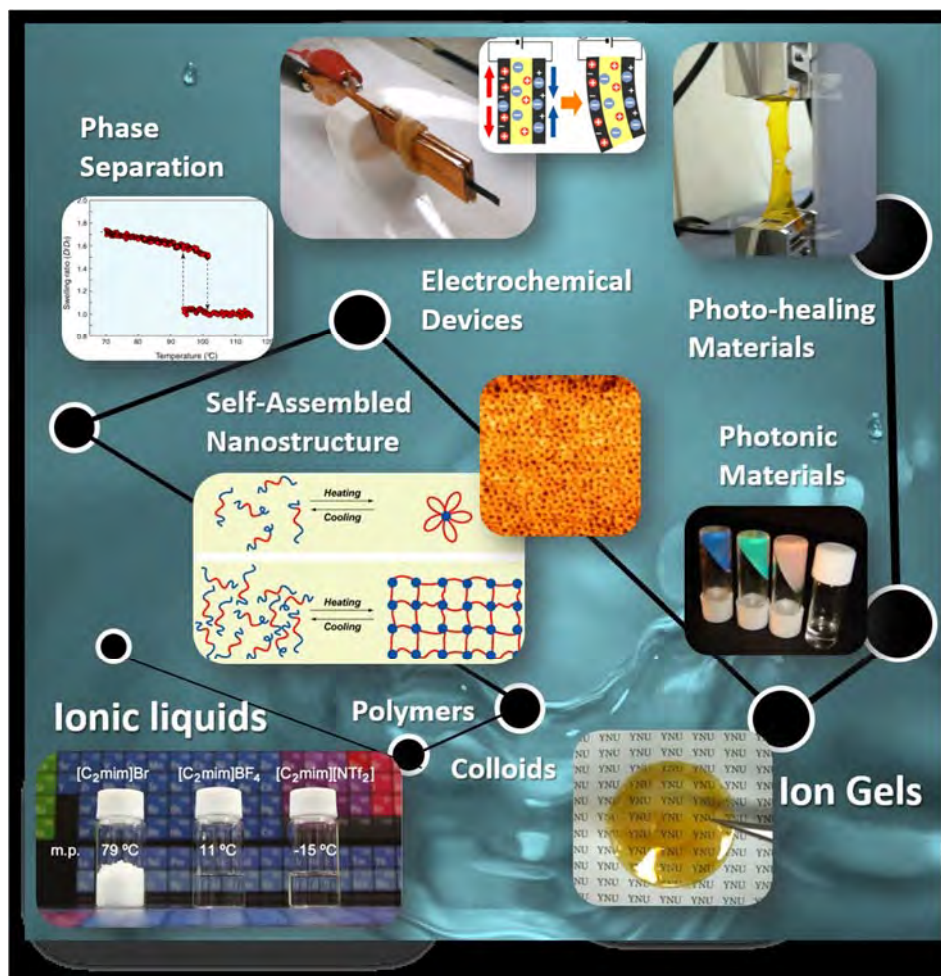
Polymers containing unsaturated *N*-heterocyclic cations (*i.e.*, imidazolium), also known as polymerized ionic liquids (PILs), have been synthesized and investigated for various applications, including alkaline fuel cells and batteries. Recently, results have shown higher alkaline chemical stability and lithium electrochemical stability for polymers bearing a saturated *N*-heterocyclic cation (pyrrolidinium) *versus* unsaturated *N*-heterocyclic cation (imidazolium). However, to date, few studies have systematically investigated polymers containing saturated *N*-heterocyclic cations with various ring sizes. In this study, homopolymers and multiblock polymers containing styrene-based saturated *N*-heterocyclic cationic chemistry was synthesized with various saturated *N*-heterocyclic cations (methylpyrrolidinium, methylpiperidinium, methylazepanium) and investigated as functional polymer membranes as it applies to alkaline fuel cells and lithium ion batteries. This work provides a fundamental understanding of the impact of polymers containing various saturated *N*-heterocyclic cation sizes on polymer properties and further introduces a promising chemistry for producing highly stable and ion conductive solid-state separators for alkaline fuel cells and lithium ion batteries.



POLY 196: Advanced materials based on polymers and ionic liquids

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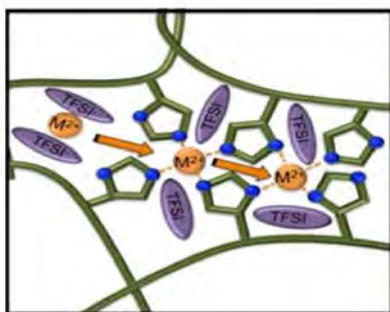
Ionic liquids (ILs) are ambient temperature molten salts, which have attracted considerable attention owing to their unique properties. In this contribution, we review advanced materials composed of ILs and polymers for the basis of a new design protocol to fabricate novel materials. As electrolytes for electrochemical devices, cross-linked polymers containing ILs (ion gels) are endowed with functional properties inherited from ILs and mechanical consistency derived from polymers. To create such materials, micro-phase separation of block copolymers and colloidal arrays in the ILs are utilized. Based on the molecular design of task-specific ILs, the resultant ion gels are applicable as electrolytes for actuator, fuel cell, and secondary battery applications. Thermo- and photo-responsive polymers in ILs are also highlighted, whereby such stimuli elicit changes in the solubility of the self-assembly of block copolymers and colloidal arrays in the ILs. Further, thermo- and photo-reversible changes in the self-assembled structure can be exploited to demonstrate sol-gel transitions and fabricate photo-healable materials.



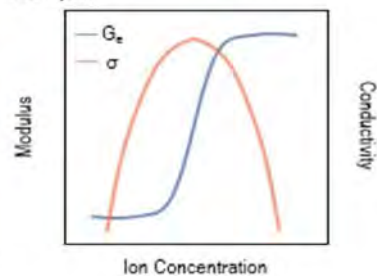
POLY 197: Role of multivalent ions on the mechanics and ionic conductivity of metal-ligand coordinating PILs

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Polymers that contain ionic liquid constituent retain many of the properties of ionic liquids including ionic conductivity. We have recently found that a polymerized cation (such as imidazolium) is an excellent host for any associated anion. As a result, polymeric ionic liquids are not just solid counterparts to IL's, but are excellent vectors for the inclusion of a variety of functionalities ranging from multi-valent ions for batteries to magnetic anions. Polymeric ionic liquids (PILs) formed via metal-ligand coordination interactions are transient in nature leading to both ionic conduction and transient-gel mechanical behavior. The molecular design of these materials allows for precise and independent control over the nature and concentration of ligand and metal, which are molecular properties critical for bulk ion conduction and polymer mechanics. In a model system composed of poly(ethylene oxide) with tethered imidazole moieties that facilitate salt dissociation of both nickel (II) bis(trifluoromethylsulfonyl)imide (NiTFSI) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), the nickel-imidazole interactions physically crosslink the polymer, increase the number of elastically active strands, and dramatically enhance the modulus while allowing Li⁺ to conduct quickly through the matrix.



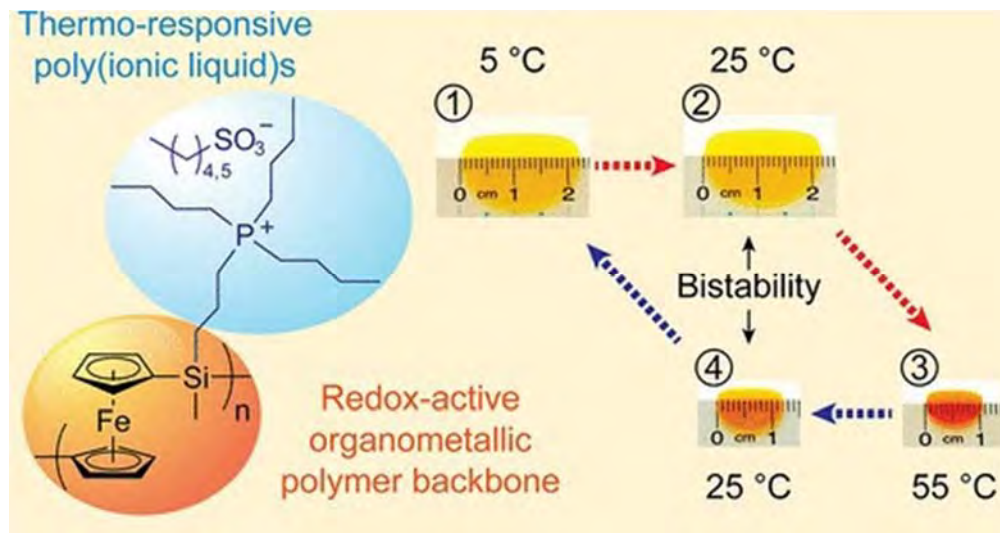
Trade-off between Mechanics and Ion Transport



POLY 198: Redox responsive polyionic liquids and their hydrogels with transition metals: Molecular design and applications as "smart" materials

Gyula Vancso¹, *g.j.vancso@utwente.nl*, Kaihuan Zhang¹, Mark A. Hempenius². (1) Univ of Twente Faculty of Chem, Enschede, Netherlands (2) University of Twente, Enschede, Netherlands

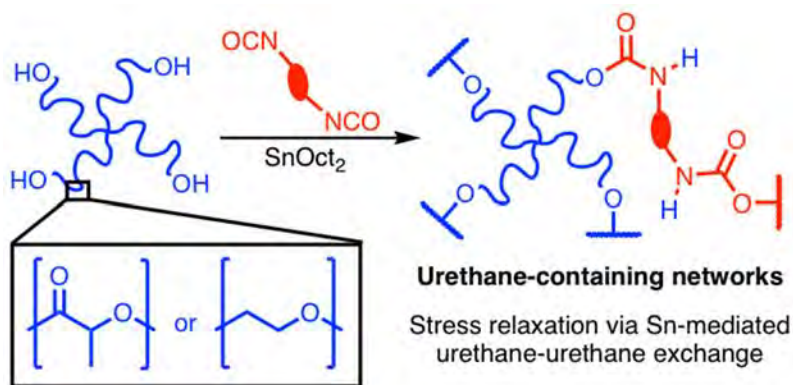
The synthesis of a new class of cross-linkable redox-responsive poly(ferrocenylsilane)-based poly(ionic liquid)s (PFS-PILs) will be discussed. PFS consists of alternating redox-active, silane-bridged ferrocene units (see Figure) with a rich palette of possible substituents attached to Si. These PILs are redox responsive due to the presence of ferrocene in the backbone and can also exhibit a lower critical solution temperature (LCST) behavior depending on the molecular structure. We describe the responsive behavior in solution, cross-talk between the two types of stimuli, as well as the responsive behavior of cross-linked hydrogels made from these PFS PILs. We show how these systems can be used to disperse CNTs and embed them in devices. In addition we demonstrate applications by changing the optical transmittance of the PIL solutions for use as smart windows. The hydrogels can display an unusual, strongly hysteretic volume-phase transition indicating non-ergodic behavior and useful thermal memory properties, which will also be elucidated (see Figure).



POLY 199: Stress relaxation in urethane-containing polymer networks

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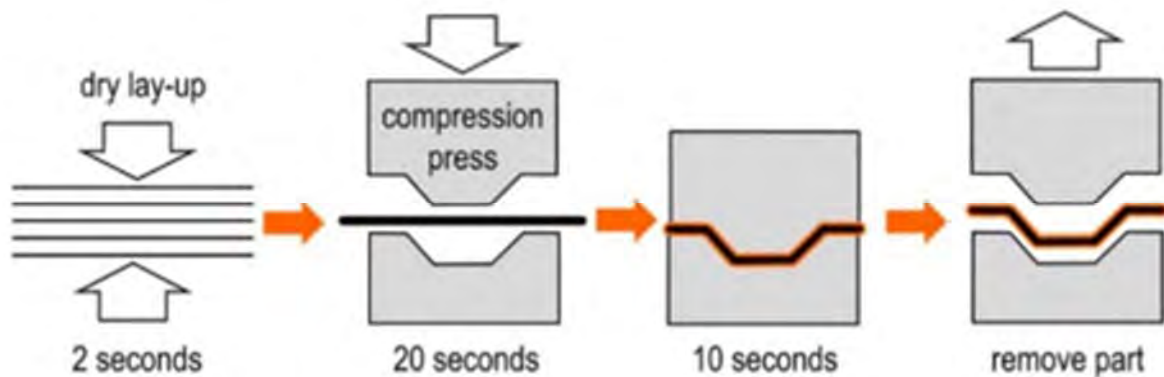
Cross-linked polymers are used in many commercial products and are traditionally incapable of recycling via melt reprocessing. Recently, tough and reprocessable cross-linked polymers have been realized by incorporating cross-links that undergo associative exchange reactions, such as transesterification, at elevated temperatures. Here we investigate how cross-linked polymers containing urethane linkages relax stress under similar conditions, which enables their reprocessing. Materials based on hydroxyl-terminated star-shaped poly(ethylene oxide) and poly((±)-lactide) were cross-linked with methylene diphenyldiisocyanate in the presence of stannous octoate catalyst. Polymers with lower plateau moduli exhibit faster rates of relaxation. Reactions of model urethanes suggest that exchange occurs through tin-mediated exchange of the urethanes that does not require free hydroxyl groups. Furthermore, samples were incapable of elevated temperature dissolution in a low polarity solvent (1,2,4-trichlorobenzene) but readily dissolved in a non-protic high polarity solvent (DMSO, 24 to 48 h). These findings indicate that urethane linkages, which are straightforward to incorporate, impart dynamic character to polymer networks of diverse chemical composition, possibly through a urethane reversion mechanism.



POLY 200: Imine-linked vitrimers applied to lightweight advanced composites

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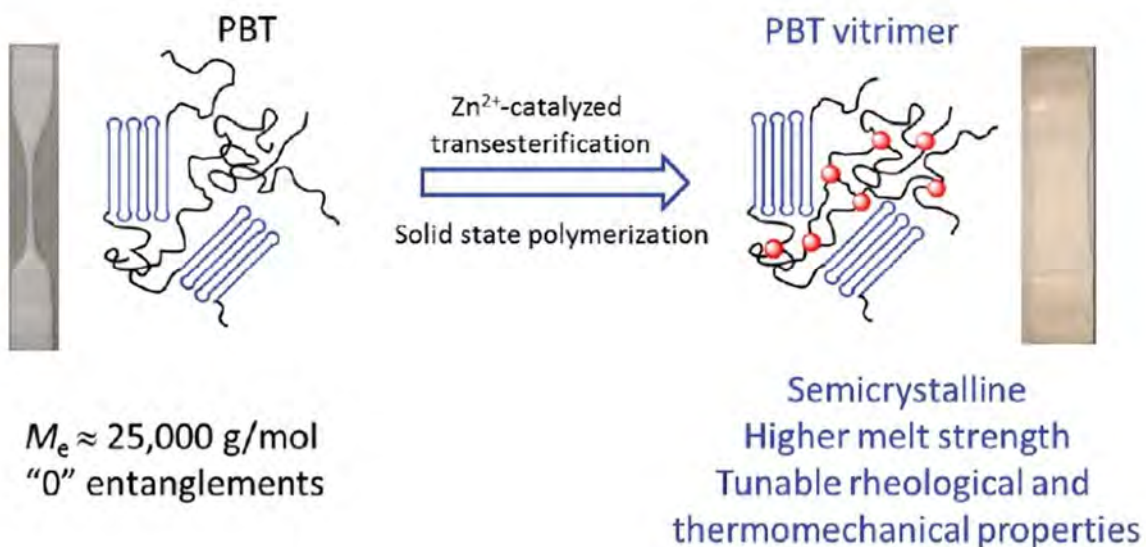
Mallinda is commercializing imine-linked vitrimers. We are focusing on application spaces where the cure time of traditional thermosets is limiting. The in-mold cure required to produce traditional thermoset composites keeps prices high and production volumes low. Vitrimer composites have the potential to revolutionize composite production by curing the material upstream of part production. The range and flexibility of the imine chemistry allows Mallinda to develop solutions for applications ranging from sporting goods and electronics to heavy machinery and automotive.



POLY 201: Semi-crystalline vitrimers via solid state polymerization

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(1) Chemical Engineering & Chemistry, TU Eindhoven, Eindhoven, Netherlands (2) T&I, SABIC, Bergen op Zoom, Netherlands

Vitrimers are a relatively new class of materials which form a "bridge" between classical thermosets and thermoplastics. These materials are covalently crosslinked, but rather than being permanent, the crosslinks are dynamic and may rearrange upon heating above the so-called vitrimer transition temperature. This leads to a greater dimensional stability and creep resistance at lower temperatures and (re)processability of the materials at higher temperatures. Recently we reported our results on the development of a new type of semi-crystalline vitrimer based on poly(butylene terephthalate) (PBT). Glycerol was incorporated as a crosslinker into the amorphous phase of PBT via solid-state polymerization using Zn^{2+} as a transesterification catalyst. It was found that the crystallization characteristics of PBT were not significantly affected by the incorporation of glycerol, leading to similar thermo-mechanical properties below the melting point. Above the melting point, however, a rubbery plateau was observed (consistent with a crosslinked material) and the modulus of this rubbery plateau could be changed by changing the amount of crosslinker. The dynamic nature of the crosslinks was confirmed via stress relaxation experiments, revealing a full relaxation at temperatures above the melting point. Furthermore, it was found that the (thermo)mechanical properties could be further tuned by using different crosslinkers and/or changing the morphology of the material. These results will be discussed in detail in the current presentation.

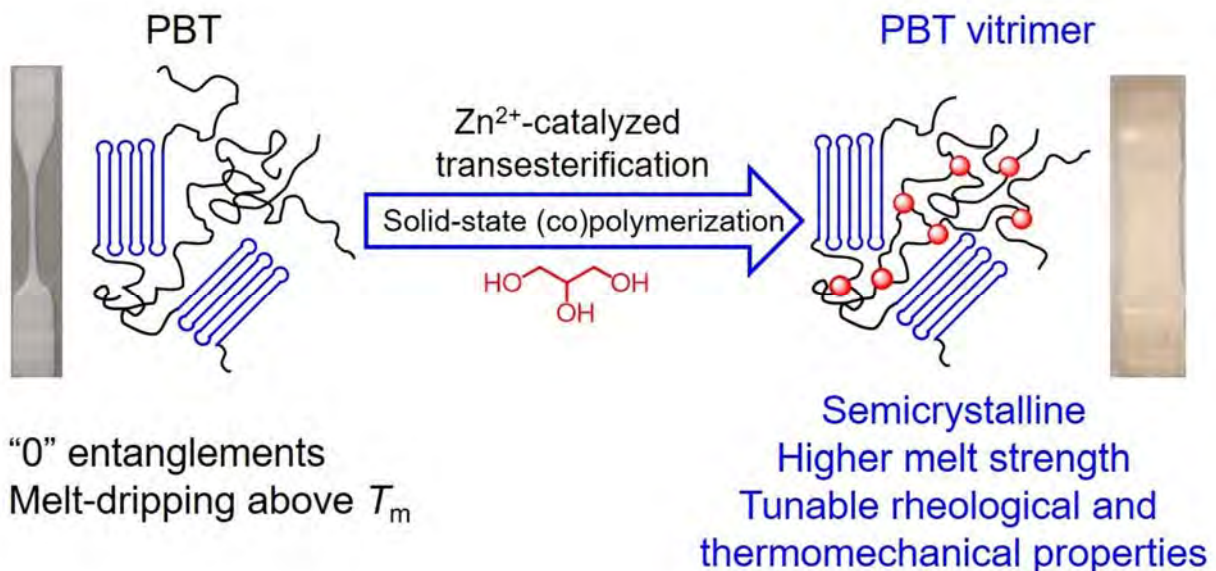


POLY 202: Poly(butylene terephthalate) (PBT)-based vitrimers: Industrial view

Han Goossens, han.goossens@sabic.com. T&I, SABIC, Bergen op Zoom, Netherlands

Poly(butylene terephthalate) (PBT) is a semi-crystalline polyester and widely used in injection-molding applications due to its high crystallization rate and good solvent resistance. However, commercial PBT, with M_n ranging from 5000 to 45 000 g/mol, is hardly entangled. Its lack of entanglements inherently gives the material a low melt strength, leading to processing challenges for techniques that involve elongational flows, such as blow molding, foaming, film, or sheet extrusion.

In this presentation we will show two ways on preparing PBT-based vitrimers, i.e. one via reactive extrusion using $Zn(II)$ -catalyzed addition and transesterification chemistry with epoxies and one via solid-state (co)polymerization to incorporate glycerol into the amorphous phase of PBT. For both systems the characteristic vitrimer behavior was demonstrated by stress relaxation and oscillatory frequency sweep experiments. Furthermore, we will focus on the effect of vitrimer chemistry on the crystallization aspects and make the connection to industrial processing conditions.



POLY 203: Thermadapt shape memory hybrid materials with healing properties

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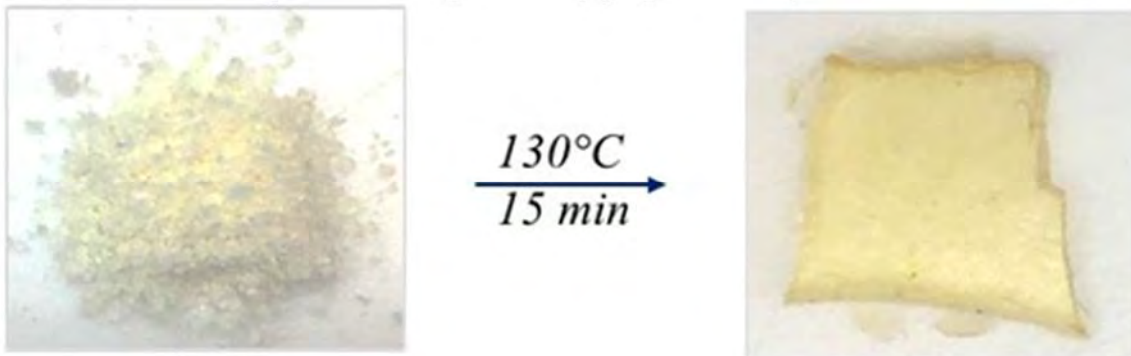
Shape memory materials have the ability to change their shape and recover their original shape upon application of an external stimulus. One possible way to trigger shape memory effect is to change and increase system temperature. These materials are called thermo-responsive. To obtain this ability, two conditions are required. First, switch domain as reversible thermal transition is necessary for temporary shape fixation and partial recovery. This shape memory transition allows to enable chain mobility to fix temporary shape and inversely recovery permanent shape. Then, a cross-linking network determine the permanent shape to prevent chain slipping.

In this study, reversible thermal transition is determined by the melting temperature of the crystalline phase of poly(ethylene-co-vinyl acetate). This polymer is cross-linked by an inorganic component as transition metal oxide via transesterification reaction to form dynamic ionic-covalent bond. The hybrid materials obtained lead to a very efficient shape memory effect. Moreover, the use of an organic-inorganic hybrid material enable to obtain custom-made material, specifically by tuning nanostructuration and nature of the hybrid interface. Indeed, hybridation allows to enhance drastically the mechanical properties and brings additional properties such as thermally induced healing properties and reprocessability.

Shape memory properties was highlighted by tensile tests to quantify material's ability to fix the temporary shape and to recover its permanent shape. Thermally induced healing and reprocessability properties was investigated by stress relaxation, creep tests and qualitative tests are shown on these pictures. Moreover, self-healing efficiency was analyzed by mechanical tests such as dynamic mechanical analysis and tensile tests.



Illustration of thermally-induced shape memory properties of hybrid material

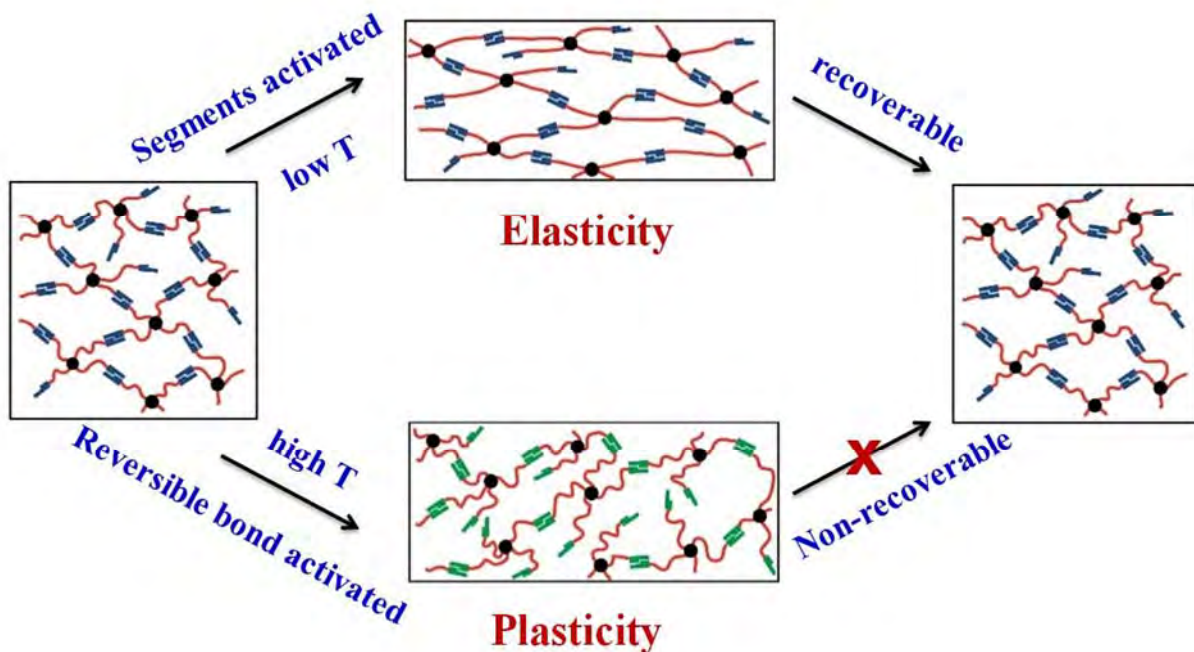


Reprocessing of hybrid material through hot press

POLY 204: Dynamically crosslinked shape memory polymer network

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In contrast to thermoplastic shape memory polymers (SMP), thermoset SMP exhibit robust shape memory behaviors, but their permanent shape is not reconfigurable. In addition, the permanent shapes of both thermoplastic and thermoset SMP are defined by traditional molding process, which limits the geometric complexity of SMP based devices. Our recent work has established a third class of SMP (thermadapt SMP) with dynamic covalent crosslinkers that overcomes the above limitations. At relatively low temperatures, the covalent linkages remain dormant, the SMP exhibits the classical elasticity-based thermoset shape memory behaviors. At sufficiently high temperature such that the dynamic linkages are activated, the permanent shape can be reconfigured repeatedly via solid-state plasticity in a mold free manner. Additional spatio-temporal controls can further enrich the morphing behavior. In particular, light-triggered crosslinking establishes spatio-selective molecular chain anisotropy, leading to opportunities to design single component soft robots. In addition, photo-thermal heating permits the introduction of digitally defined stress distribution in a free-standing flat film that can be used for encoding invisible information.

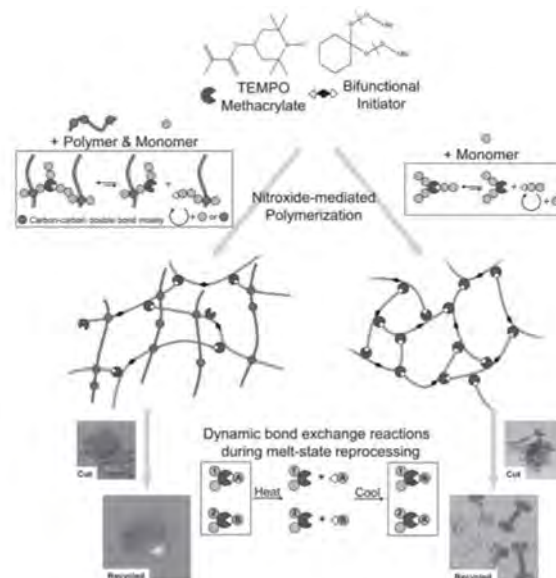


Network with distinct elasticity and plasticity.

POLY 205: Dynamic polymer networks and network composites: Reprocessing leading to full property recovery associated with cross-link density for models of rubber tires and non-isocyanate polyurethane networks and a quantitative approach to suppress creep in vitrimers

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Northwestern University, Evanston, Illinois, United States

Thermosets are covalently cross-linked networks that cannot be recycled by melt processing because the percolated network prevents melt-state flow. Although much research has focused on making networks melt-reprocessable or malleable via cross-links that are reversible or that undergo exchange reactions, very little success has been reported in achieving full property recovery after reprocessing associated with cross-link density. Here, we describe results of two studies in which we achieve full recovery of cross-link density as determined by rubbery plateau modulus. The first exploits nitroxide-mediated polymerization (and its reversible radical capping/uncapping step) in a novel way to achieve dynamically cross-linked polybutadiene and polyisoprene both without any filler and with substantial levels of carbon black and other fillers as models for rubber tires. With reprocessing conditions comparable to those used in commercial tire molding operations, results show full recovery of cross-link density after multiple reprocessing steps for both polymer networks and appropriately designed network composites. The second demonstrates that, under appropriate catalyzed reprocessing conditions promoting reversible and exchange reactions, polyhydroxyurethane (PHU) networks achieve full recovery of cross-link density after multiple reprocessing steps. Such PHUs are potential substitutes for isocyanate-based polyurethane networks. We will also describe a study aimed at addressing an "Achille's heel" of vitrimers, that being their propensity to creep, which results from the presence of exchange reactions above the vitrification temperature. We have developed a novel approach that substantially reduces creep in vitrimers and using a modification of Flory-Stockmayer theory have quantified conditions under which this approach is expected to work.



POLY 206: Hybrid materials: A concept for healing networks

Alice Tonnelier¹, *alice.tonnelier@gmail.com*, **Stéphane Delalande**², **Rémi Perrin**³, **Lionel Nicole**¹, **Laurence Rozes**¹. (1) *Laboratoire de Chimie de la Matière Condensée de Paris, Paris, France* (2) *PSA Group, Vélizy Villacoublay, France* (3) *Soprema, Strasbourg, France*

Over their lifetime, polymers suffer from damages which lead to irreversible mechanical degradation and a loss of functionality. Being a part of smart materials, self-healing materials have emerged to prevent or slow down the loss of mechanical properties. To this end, the reversibility of covalent or supramolecular bonds is chosen to enable a material to self-heal or to heal upon application of an external stimulus.

Metal-organic bonds can also play the role of the reversible link. This strategy is exploited in some hybrid materials in which both organic and inorganic components coexist, one of them at least being nanoscaled. The amount and chemical nature of organic/inorganic interfaces is crucial to enhance and tune the mechanical properties and can also confer new attractive properties. For instance, hybrid materials are now employed in impact detection, anti-fogging, anti-adhesion... Interestingly, coordinative chemistry dealing with polymers and metallic cations also offers both advantages of versatility of the complexing function in polymers and wealth of properties thanks to metallic cations (photochromism, oxydoreduction...).

We synthesized healing hybrid materials using polyurethane macromolecular chains crosslinked by a transition metal oxide. The inorganic component led not only to crosslinking, but also to a material reinforcement. The ability to heal itself upon an increase of temperature was also evidenced as a result of the exchange dynamic brought by the bonds reversibility at the hybrid interface. Moreover, the redistribution of the bonds enables the network to rearrange without any loss of its integrity as vitrimers. Thus, both thermoforming and self-healing were obtained. In our materials, healing and thermoforming occur without catalyst and at a temperature depending on polymer chemistry. It was demonstrated by scanning electron microscopy (Figure 1), creep, stress relaxation and dynamic mechanical analysis. The determination of healing efficiency was also obtained using tensile testing. For example, crosslinked and hybrid polyurethane prepolymer materials have a high healing efficiency near of 100% and a critical temperature of 60 °C from which healing is observed.

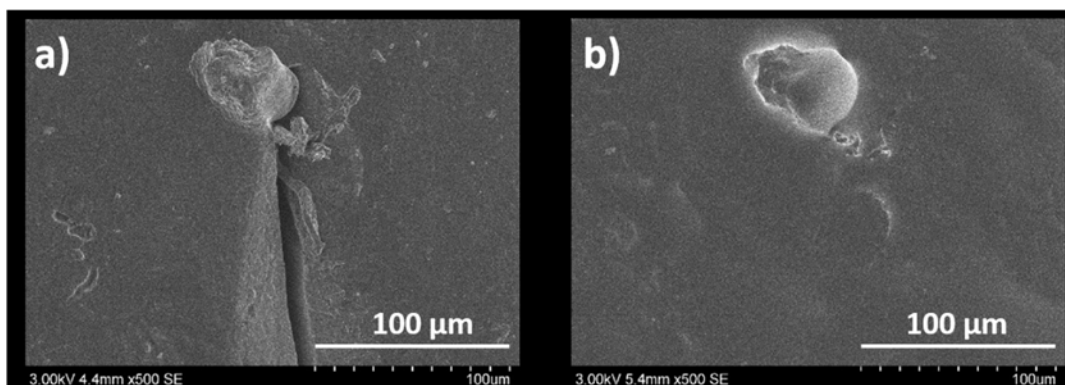
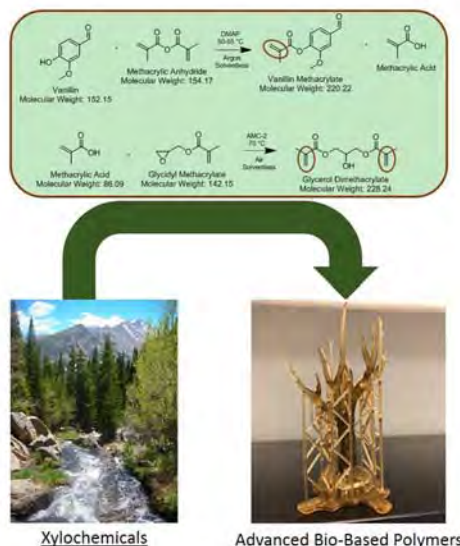


Figure 1: Scratch before (a) and after thermal treatment (b)

POLY 207: Advancement of bio-based polymers and composites for military applications: Pushing the envelope via strategic assemblies of xylochemicals

Joseph F. Stanzione¹, stanzione@rowan.edu, **Giuseppe R. Palmese**³, **Joshua M. Sadler**⁴, **John La Scala**². (1) Department of Chemical Engineering, Rowan University, Glassboro, New Jersey, United States (2) Department of the Army, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States (3) Department of Chemical & Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States (4) Army Research Laboratory, RDECOM, Aberdeen Proving Ground, Maryland, United States

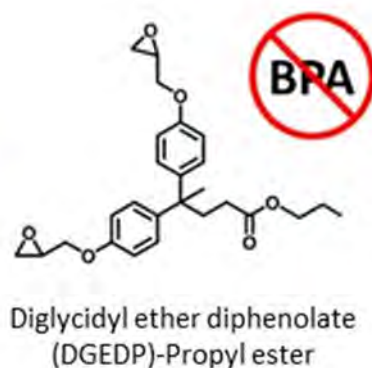
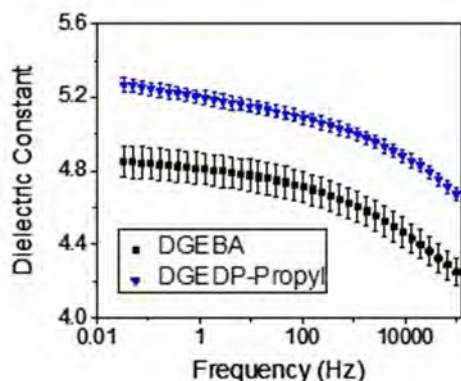
The utilization of wood-derived building blocks (xylochemicals) and other abundantly available, non-food biomasses to replace fossil-based precursors is an attractive research subject in modern polymer science and engineering. The continuing development of economically viable bio-based feedstocks and subsequent, new platform chemicals opens opportunities to increase the resource base from which chemical and materials engineers can draw to meet specific polymer and composite property requirements. Recently, significant efforts have transpired to obtain bio-based polymers and composites with enhanced thermal and physical properties for a wide variety of applications, from packaging to coatings to adhesives to energy storage devices. In continuing these efforts and to push the envelope, we have strategically assembled xylochemicals via our molecularly hybrid approach and have prepared and examined a variety of bio-based thermoplastics, thermosets, and composites, including epoxies, vinyl esters, allyl ethers, polyesters, and polycarbonates, all focused for utility in military applications. These novel materials are largely based on lignin-derived, (hemi)cellulose-derived, and cashew nut shell liquid-derived platform chemicals, but also contain components sourced from alternative bio-based feedstocks such as birch bark and agriculture wastes. This presentation will highlight our work on fundamentally understanding the processing-structure-property-toxicity relationships of our bio-based polymers and composites via thermal analysis and mechanical testing techniques. Furthermore, their utilities in military applications will be discussed.



POLY 208: Dielectric properties of bio-based diphenolate ester epoxies

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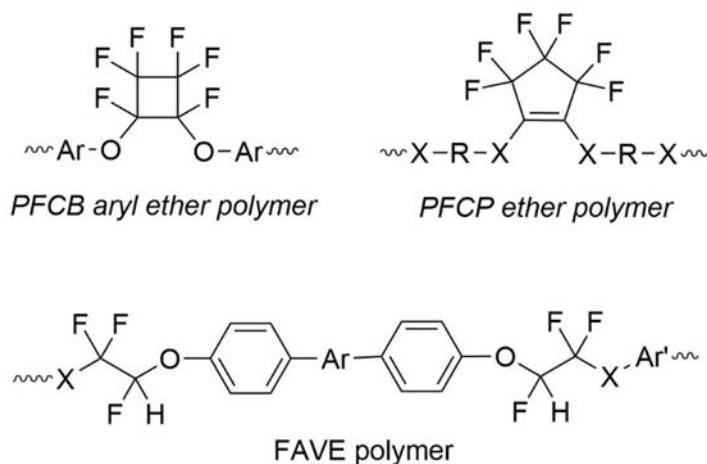
Structural capacitors require both high mechanical strength and dielectric constant. They substitute for existing structural components of products (e.g. vehicle doors, electronics cases etc.) while also functioning for energy storage. To this end, thermoset bio-based diglycidyl ether of diphenolate esters (DGEDP) **exhibit comparable** mechanical properties as petroleum-derived diglycidyl ether of bisphenol A (DGEBA), while DGEDP is derived from levulinic acid, a safe and readily renewable feedstock. A series of DGEDP-esters (i.e. methyl, ethyl, propyl and butyl esters) were synthesized and studied to determine the potential replacement of DGEBA structural dielectric materials. It was found that that DGEDP-propyl has the highest dielectric constant in the series, comparable to DGEBA. To understand this, we consider the structure-property relationships within the DGEDP ester series, as well as the effect of varying the cross-link density. This reveals differences in the dielectric properties of DGEDP-esters which are attributed to the interplay of segmental, small local, and side-chain motions on one hand and free volume and steric hindrance on the other.



POLY 209: Advances in efficient strategies towards high use temperature polymers and networks from fluoroalkenes

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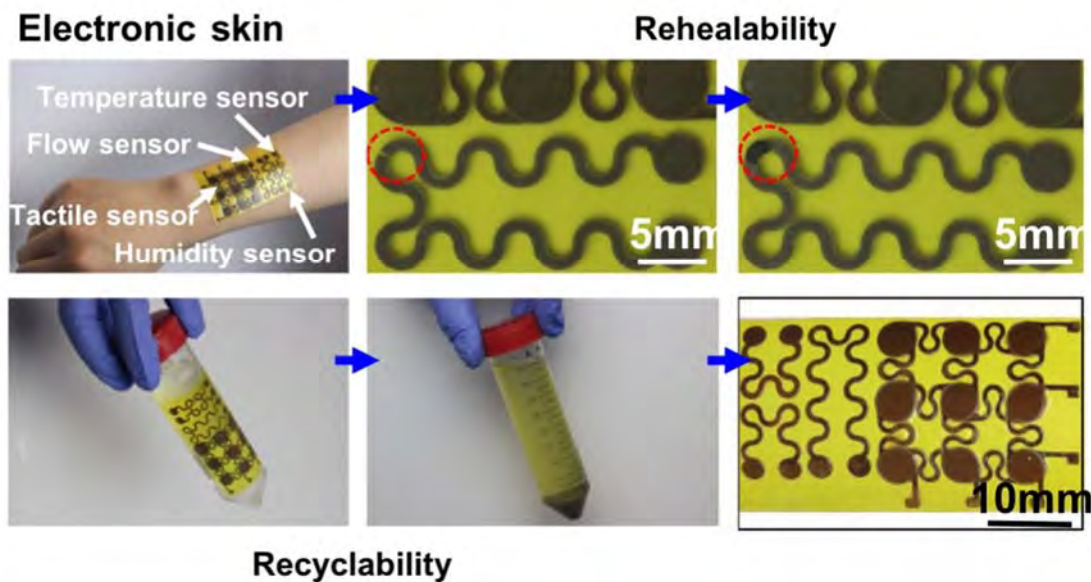
Many of the desired properties of high use temperature aromatic polymers are shared with fluoropolymers. A logical approach would be to incorporate fluorinated functionality into the framework of the polymer that would improve solution processability of such rigid systems. Recently, we have developed a pool of new fluorocyclic-containing polymers that includes poly(aryl ether)s, fluorinated organically modified silica gels, aromatic-containing fluorosilicones, and resins derived from cyanate esters and benoxazines. These unique materials have shown marked improvement in processability, mechanical strength, and filler compatibility as hybrid composites while retaining high use temperature in excess of 450 °C in air-rich environments. This work will highlight new synthetic routes for monomer preparation, step-growth polymerization methodologies, and processing of these systems.



POLY 210: Novel dynamic covalent polymer networks and their functional composites with rehealability and full recyclability

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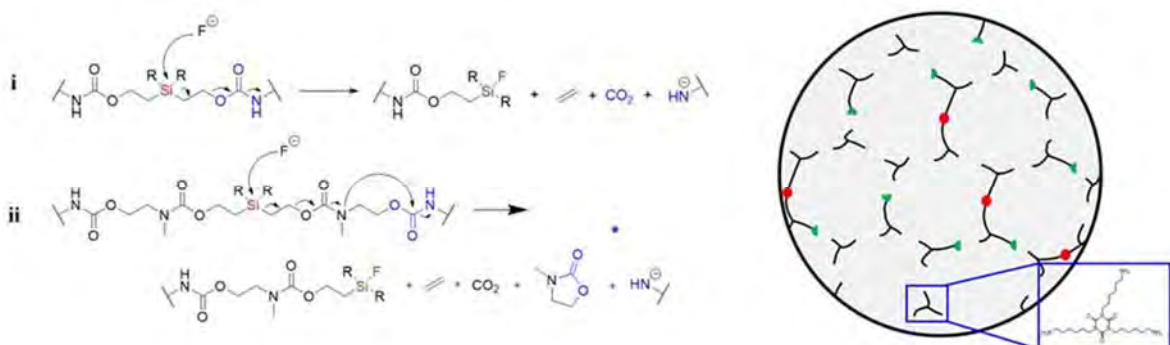
Conventional crosslinked polymers, commonly called thermosets, are mechanically tough, but are not able to be repaired or recycled. Malleable network polymers represent a new class of materials, wherein reversible covalent bonds are employed. These materials can exhibit mechanical properties of typical thermosets under ambient conditions, yet under external stimuli they can be reprocessed and recycled through a cross-link exchange and rearrangement process, usually with the aid of catalysts. This presentation will focus on the development of a catalyst-free network polymer, which becomes malleable by application of either heat or water. Such malleable thermosets and their functional composites (e.g., solid-state electrolyte membrane, carbon fiber reinforced composites, or electronic skin) take advantage of dynamic covalent reaction to achieve its unique processability, rehealability and full recyclability, while retaining tough mechanical properties.



POLY 211 Cross-linked polymer networks that selectively and controllably disassemble on-demand via cascading bond cleavage

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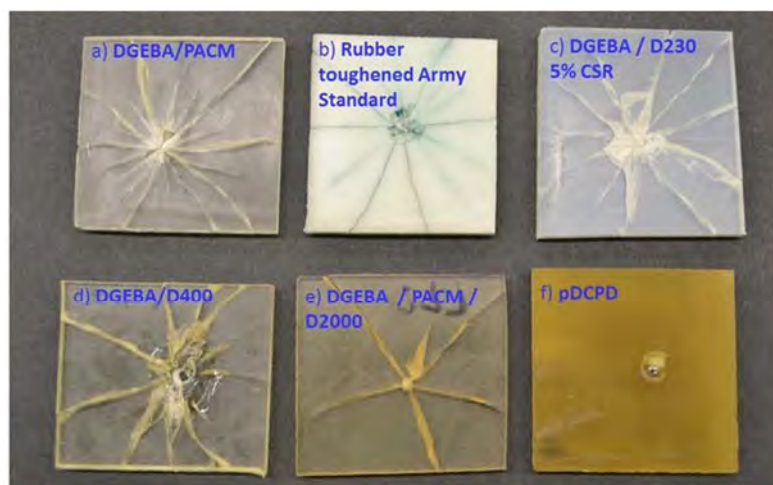
Cross-linked polymeric materials are utilized in numerous consumer and industrial applications due to their unique properties. However, these materials require harsh chemical treatments in order to degrade their cross-linked networks, leading to environmental and safety issues. This work describes the first silyl-containing polyurethane thermosets, formed from aliphatic isocyanates and synthesized silyl-diols with different electrophilicity and chain lengths to control disassembly rates. The synthesized thermosets displayed high thermal stability, rigidity, and high cross-link density, yet have the ability to disassemble via cascading bond cleavage in multiple directions upon exposure to a selective and mild chemical stimulus. Disassembly was initiated by reaction with fluoride ion to release small molecules. Unlike previously reported degradable cross-linked materials, the silyl-containing thermosets were resistant to disassembly with strong acid and base, displaying their selectivity and robustness. This technology has numerous potential applications, such as in the selective removal of coatings from organic composites.



POLY 212: Rate dependent mechanics of crosslinked polymer networks

Joseph Lenhart, *joseph.l.lenhart.civ@mail.mil*. WMRD, US Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

This presentation will cover a comprehensive program in crosslinked polymer networks at the US Army Research Laboratory, investigating the rate dependent mechanical response over a broad range of crosslink density. For soft networks we have investigated the role of chain entanglement on the mechanical response, and are developing these materials as testing media and tissue simulants for the assessment of military protective equipment. For rigid materials we have focused on highly crosslinked epoxies and Ring Opening Metathesis Polymerized (ROMP) resins based on polymeric dicyclopentadiene (pDCPD). For the ROMP resins, the molecular weight between crosslinks (M_c) was systematically varied by co-polymerizing DCPD with either 5-ethylidene-2-norbornene (ENB), a chain extender that increases M_c , or 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene, a di-functional crosslinker (CL), which decreases M_c . A critical M_c of 500 ± 100 g/mol was identified that dictated the failure process of these resins. Resins with M_c above this value were ductile over a broad range of strain rates. Resins with M_c below this value were brittle, exhibiting low mode I fracture toughness, poor elongation to break during quasi-static tensile deformation, and substantial radial fracture during high velocity impact. By formulating DCPD copolymers with ENB we were able to make crosslinked resins with a glass transition temperature (T_g) of 150 °C that maintained ductility deep in the glassy regime at quasi-static to ballistic strain rates, which is in stark contrast with crosslinked epoxy resins that are typically brittle even with T_g as low as 50 °C. Molecular dynamics simulations showed that resins with lower M_c were more prone to forming molecular scale nano-voids. We postulate that the higher chain stiffness in low M_c resins inhibits relaxation and plastic deformation in the vicinity of these nanovoids, causing embrittlement. The experimental and computational results suggests that when M_c approaches the persistence length of the crosslinking chains, that the glassy network becomes brittle.

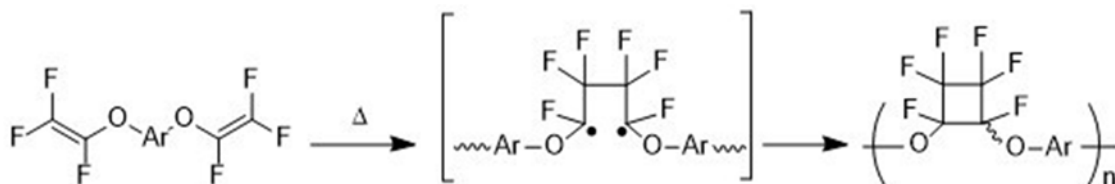


pDCPD exhibits a ductile like failure during ballistic impact with no large scale radial fracture

POLY 213: Polynaphthalene networks and semi-fluorinated aromatic ether polymers and for advanced composites

Ganesh Narayanan¹, Andrzej Sygula², **Dennis W. Smith¹**,
dsmith@chemistry.msstate.edu. (1) Department of Chemistry, Mississippi State University, Starkville, Mississippi, United States (2) Chem Dept, Mississippi State University, Mississippi State, Mississippi, United States

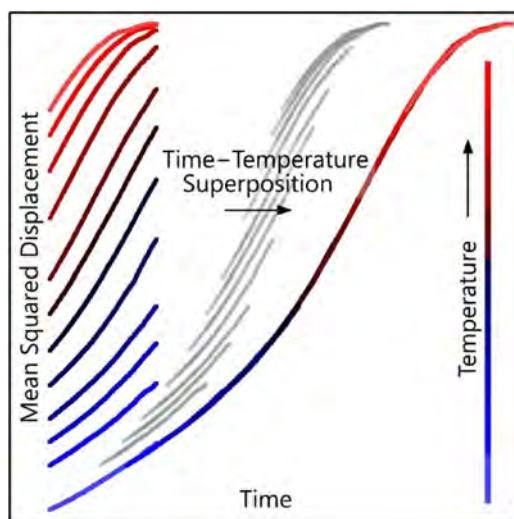
Two platform technologies including (1) polynaphthalene networks and (2) semi-fluorinated aromatic ether polymers are presented with particular emphasis on applications for advanced composites. Polynaphthalene networks are produced via the thermal cyclopolymerization of bis-*o*-diynylarene (BODA) monomers affording intermediate resins which can be melt processed and thermally cured ($T_d > 400$ °C). As a special class of enediynes, BODA monomers are prepared in three steps from commercial bis-phenols and undergo radical mediated Bergman cyclization and overall step-growth propagation to variable molecular weight reactive resin intermediates. Upon thermal processing via extrusion, infusion, coating, or micro/nano-molding and final cure, the resulting polyarylene networks are studied for applications such as thin film dielectrics, carbon fiber matrix composites, carbon-carbon composites, light emitting diodes, and photonic/electronic sensors. Semi-fluorinated aromatic polymer are prepared via the unique step-growth polymerization of fluoroalkenes. Perfluorocyclobutyl (PFCB) aryl ether polymers are prepared via step-growth thermal cyclopolymerization of aryl trifluorovinyl ether (TFVE) monomers for a variety of applications desiring an optically tunable, thermally stable, and processable fluoropolymer. More recently, fluorinated aryl vinylene ether (FAVE) polymers were prepared from the condensation of functionalized bisphenols with TFVEs. These fluoropolymers are solution processable, exhibit excellent thermal stability, and possess the ability to undergo thermal crosslinking without the use of post-curatives. In addition, we have reported a new class of perfluorocycloalkene (PFCA) polymers from commercial perfluorocycloalkene monomers and bisphenols. The synthesis, processing, and characterization for these platform technologies will be presented with special emphasis on advanced composites for aerospace and other composites applications.



POLY 214: Bridging the vast mismatch in the time scale of atomistic simulations and experiment for cross-linked epoxy using time-temperature superposition

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Many defense applications rely on the thermomechanical response of network polymers to ballistic strain rates. At such conditions, the design of controlled experiments can be challenging. Atomistic simulations, on the other hand, are well-suited to study thermomechanical behavior at such exceptionally high rates while preserving specific chemical interactions within the network that can provide structure-property insight. The associated computational cost, however, limits the accessible time scale and hence makes the quantitative comparison and the integration of computation and experiment nebulous. Here, we perform atomistic simulations of a cross-linked epoxy network to study the dynamics within the network. We find that the time-temperature superposition principle can be successfully invoked for the simulation trends to create a master curve that extends to experimentally relevant time scales. Thus, the dynamics studied via simulations can be directly compared with experimental data on mechanics for the same network that is available in the literature. By bridging these time and length scales, we are able to consider the molecular origin of dynamic heterogeneity in the system, which is of great relevance for applications ranging from metrology to mechanical toughening. We believe that our approach should be generally applicable to other glass-forming systems, where rate effects on thermomechanical behavior are an important consideration.

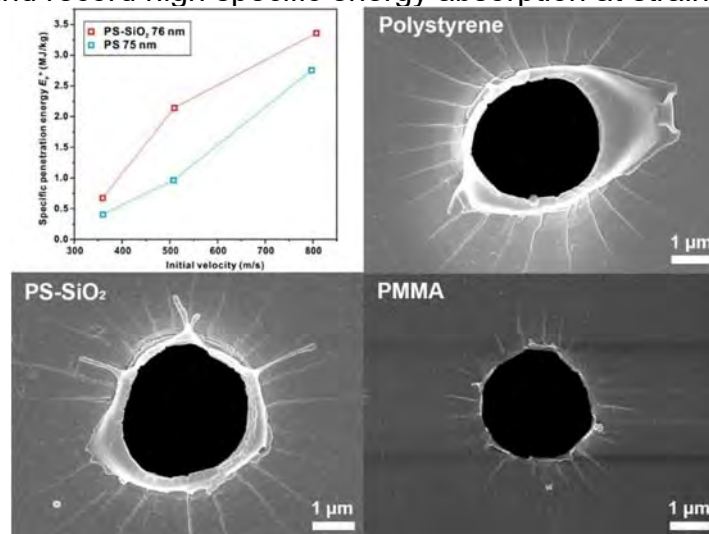


POLY 215: Specific energy absorption of freestanding glassy homopolymer and homopolymer grafted nanoparticle thin films at extreme strain rates

Jinho Hyon¹, *jhyon@rice.edu*, **Edwin L. Thomas**¹, **Jason Streit**², **Richard A. Vaia**². (1) *Material Science & NanoEngineering, Rice University, Houston, Texas, United States* (2) *US Airforce Rsrch Lab, Wright Patter, Ohio, United States*

The yield stress of a polymer increases with strain rate but the fracture stress is almost constant, inducing a ductile to brittle transition. At 20 °C polystyrene (PS) is a brittle, glassy polymer. Under tensile loading, fracture of PS is preceded by crazing, a dilational plastic deformation mechanism that leads to local energy dissipation ahead of the propagating crack. Plastic deformation can also induce shear bands. If crazing and shear banding can be made extensive, plastic deformation can dissipate large amounts of energy, and if occurring at very high loading rates, substantial sample heating can lower both the crazing stress and the yield stress leading to further adiabatic heating and plastic flow rather than brittle behavior.

Chains near the surface regions of free standing glassy polymer films have a higher mobility and lower entanglement density lowering the crazing and yield stresses. We investigate PS and PMMA films of various molecular weights (30-400 kg/mol) and thicknesses (30-300 nm), impacted by μ -size spherical projectiles at incident velocities of 350-800 m/s. Additionally, we explore polymer grafted nanoparticle films (\sim 1-5% v/v NPs) in order to observe the influence of the 100's of chains covalently anchored to each NP on the deformation. We find unprecedented energy absorption for entangled PS films and even greater energy absorption for entangled PS grafted to NPs. The observed deformation is comprised of extensive multiaxis crazing, tangential craze widening with strong adiabatic heating of the impact region leading to plastic flow of a viscoelastic melt and record high specific energy absorption at strain rates of $\sim 10^7/s$.



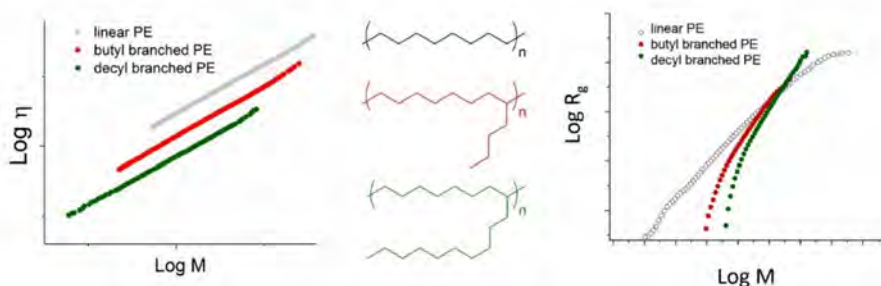
Specific energy absorption vs. velocity for PS and PS-SiO₂ films. SEM images of perforations viewed at normal incidence of the film exit surface. Extensive multiaxis crazing and adiabatic heating lead to large plastic deformation and viscoelastic melt flow with high energy absorption for the PS and PS-SiO₂ thin films. The deformation in the PMMA film is localized with very little energy absorption.

POLY 216: Characterization of polyolefins with precise control of branch frequency and branch length

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Separations of commercial polyolefins, which often involve mixtures and copolymers of linear, short-chain branched, and long-chain branched polyethylenes, can be very challenging to optimize as species with similar hydrodynamic sizes or solubility often co-elute using various chromatographic methods. To better understand the effects of polyolefin structure on the dilute solution properties of polyolefins, a family of short-chain branched polyolefins with control of alkyl branch frequency and branch length were synthesized by ring-opening metathesis polymerization (ROMP) of 1-alkyl-*trans*-cyclooctene monomers. This synthetic approach utilizes highly strained cyclic alkenes to generate controlled, regioregular polyalkenamers. Quantitative post-polymerization hydrogenation generates the final branched polyolefins with ideal head-to-tail addition of monomer, resulting in a fixed branch frequency and branch length across the molar mass distribution.

A series of linear polyolefins with comparable molar masses, but varied short-chain branch length, were analyzed by high-temperature size exclusion chromatography with infrared, refractive index, viscometric, and multi-angle light scattering detectors to quantify molar mass, molar mass distribution, intrinsic viscosity ($[\eta]$), radius of gyration (R_g), and degree of short-chain branching. A systematic decrease of intrinsic viscosity is observed with increasing branch length across the entire molar mass distribution. R_g measurements were also confirmed by offline high-temperature small angle neutron scattering measurements (SANS). These short-chain branched polyolefins can serve as useful standards to calibrate the branching index factor as a function of molar mass so long-chain and short-chain branching distributions in polyolefins can be more accurately measured. Statistical and block copolymers of branched and linear polyethylenes were also synthesized. Comparative analysis of $[\eta]$ and R_g of the copolymers with fixed branch frequency homopolymers was also conducted to determine differences in the polymer persistence length.

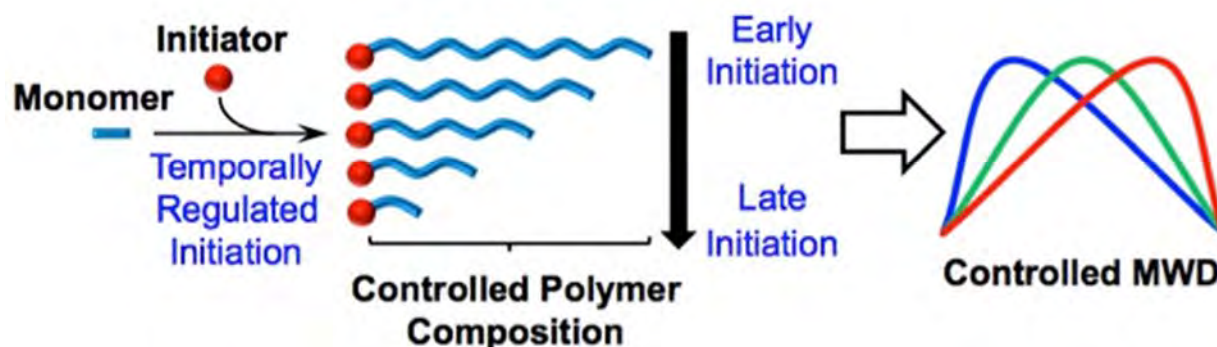


Intrinsic viscosity and conformation plots of the model branched polyolefins as a function of molar mass.

POLY 217: Using the higher moments of a polymer's molecular weight distribution to tune properties

Brett P. Fors, bpf46@cornell.edu. *Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States*

A polymer's molecular weight distribution (MWD) has an impact on its properties – from processability to changes in the phase behavior of block polymers. Dispersity is the most common measure of MWD and provides information on the relative breadth of molecular weights in a sample; however, dispersity is not a thorough description of the distribution. On this basis, our group investigates the influence of the MWD skew on polymer properties. This presentation will detail the development of a modular synthetic strategy that provides deterministic control over the M_n , breadth, and skew of a polymer's MWD and will examine the influence of MWD shape on polymer properties. Specifically, the influence of skew on polymer processability and diblock copolymer phase behavior will be discussed.



POLY 218: Novel strategy for radical ring-opening polymerization of strainless macrocyclic monomers

Jia Niu, *jia.niu@bc.edu*. Department of Chemistry, Boston College, Chestnut Hill, Massachusetts, United States

As a fundamental polymer synthesis strategy, ring-opening polymerization (ROP) demonstrated great utility in the preparation of synthetic polymers with heteroatoms and functional groups in the backbone, but controlled ROP of strainless macrocyclic monomers for the incorporation of extended main-chain functionalities still remains challenging. In this work, we address this challenge by developing a novel chain-growth, triggered ring-opening polymerization (TROP) approach for the rapid and controlled ROP of strainless macrocyclic monomers (Figure 1). A systematic study correlating various designs of the ring-opening trigger and polymerization control were designed to allow optimized ROP kinetics and reaction control. The optimized TROP conditions were then employed to prepare glycomimetic multi-block copolymers with predefined block sequences and main-chain carbohydrate functionalities that are inaccessible by previous polymerization techniques, thereby significantly broadening the structural and functional scopes of glycomimetic polymers.

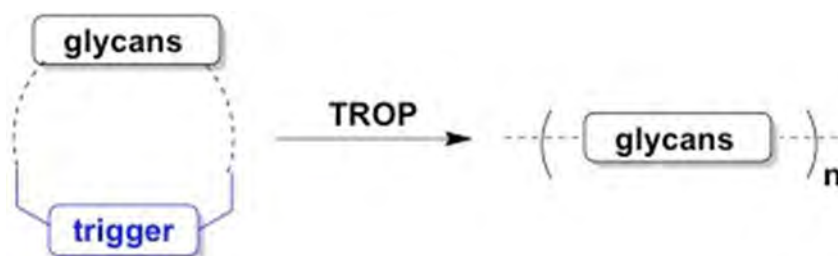
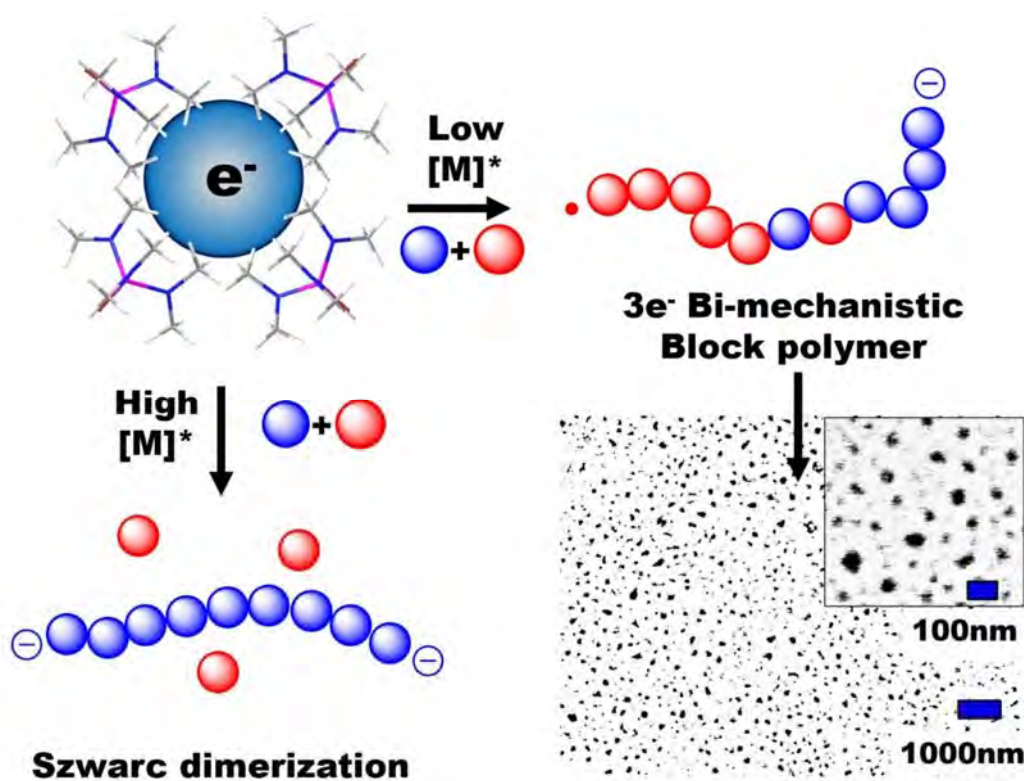


Figure 1. Scheme of TROP

POLY 219: Rapid bimechanistic synthesis and self-assembly of block co-polymers using free electron initiators

Martin M. Thuo¹, *mwangi.m@gmail.com*, **Boyce S. Chang**². (1) *Materials Science & Engineering, Iowa State University, Ames, Iowa, United States* (2) *Iowa State University, Ames, Iowa, United States*

Polymers, from DNA, cellulose, to poly-olefins, are ubiquitous to human existence. Polymer synthesis, however, has been limited to a set of methodologies with kinetics playing a critical role in the quality of material obtained. For hydrocarbon-based polymers, the use of initiator moieties—often needed to induce asymmetry in the electron density, is the first challenge in their synthesis. In free-radical chain growth, for example, addition of a single electrons to an olefin introduces an odd-electron activated monomer albeit with an appended initiator fragment. The initiator moiety can, however, be eliminated by use of a free-electron initiator. Use of free (solvated) electrons in co-polymerization of so-called ‘armed-disarmed’ monomer pairs will be discussed. Exploiting solubility and quantum mechanics dominated properties of the free electrons, challenges in diffusion limited reactivity can be overcome. This coupled approach allows for rapid polymerization where the odd-symmetry in electron density can be exploited in a bimechanistic (concurrent radical and anionic) reaction. We extended this approach to synthesis of block co-polymers of complex architecture that given unprecedented neoteric micro-structures.

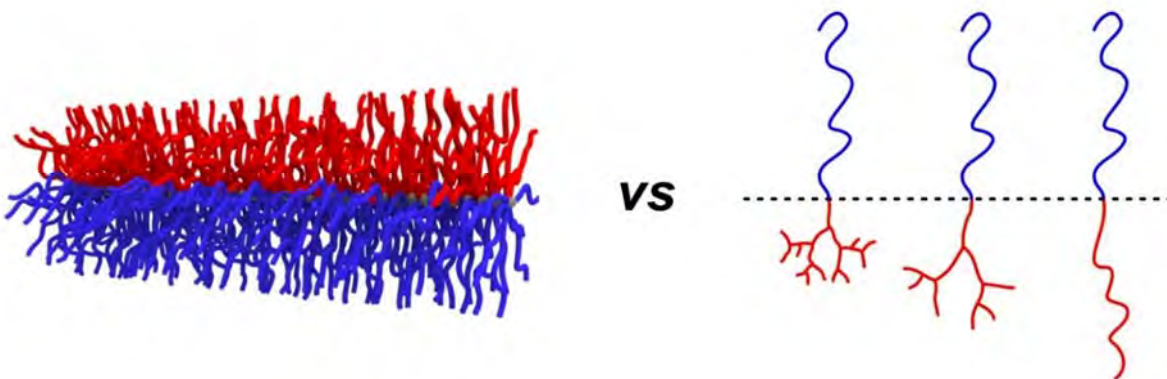


Free-electron initiated bimechanistic synthesis of block co-polymers that self-assembled into complex patterns

POLY 220: Tunable polymer nanostructures enabled by controlled branching

Mingjiang Zhong¹, mingjiang.zhong@yale.edu, Zi-Hao Guo¹, Feng Li², An Le³, Mengxue Cao⁴. (1) Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States (2) Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States (3) Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States (4) Yale University, New Haven, Connecticut, United States

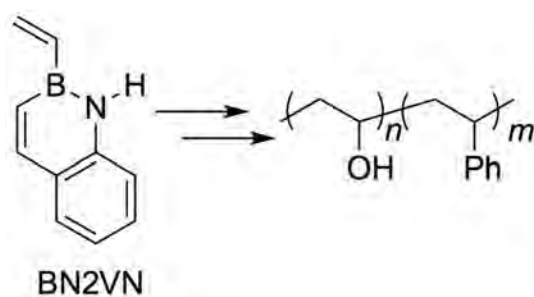
Branched macromolecules have found broad applications ranging from thermoplastics, rubbers, and adhesives to biomaterials. Recent developments in living polymerization techniques enabled the synthesis of diverse branched macromolecules of controlled composition and functionality. In the first part of this talk, the presenter will report their recent progress on the controlled synthesis and characterization of bottlebrush block copolymers containing quasi-alternating sidechains. Interesting phase separation behaviors that result in the formation of sub-5 nm nanodomains and independently tuned thermomechanical properties will be discussed. The concept of precision synthesis will then be extended for the preparation of hyperbranched polymers in the second part of this talk. A chain-growth type hyperbranched polymer was realized through a polymerization-induced radical generation process. This approach was utilized for the integration of hyperbranched building blocks into a variety of hierarchically-structured materials.



POLY 221: Organoborane strategy for tunable polar content in polystyrene

Rebekka S. Klausen, *klausen@jhu.edu*. JHU/Chemistry Dept., Baltimore, Maryland, United States

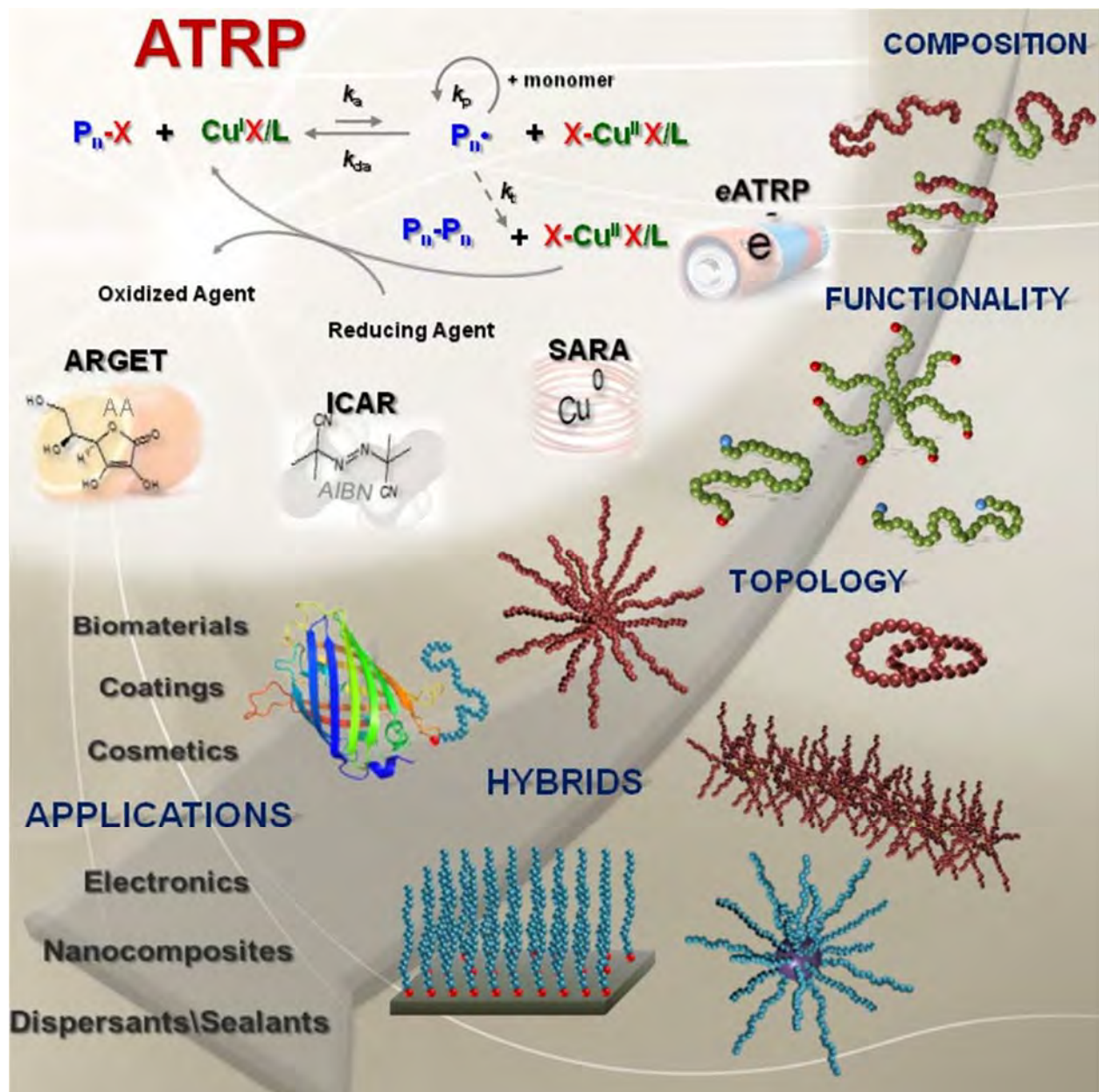
BN 2-vinylnaphthalene, a BN aromatic vinyl monomer, is copolymerized with styrene under free radical conditions. Chemoselective organoborane oxidation yields styrene-vinyl alcohol (SVA) statistical copolymers with tunable hydroxy content. Comprehensive spectroscopic investigation provides proof of structure. Physical properties that vary systematically with hydroxy content include solubility and glass transition temperature. BN aromatic polymers represent a platform for the preparation of diverse functional polymeric architectures via the remarkable reaction chemistry of C-B bonds.



POLY 222: Nanostructured polymers by ATRP

Krzysztof Matyjaszewski, km3b@andrew.cmu.edu. CMU, Pittsburgh, Pennsylvania, United States

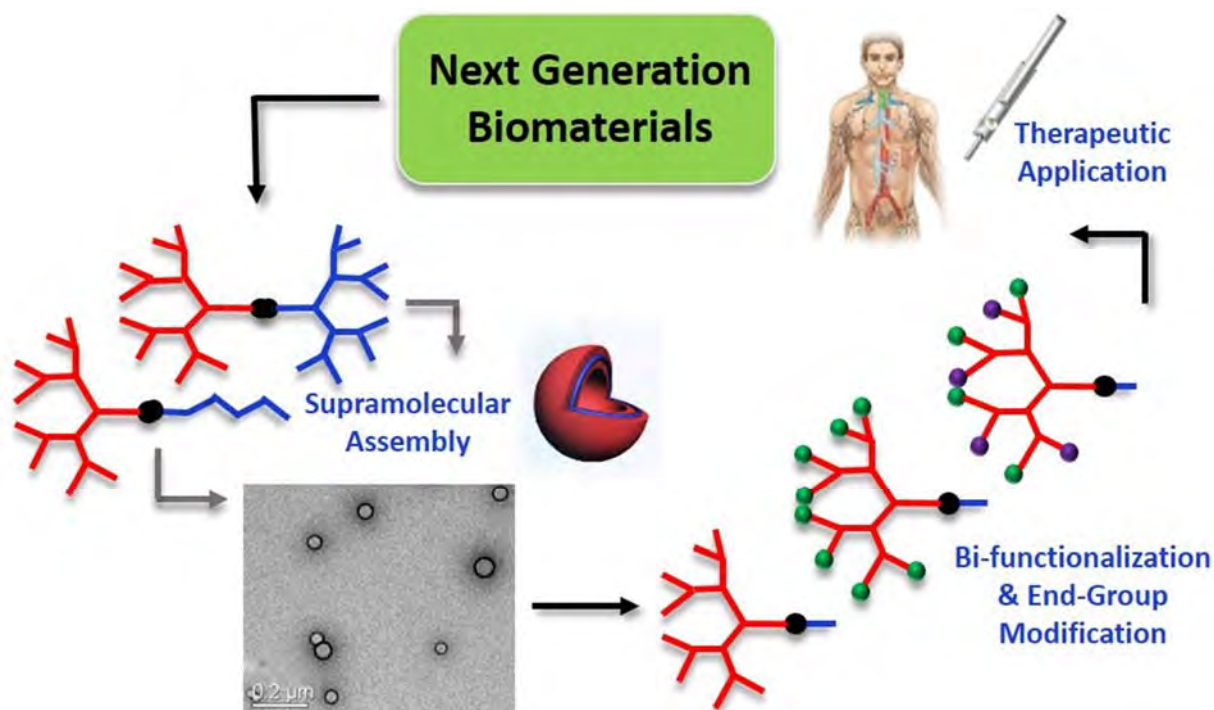
Atom transfer radical polymerization (ATRP) has been successfully used to synthesize various nanostructured polymers with controlled composition, topology and functionality. They include block, graft and gradient copolymers, stars, densely grafted molecular brushes and telechelics. In addition organic/inorganic hybrids and bioconjugates with proteins and nucleic acids were prepared. Their properties and some applications will be discussed.



POLY 223: Heterobifunctional linear-dendritic block copolymers (LDBC) as multifunctional carriers for targeted drug therapy

Davita L. Watkins, watkindl@gmail.com. Chemistry and Biochemistry, University of Mississippi, University, Mississippi, United States

Linear-dendritic block copolymers (LDBC) combine the advantageous properties of both linear and dendritic polymers to afford nanomaterials with superior mechanical properties. However, the practical application of these materials for clinical use are marginal due to limitation in specificity, size, and molecular constructs. Herein, we report the synthesis and characterization of heterobifunctional linear-dendritic block copolymers (LDBC) comprised of a hydrophilic polyamidoamine (PAMAM) dendron covalently linked to a hydrophobic polyester. Heterobifunctional groups were incorporated at the hydrophilic block to investigate the interfacial behavior of the nanoparticle surface. These additional structural modifications are important as they provide several biological advantages such as resistance against plasma proteins and efficient cell penetrating ability. The synthesis of well-defined PAMAM-polyester LDBC was confirmed via spectroscopic and chromatographic analysis. Microscopy and light scattering techniques afford evidence of nanoparticle formation. Results of the study confirm materials applicable for targeted drug delivery.

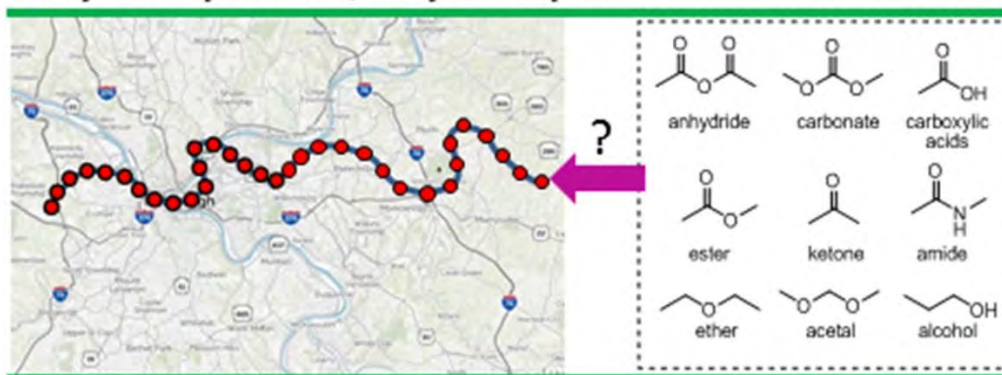


POLY 224: Tailoring the hydrophobic/hydrophilic balance of functional materials

Robert T. Mathers, rtm11@psu.edu. Chemistry, Pennsylvania State University, New Kensington, Pennsylvania, United States

Functional polymers often require a particular hydrophilic/hydrophobic balance to achieve desired physical properties and performance. This presentation will discuss our recent efforts and collaborations to explore new avenues to predict hydrophobicity of linear, branched, and crosslinked polymers. Using computational partition coefficients (LogP) of oligomeric models, this systematic method guides synthetic efforts and determines the influence of functional groups on hydrophobicity. Experimental validation with solvatochromatic experiments, swelling studies, contact angles, and HPLC retention times underlies the predictive nature of computational LogP values. Recent applications includes tailoring thermoresponsive behavior, designing diblock copolymers for crystallization driven self-assembly (CDSA), and functionalizing polyesters with B Vitamins.

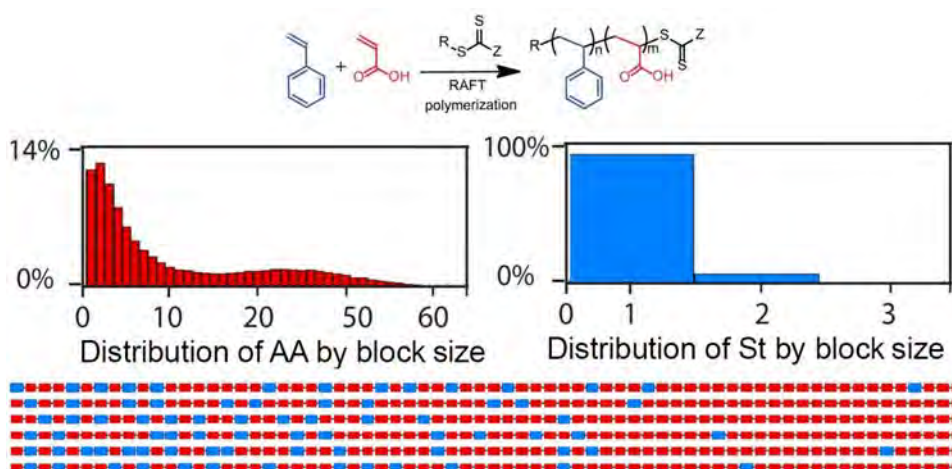
Roadmap for Tailoring Hydrophilic/Hydrophobic Balance



POLY 225: Practical prediction of monomer composition and drift in controlled radical polymerizations

Anton A. Smith¹, aaas@berkeley.edu, Vincent Wu², Aaron Hal², Ting Xu². (1) Stanford University, San Francisco, California, United States (2) Material Sci Eng, UC Berkeley, Berkeley, California, United States

Polymer chemists still look to proteins with envy. The unparalleled control of monomer distribution and dispersity of proteins is well beyond the reach of modern polymer chemistry. However, simple measures of control is possible, as the theoretical understanding needed to exert control of gradient to gradient-block copolymers is well developed, though experimentally it is rarely utilized, likely due to the complexity of design and analysis involved. While comprehensive software packages for predicting polymerizations have been developed, their complexity renders them difficult to approach when doing exploratory experimental work. Compositional drift in batch polymerizations due different reactivity of monomers is a well-known phenomenon. This drift can lead to the formation of a gradient in composition when the polymers are synthesized using controlled polymerization methodologies, such as RAFT. By knowing the apparent reactivity ratios of the polymerization, the drift can be controlled by adjusting polymerization conditions to create gradient copolymers towards a desired design. The same methodology can also be applied to predict composition in non-drifting polymerizations. Despite the low complexity of doing so, neither are seldom done, likely due to the perceived difficulty. We seek to remedy this through 'Compositional Drift'; an easy-to-use program enabling the prediction of drift in polymer composition based on the use of the Mayo-Lewis model and Monte-Carlo methodology. This tool has guided experimental design and allowed an understanding of polymer compositions in complicated heteropolymers. We wish to supply this tool to the community, showcasing two recent examples of use in the literature.^{1,2}

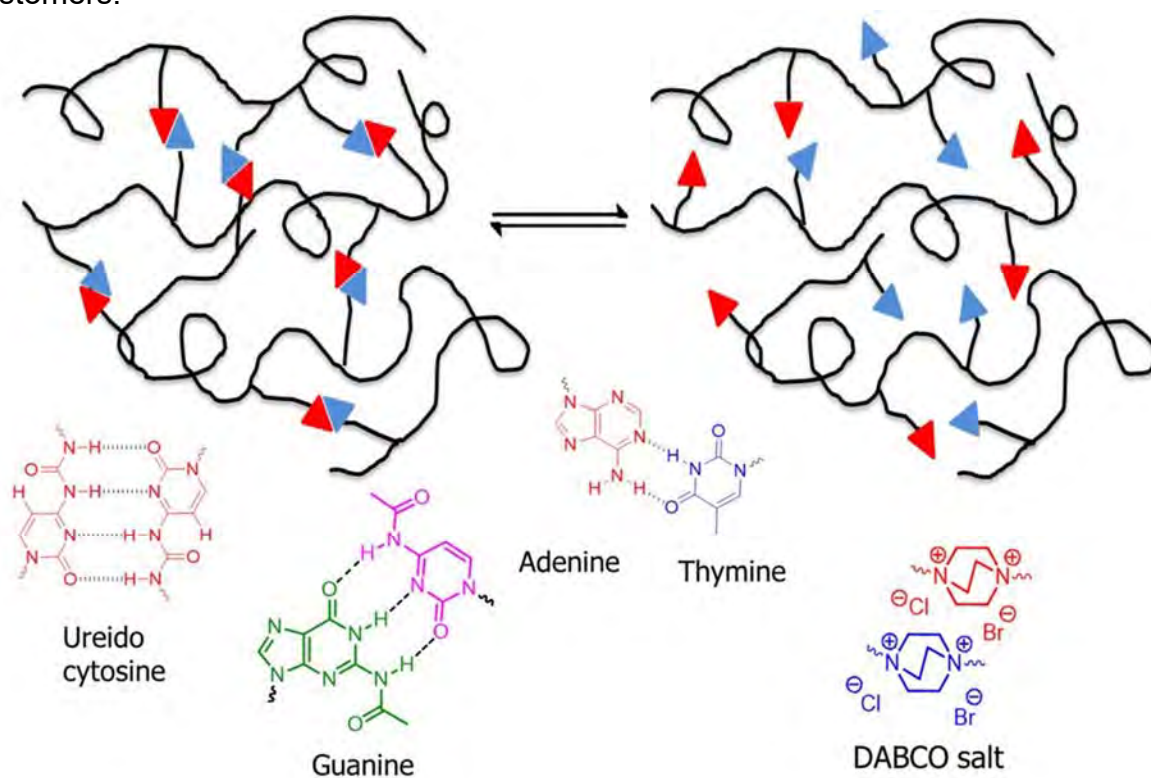


Simulated distributions of styrene (St) and acrylic acid (AA) in idealized polymer chains made by RAFT. Bottom: examples of polymer compositions, with each individual row representing one polymer.

POLY 226: Designing acrylic ABA triblock copolymers with multiple hydrogen bonding or multiple ionic bonding

Xi Chen², Keren Zhang², Kevin Drummey¹, **Timothy E. Long**¹, telong@vt.edu. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

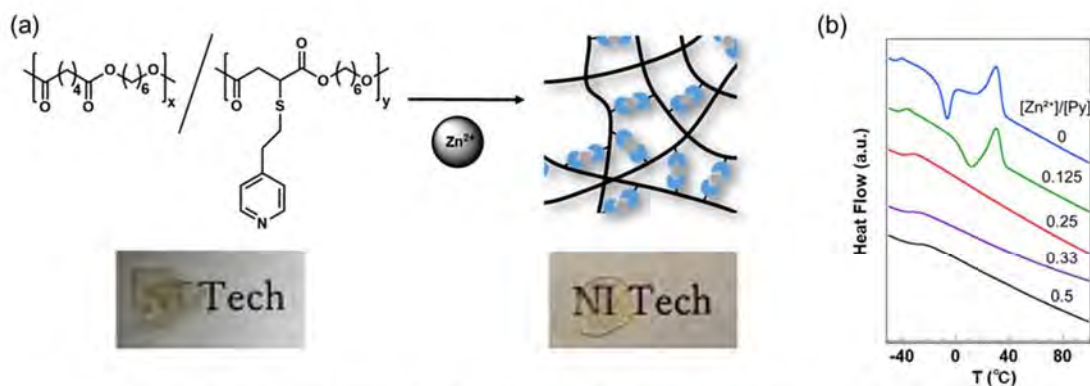
The dynamic characteristics of hydrogen and ionic bonding contributes to the reversible properties of acrylic polymers, opening new avenues for designing materials with flexibility and processability. Incorporation of multiple hydrogen bonding or ionic bonding provides acrylic polymers with enhanced structural and mechanical integrity. Inspired by complementary hydrogen bonding interactions between nucleobase pairs in DNA, a series of bioinspired nucleobase-acrylic monomers such as adenine acrylate (AdA), thymine acrylate (ThA), cytosine acrylate (CyA), ureido-cytosine acrylate (UCyA) were designed, whose synthesis were afforded by aza-Michael addition. Additionally, a facile 2-step synthesis provided doubly-charged styrenic-DABCO Br-Cl monomers. Reversible addition-fragmentation chain transfer (RAFT) polymerization enabled the preparation of multiple nucleobase- or ion-containing acrylic triblock copolymers with varied compositions, controlled molecular weight, and low polydispersity. Thermal and mechanical analysis demonstrated superior properties attributed to the presence of efficient physical crosslinking of dynamic bonds. Moreover, the soft acrylic backbone increased chain mobility and facilitated self-assembly, promoting microphase-separated morphological behavior. The hydrogen and ionic bonding-containing polymers offer great promise for many applications as pressure sensitive adhesives and thermoplastic elastomers.



POLY 228: Crystallization and thermal property control of metallo-supramolecular polyesters prepared via multiple coordination bonds

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So far, there have been many reports of metallo-supramolecular polyesters containing coordination ligands at the chain ends, where the metal-ligand coordination bonds are formed only between the end-groups. For further development of functional polyesters, we here prepared metallo-supramolecular polyesters containing multiple coordination ligands along the chain. We first synthesized polyesters containing thiol-groups along the chain via polycondensation, using 1,6-hexanediol, adipic acid and thiomalic acid as monomers ($M_n=3.2 \times 10^4$, the average number of thiol-groups per chains was approximately 35). Coordination ligands, that is, pyridine units (Py), were introduced via Michael-Addition reaction between thiol-groups and 4-vinylpyridine. Obtained polyesters were dissolved into a pyridine-water (9:1) mixed solvent. We also prepared another solution of zinc chloride ($ZnCl_2$) with the same solvent. By blending these two solutions and subsequently evaporating the solvents slowly, we prepared metallo-supramolecular polyester bulk films. We prepared various blends with varying the mole ratio of $ZnCl_2$ to Py, $[Zn^{2+}/Py]$, to figure out effects of the numbers of Py on the thermal properties and crystallizability. From the result of FT-IR, we confirmed coordination bonds were formed and the fraction of coordinated Py were increased by increasing $[Zn^{2+}/Py]$. The DSC measurement showed a systematic increase of glass transition temperature with $[Zn^{2+}/Py]$ increasing. Furthermore, interestingly, the crystallization / melting peaks in the thermogram disappeared as more than a certain amount of $ZnCl_2$ ($[Zn^{2+}]/[Py]>0.25$) was added. The result of SAXS showed the disappearance of crystalline domains, which well agrees with the result of DSC measurement. Macroscopically, we confirmed the samples forming coordination bonds were highly transparent while the neat polyester before adding $ZnCl_2$ was opaque. Those phenomena were probably based on the mechanism that the homogeneously dispersed $ZnCl_2$ through coordination bonds prevented the chain arrangement required for crystallization.



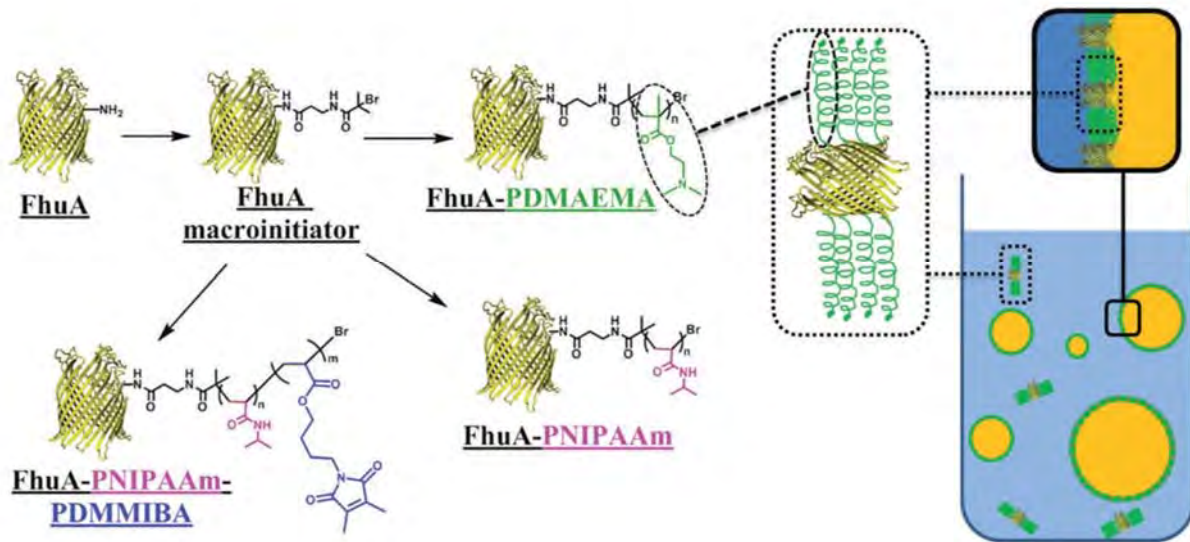
- (a) Chemical structure of synthesized polyester and probable network structure with dispersed $ZnCl_2$. Images of obtained samples before and after addition of $ZnCl_2$ are also shown.
- (b) DSC 2nd heating curve with varying $[Zn^{2+}]/[Py]$.

POLY 229: Incorporation of biological functions into polymer materials: The use of protein-polymer-conjugates

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This work aims at imparting biological functions into polymeric materials. We introduce a new strategy using engineered natural protein channels decorated with polymer chains followed by self-assembly at various interfaces to form ultrathin, permeable and highly selective membranes.

This approach diversifies membrane technology since various sizes and shapes of proteins can be used in addition to different responsive polymers generating a platform for “smart” self-assembled membranes, which can also be extended to immobilize enzymes in thin polymer films yielding active membranes for effective bioreactor design.



Synthesis and self-assembly of protein-polymer conjugates to form nanoporous capsules and membranes

POLY 230: Tailored mucoadhesive emulsions for the delivery of therapeutic agents

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A series of novel branched polymeric surfactant architectures incorporating hydrophobic and hydrophilic chain ends have been synthesised by atom transfer radical polymerisation (ATRP). A range of stable emulsions have been generated to study the role and ratio of hydrophobic/hydrophilic chain ends, leading to the discovery that up to 90 mol% of chain ends can be removed while maintaining emulsion stability and comparative droplet size. As such, functionality may be added to the branched copolymer emulsifiers and the resulting emulsions. Thiolated polymers, thiomers, have long been shown to have mucoadhesive properties, forming strong disulphide linkages between the thiol-functional polymers and mucus glycoproteins. Herein, we present a novel oil-in-water emulsion stabilised by hyperbranched polymers that display tunable mucosal interactions. Tailoring of the highly stable emulsions to either the macro or nano scale may also be achieved by varying the emulsification technique.

Macroemulsions, despite being highly stable for many weeks, strongly interact with mucosal surfaces, giving a burst release of oil as shown in Figure 1. Nanoemulsions, conversely, adhere fully to mucosal surfaces, with potential to deliver oil-soluble payloads. Mucoadhesion was quantitated by a flow-through model passing nanoemulsions with varying thiol content over synthetic biosimilar mucus, showing greater adhesive properties as the thiol content was steadily increased. Ex vivo multiple particle tracking of fluorescently labelled nanoemulsions further corroborated the trend while tracking the movement of individual droplets through the mucosal layer, showing control of mucous-diffusion. In vitro testing included cytotoxicity and efficacy testing of nanoemulsions loaded with drugs typical for treating corneal diseases into nanoemulsions on mucus secreting Human Conjunctival Epithelium cells (HCjE-Gi).

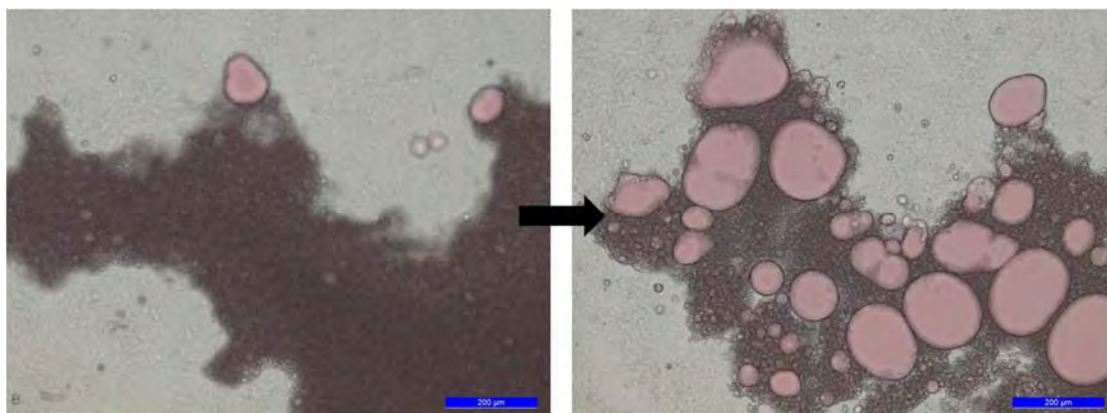
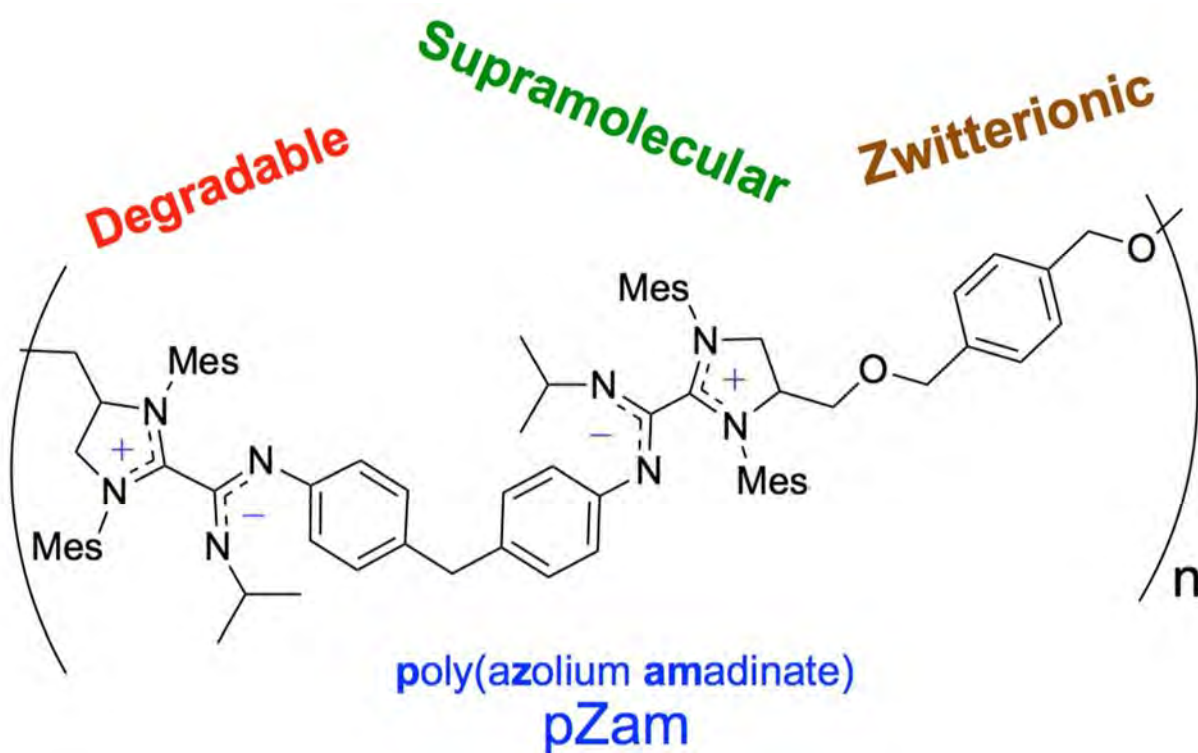


Figure 1 – Optical microscopy images, 10x magnification, of the breakdown of a stable oil-in-water macroemulsion containing a hydrophobic drug mimic when in contact with a mucosal surface.

POLY 231: Supramolecular polymers based on zwitterionic N-heterocyclic carbene carbodiimide (NHC-CDI) linkages

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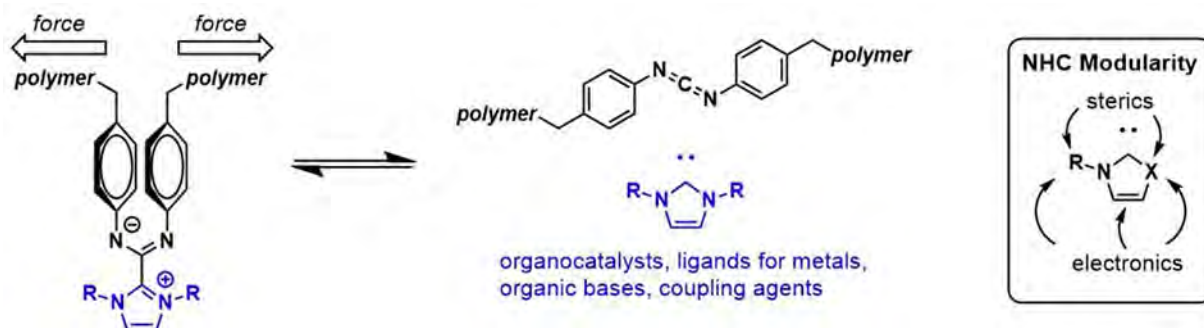
Polyzwitterions attract broad interest across a range of fields due to their favorable biocompatible, antifouling, and ion-conductive properties. Such polymers are usually synthesized from the polymerization of alkenes with pendant zwitterions, leading to polymers which are not easily degradable and have a limited degree of property control. In this talk, the design and synthesis of supramolecular main-chain polyzwitterions will be discussed using *N*-heterocyclic carbene (NHC) chemistry. These materials offer a high degree of tunability over the resulting polymer water solubility, (thermo)dynamics, end-group functionality, and degradability.



POLY 232: Flex activated mechanocatalysts based upon N-heterocyclic carbene adducts

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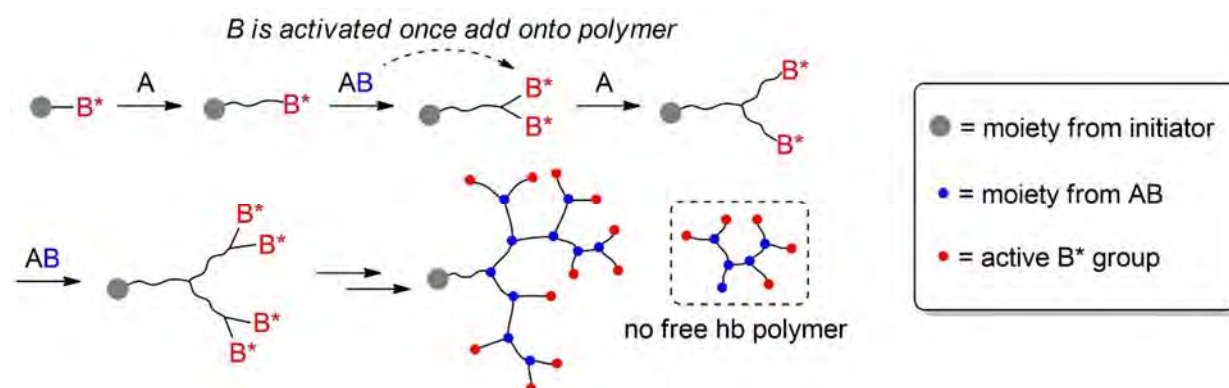
We have investigated a series of mechanophores based upon adducts of N-heterocyclic carbenes (NHCs) and carbodiimides. Polycarbodiimides were first prepared and then reacted with NHCs in solution. The solid polymeric materials were found to release NHCs in active forms upon application of mechanical load. Our investigations aim to correlate mechanophore activation with NHC structure, identify useful downstream applications of the mechano-activated NHCs, and identify fundamental guidelines for the use of these mechanophores in functional materials.



POLY 233: Chain-growth type (hyper)branched radical copolymerization: A promising approach to functional materials with controlled incorporation of branching motifs

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Dendrimers and hyperbranched polymers (HPs) have demonstrated a wide array of potential applications, including cosmetics, drug delivery, and lubricants. A variety of synthetic methods have been developed to realize dendrimers and HPs as well as their hybrid derivatives. In contrast to dendron-type polymers that require multi-step syntheses, HPs are more synthetically accessible as they can be prepared through single-step strategies. Development of a site-specific initiation is yet needed to enable efficient and precise incorporation of HPs for the synthesis of hybrid materials. Yamago and coworkers recently reported a chain-growth type HPs synthesis. A vinyl telluride monomer of a hierarchical reactivity was copolymerized with methyl acrylate under organotellurium-mediated living radical polymerization (TERP) condition, resulting in HPs with controlled degree of polymerization and branching.[i] Inspired by this work, we hypothesize that similar concept could be translated to atom transfer radical polymerization (ATRP) and HPs containing diverse functional side-groups can be grafted from target sites in a controlled manner. As shown in scheme 1, we copolymerized *α*-bromo vinyl containing monomer (AB) with other common monomers (A), e.g., acrylate and styrene, under copper-catalyzed ATRP conditions. HPs grown exclusively from ATRP initiator (B^*) were realized. The carbon-bromo bond of AB cannot be activated by copper catalyst until the vinyl group is polymerized in to a polymer chain, and a branching point in the polymer chain is thus generated upon the incorporation of an AB monomer. By tuning the feeding ratio of AB and A, HPs with different branching density were obtained.

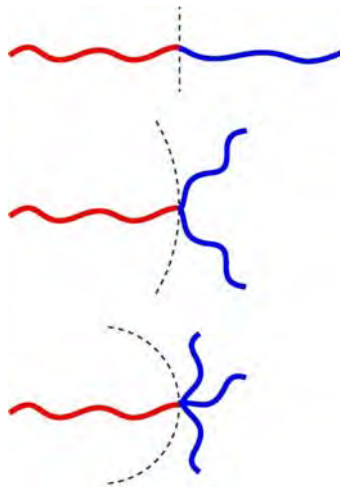


Scheme 1. Polymerization mechanism.

POLY 234: Miktoarm architectural effects in block polymer self-assembly

Christopher Bates, cbates@ucsb.edu. *Materials and Chemical Engineering Departments, University of California, Santa Barbara, Santa Barbara, California, United States*

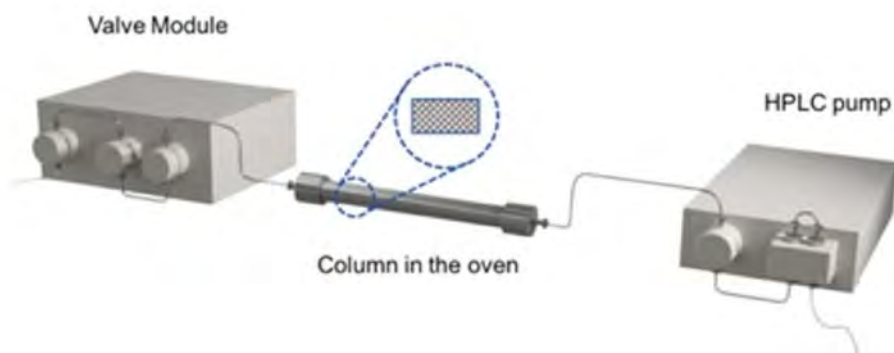
Miktoarm star polymers provide potential performance advantages in a variety of applications including viscosity modifiers and thermoplastic elastomers. The asymmetry in arm connectivity inherent to this polymer architecture introduces significant synthetic challenges that render exhaustive exploration of material design and phase space difficult. Here, we report experimental efforts to circumvent these obstacles by describing new synthetic concepts to access miktoarm star block polymers. These studies are complemented by self-consistent field theory to rationalize self-assembly behavior.



POLY 235: Linear and linear-hyperbranched block copolymers by continuous flow chemistry polymerizations

Rigoberto C. Advincula, *rca41@case.edu*. *Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States*

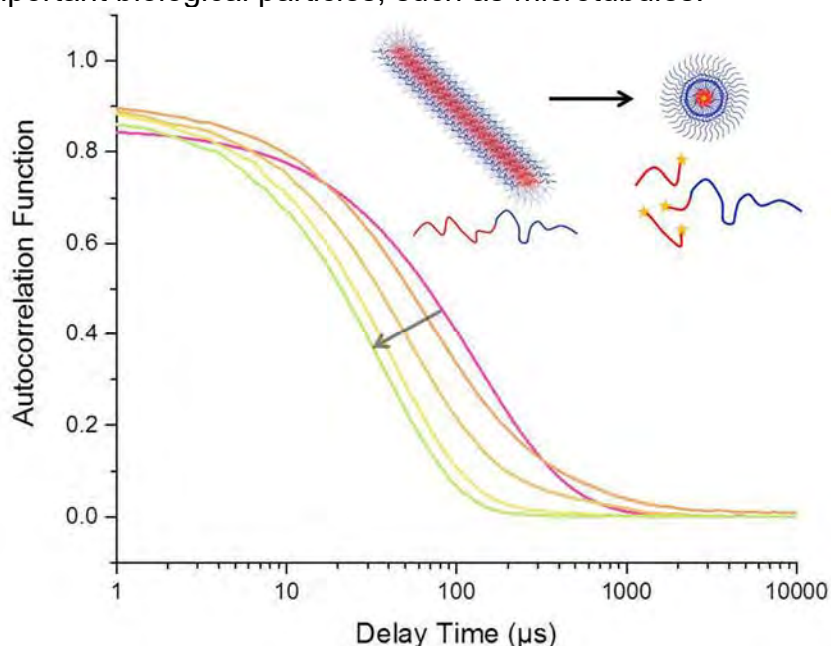
The advent of controlled process chemistry by using flow parameters and micro-confinement or micromixing has enabled far more efficient and high yielding reactions especially in organic synthesis and the development of new pharmaceuticals or drugs. However, not much has been reported on its application in block copolymerization and nanoscale materials synthesis. The continuous flow synthesis of polymers allows for the in-situ and real-time production of materials necessary for the production of plastics, hydrogels, surfactants, proteins, etc. Nanomaterials that include metal, metal oxide, carbon, and silica are important for utilization in catalysis, dyes, sensors, drug delivery, etc. In this talk, we will show the possibilities for block copolymer polymerization and hyperbranched polymer synthesis under continuous flow chemistry conditions and their possible using in nanostructuring and nanomaterials synthesis including grafted particles. This can be done by producing better pressure, volume, and temperature control often reaching supercritical or optimized flow conditions. For example, better polydispersity, molecular weight, block copolymer and branching efficiencies have been reported in flow chemistry. We will also report our recent results in living free radical polymerization and microparticle modification methods.



POLY 236: Rapid morphological transitions in poly(butadiene-*b*-ethylene oxide) aggregates induced by olefin metathesis

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Olefin metathesis represents a powerful class of reactions for the controlled synthesis, degradation, and functionalization of a variety of monomeric and polymeric substrates. In particular, polybutadienes comprised of predominantly 1,4 isomers experience chain cleavage and ring-closure upon exposure to Grubbs' catalysts, leading to a reduction in a molecular weight. We demonstrate that this phenomenon can be exploited to induce rapid morphological transitions in aqueous, self-assembled aggregates of poly(butadiene-*b*-ethylene oxide) (PB-PEO). When pre-formed PB-PEO aggregates are exposed to Grubbs' catalyst, the catalyst is sequestered within the hydrophobic PB cores. As metathesis subsequently occurs, the associated reduction in PB molecular weight increases the preferred interfacial curvature of the aggregate. Small angle x-ray scattering, dynamic light scattering, optical microscopy, and transmission electron microscopy show that the aggregate morphology transforms from vesicles or wormlike micelles to spherical micelles within minutes. The ultimate morphology and its characteristic length scales are highly controllable *via* the ratio of catalyst to polymer. In addition, the degraded PB chain ends within the aggregated cores are functionalized with a Ru ligand, enabling further metathesis reactions (*e.g.*, polymerization of a new species) to be initiated. In this manner, we believe that olefin metathesis can be exploited as a new strategy by which to synthetically mimic unique, dynamic behaviors exhibited by important biological particles, such as microtubules.



POLY 237: Responsive triblock copolymer particles with tuneable size and shape

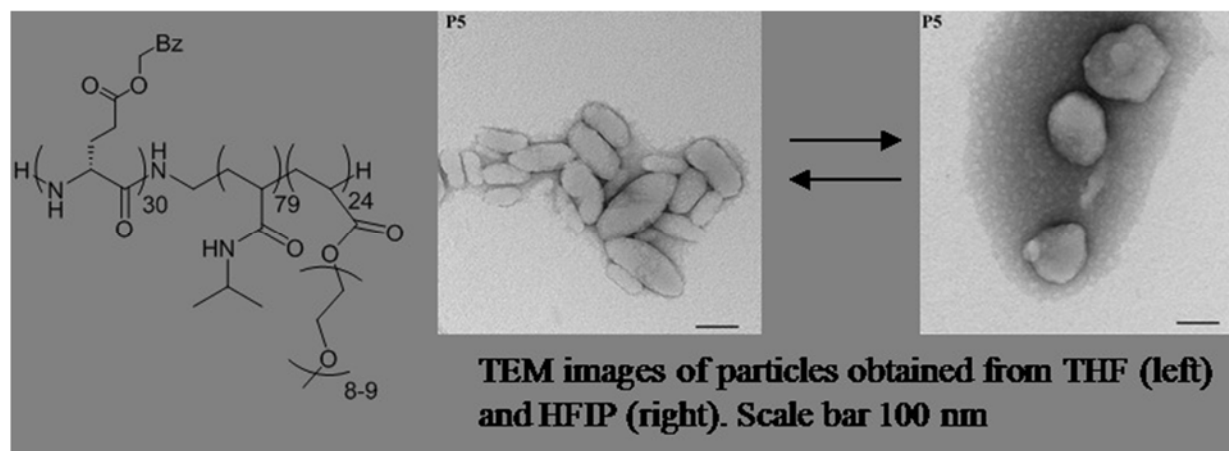
Elena Bobbi¹, elenabobbi@rcsi.com, Sally-Ann Cryan³, Andreas Heise^{2,1}. (1) Pharmaceutical and Medicinal Chemistry, Royal College of Surgeons in Ireland, Dublin, Ireland (2) School of Chem Sciences, Dublin City University, Dublin, Ireland (3) School of Pharmacy, Royal College of Surgeons in Ireland, Dublin, Ireland

We have designed a set of triblock copolymers containing hydrophilic poly(poly(ethylene glycol) methyl ether acrylate) (PPEGA) and hydrophobic poly(benzyl-L-glutamate) (PBLG) separated by a temperature-responsive PNIPAM middle block. Triblock copolymers were synthesized combining RAFT and NCA-ROP polymerizations systematically varying the length of the PPEGA and PBLG blocks to obtain a series of copolymers with different hydrophilic/hydrophobic ratios.

Following a solvent exchange procedure all the polymers formed particles in water. DLS analysis confirmed that the thermoresponsive behaviour depended on the triblock copolymer composition. Triblock copolymers with short and long PPEGA blocks behaved as hypothesized, i.e. they became smaller with increasing temperature due to the shrinkage of the NIPAM block. On the contrary, the ones with the intermediate PPEGA block increased in size probably due to changing hydrogen bonding interactions between NIPAM and PPEGA with temperature.

TEM analysis confirmed a non-spherical shape of all particles in the dry state, which is caused by the alignment of the α -helix secondary structures of the central hydrophobic PBLG block as confirmed by CD and FTIR. Advanced Field Flow Fractionation experiments further confirmed that the non-spherical morphology is indeed present in solution. Moreover, when a helix breaking solvent such as HFIP was used in the particles formation process TEM images revealed that their shape switches to spherical because of the destabilisation of the helix-helix hydrogen bonds.

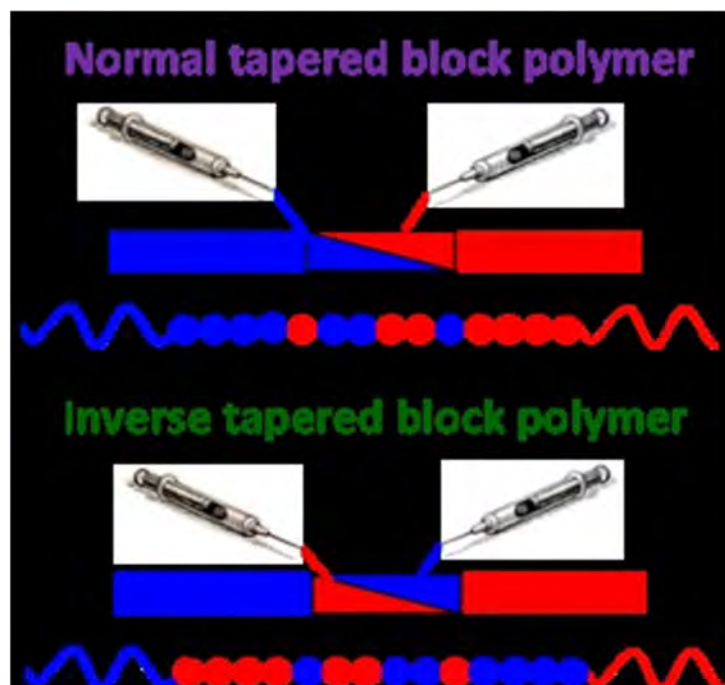
In conclusion, we have synthesized and characterized a triblock copolymer system which can form spherical or rod-like particles in water and can either shrink or swell following an increase in temperature depending on the triblock copolymer composition and formulation conditions.



POLY 238: Tapered block polymers: Manipulating monomer segment distributions to tune self-assembly and macromolecular properties

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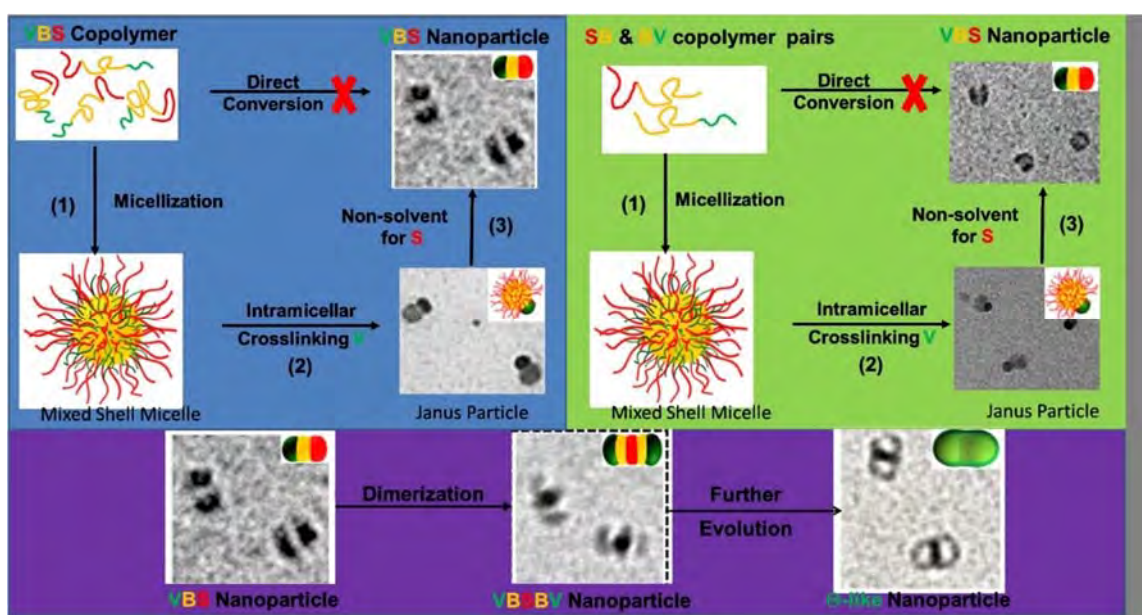
The self-assembly of block polymers (BPs) presents unique opportunities to design materials with attractive chemical and mechanical properties based on the ability of BPs to form periodic structures with nanoscale domain spacings. One area of recent progress in our group focuses on the behavior of tapered BPs (Figure 1) in which the segment distribution at the interface between blocks is synthetically varied to tune morphology, domain density profiles, thermal transitions as well as mechanical and transport properties. Two application targets for these materials are lithium-ion conducting membranes for batteries and nanostructured thin films for nanotemplates and barrier membranes. In the first target area, we found that the taper volume fraction and composition allow us to manipulate the self-assembly of salt-doped BPs in a well-defined manner that permits optimization of morphology and ion-content. Additionally, we found that the tapered interfaces influence the glass-transition behavior of the ion-conducting block leading to significant changes in lithium-ion transport (ion conductivity). In the second target area, we found the taper content alters the rate of self-assembly as well as the rate of island/hole formation (and ultimate island/hole size) upon thermal annealing. Additionally, using reflectivity techniques, we probed the domain density profiles as a function of taper composition and linked these profiles to changes in domain spacing and glass transition temperature. Overall, these studies show the versatility of tapering to provide a unique handle for simultaneously optimizing multiple materials properties.



POLY 239: Structural evolution from AB/ABC block copolymers to AB/ABC-segmented particles

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Current and prospective developments in nanoscience and nanotechnology require nanostructures with not only high complexity but also high regularity whose fabrication in turn pose great challenges. In those structures, the well-defined hierarchically nanostructured polymeric nanoparticles have attracted attention in the fields of polymer science, biomedical science, etc, and are believed as the better versatile platforms than simple structured micelles and vesicles. Therefore, the versatile and efficient fabrication method of complex and highly regular polymeric structure is highly demanded but very limited. Here, we propose a thermodynamically controlled pathway for preparing such well-defined polymeric particles with complex structures and also in a high yield. Starting from diblock copolymer pairs (A-*b*-B and partner C-*b*-B) as the precursor, A-*b*-B was first co-assembled in the solution with a partner diblock copolymer C-*b*-B to form the mixed shell micelles (MSMs) with B core and A/C mixed shell. Then, A block chain was intramolecularly covalent cross-linked, and resulted in the complete phase separation of A and C domain in the shell (Janus particle). As the results, the conversion efficiency is close to 100%. Such precise self-assembly pathway can be extended to the A-*b*-B-*b*-C triblock copolymer. An ABC-segmented particle with A, B, C domain linearly connected was obtained. The B domain is sandwiched between A and C domains. This conversion is also highly efficient and almost all the A-*b*-B-*b*-C triblock copolymer was converted to the ABC-segmented particle in solution. Furthermore, it can be further assembled to ABCBA five-segmented particle and θ -shaped particle with even higher complexity.



POLY 240: Janus graft block copolymers: Design of polymer architecture for independently tuned nanostructures and polymer properties

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A remaining challenge that limits the widespread application of block copolymers (BCPs) is a lack of independent control of the self-assembled nanostructure and bulk properties in a single polymer material, as both are dependent on the molecular structure of the BCP, described in part by the following parameters: degree of polymerization (M), Flory-Huggins parameter (χ), and volume fraction of the different polymer blocks (f). In this work, we demonstrate that Janus graft BCPs (GBCPs) synthesized via ring-opening metathesis polymerization of poly(lactic acid) and polydimethylsiloxane containing branched macromonomers offer such tunability, with the length of the side chains dictating the domain spacings achieved and the length of the backbone independently controlling the thermomechanical properties of the GBCP (Figure 1). Covalent preorganization of the block interface allows for stable self-assembled nanostructures with ultra-small domain sizes (down to 5.68 nm), and compared to linear BCPs, the self-assembly is less dependent on χ , broadening the scope of polymers that can be utilized for nanostructured polymeric materials. Ongoing work includes application of Janus GBCPs in electrospun nanofibers as a precursor for hierarchically porous carbon materials in which mesopore size is tuned by the GBCP side chain length and processability is controlled by the backbone length.

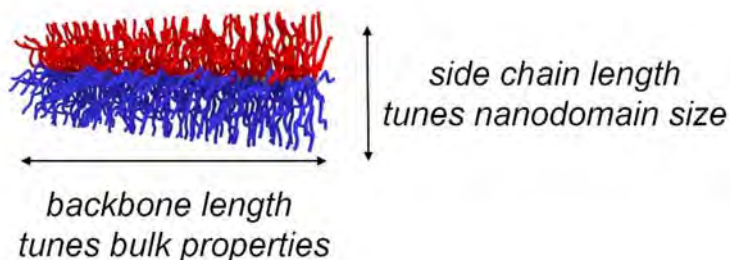
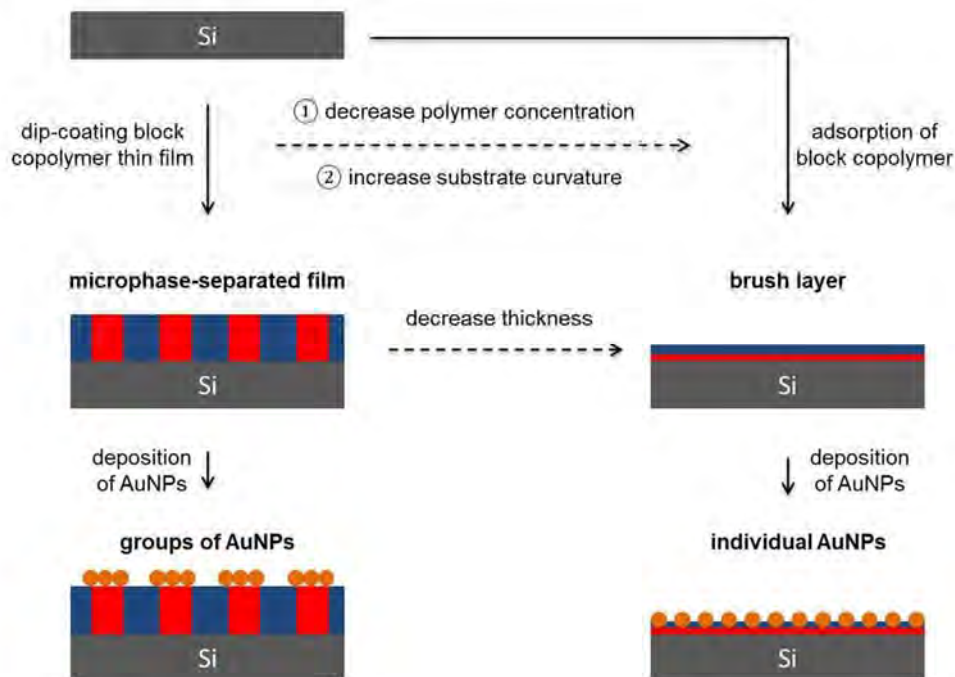


Figure 1. Architecture design of Janus GBCPs

POLY 241: Monolayer arrays of nanoparticles using block copolymer brush templates

Hu Zhu, hu.zhu@umontreal.ca, Jean-Francois Masson, C. Geraldine Bazuin. Dép. de chimie, Université de Montréal, Montréal, Quebec, Canada

Block copolymer (BCP) thin films self-assembled on surfaces are good templates for 2D patterning of metal and semiconductor nanoparticles. Previous research relied on relatively thick BCP films having microphase-separated nanostructures with distinctive surface patterns for guiding the deposition of phase-selective nanoparticles. We show that ultrathin BCP films formed from an adsorbed brush layer are also suitable templates for producing dense nanoparticle arrays. To achieve this, polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) thin films were dip-coated on silicon substrates and used to template 15-nm gold nanoparticles (AuNPs). The effect of polymer solution concentration on template thickness, surface morphology and AuNP pattern, determined by ellipsometry, AFM and SEM, respectively, was investigated. For high BCP solution concentrations, film formation is dominated by BCP deposition upon substrate withdrawal, leading to P4VP surface micelles (dots) in a PS matrix. For low BCP concentrations, it is dominated by adsorption of a featureless brush layer during substrate immersion in solution. Both film types yield dense AuNP deposition, but differing in surface pattern, the former producing AuNP clusters on the P4VP dots and the latter individual AuNPs. Dense individual AuNP deposition also occurs on 1- μm diameter fibers coated by a BCP brush layer after dip-coating in concentrated BCP solutions, where increasing curvature parallels the effect of decreasing solution concentration. This enables the development of surface-enhanced Raman scattering (SERS) optophysiology probes capable of detecting multiple targets.



POLY 242: Quantitatively accurate simulations for block copolymer melts

Mark Matsen, mwmatsen@uwaterloo.ca. *Chemical Engineering , University of Waterloo, Waterloo, Ontario, Canada*

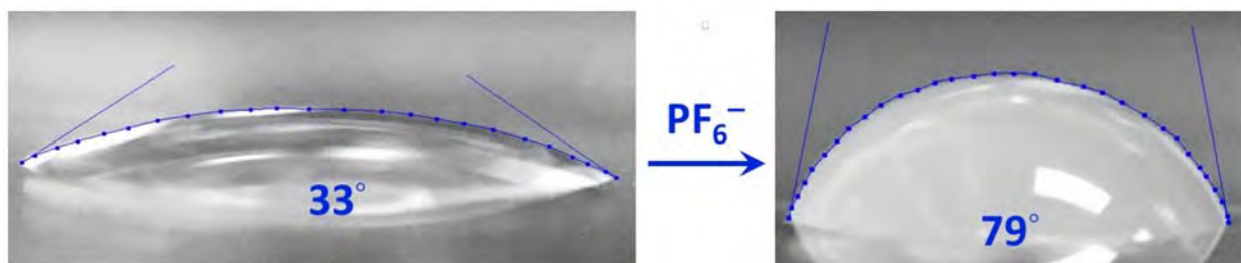
Ideally, we would like to have first-principles simulations capable of quantitatively accurate predictions for any block copolymer system. Usually, our choice of model involves balancing the complexity needed to faithfully represent an actual experimental system and the simplicity required to make the simulation tractable. Fortunately, block copolymer phase behavior is believed to become universal in the high molecular-weight limit, which foregoes the need for detailed models. We illustrate how this universality can be used to make accurate predictions for a diblock copolymer melt from simulations using a simple lattice model. Nevertheless, simulations of blends and/or complex architectures are still extremely challenging even with the simplest of models. We conclude by discussing how this last obstacle could be overcome with field-theoretic simulations.



POLY 243: PIL by condensation – Resins, dispersions, and stabilizers

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Condensation polymerization or step-growth polymerization has been a standard approach to creating ionenes and many different types of commercially important thermoplastic and thermosetting polymers. We extend these studies in polymerized ionic liquids (PIL) to show that molecular design can be used to mimic functional PIL produced previously by chain radical polymerization and controlled radical polymerization. We illustrate fabrication of bulk gels and coatings that undergo anion exchange and solvent induced stimuli-responsiveness, thermodynamically stable and self-dispersing particles extending to very small sizes (< 20 nm), and dispersing aids that transform the osmotic brush concept into a commercially viable formulation tool.

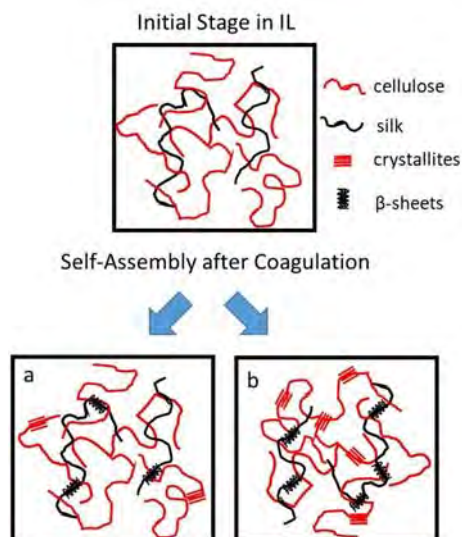


Contact angle stimuli-responsiveness induced by hexafluorophosphate exchange with bromide in coating of glycerol/PPO-diOH/1-HOC₁₁ClImBr/C₆H₁₂-diNCO self-dispersing PUD.

POLY 244: Morphological and thermal characterization of polysaccharides/protein biocomposites regenerated from ionic liquids

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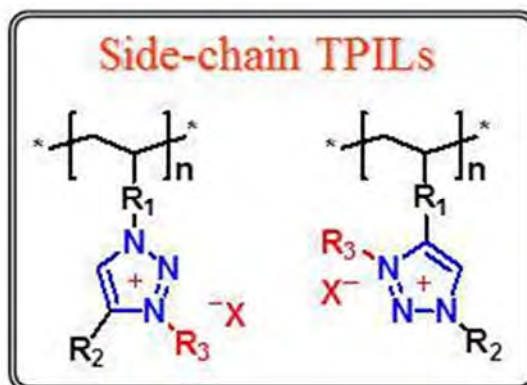
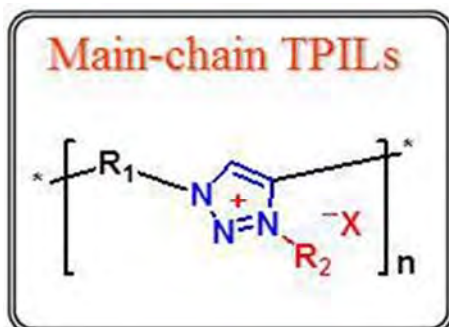
In biological systems, most structural materials are composites formed from a dispersed phase, typically biomacromolecules arranged in a hierarchically assemblage by molecular interactions. For example, in wood, cellulose is the dispersed phase, and interacts within a matrix composed of xylan and lignin. In another example, in the exoskeleton of arthropods, chitin is the dispersed phase within a matrix of silk-like proteins. Recent reports characterizing the fabrication of biomaterial composites (biocomposites) using natural materials such as silk and cellulose have identified changes in physicochemical properties as a function of fabrication method and material composition. However, the relationship between hierarchical and secondary structures during materials formation is important but still astonishingly unclear. In this study, the effect of ionic liquid and coagulation agent (water, alcohol or peroxide) are evaluated to understand the morphological and thermal properties in cellulose/silk biocomposites. Various techniques were implemented to investigate the biocomposite films, including FTIR, SEM, TGA, DSC, AFM, Confocal Microscopy, and X-ray scattering. Results show that the type of ionic liquid and coagulation agent has strong influence on the structure and thermal properties of the biocomposite. The type of ionic liquid can induce crystallization and as the alcohol content increases the formation of beta sheets increase while maintaining a constant alpha-helix formation. On the other hand, low concentrations of peroxide seem to show a decrease in the beta sheets while maintaining a similar level of alpha helices as seen in the alcohols. Topological and textural imaging in combination with X-ray scattering provide information to support our findings. The overall characterization results confirm that the level of interaction between both polymeric chains can be tuned by fabrication method.



POLY 246: Poly(1,2,3-triazolium ionic liquid)s: A new class of functional polymer electrolytes

Mona Obadia, Antoine Jourdain, Anatoli Serghei, **Eric Drockenmuller**,
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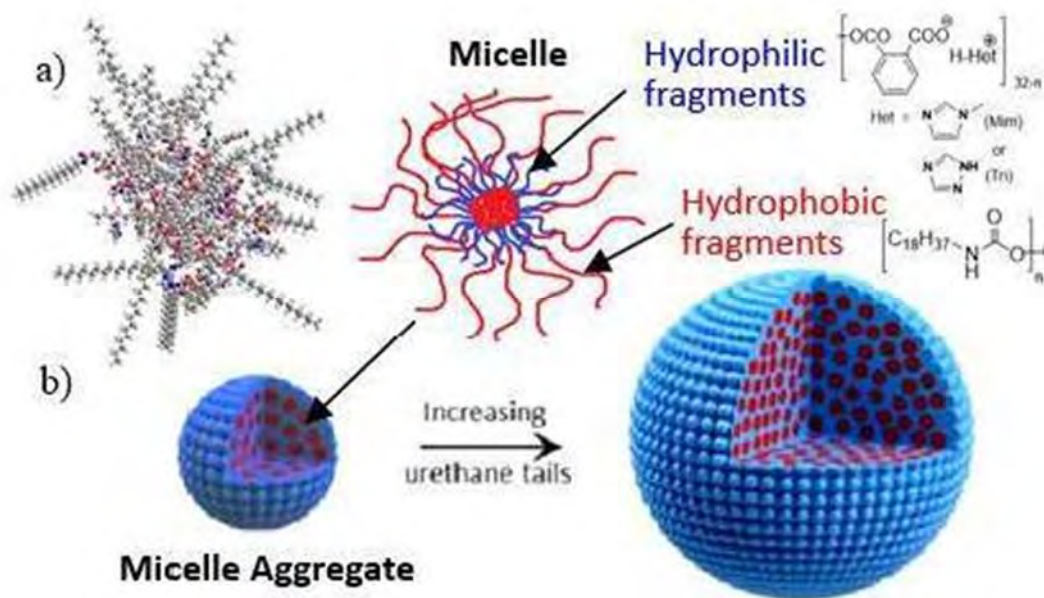
Poly(ionic liquid)s (PILs) combine the best features of ionic liquids (high ionic conductivity, thermal and chemical stabilities) with those of polymers (mechanical stability, processing and tunable macromolecular design). We have pioneered a new class of PILs having 1,2,3-triazolium cations within the repeat unit (TPILs). Their synthesis merges the robust and orthogonal nature of CuAAC, *N*-alkylation of 1,2,3-triazoles, and anion metathesis together with chain growth or step growth polymerizations as well as post-polymerization efficient chemical modifications. Sharp structure/properties relationship studies allowed reaching TPILs having high thermal, chemical and electrochemical stabilities as well as high ionic conductivity. The use of the 1,2,3-triazolium chemistry demonstrates the ability to tackle new synthetic challenges and broaden the structural variety of PILs.



POLY 247: Assemblies of linear and branched poly(ionic liquid)s

Vladimir V. Tsukruk, vladimir@mse.gatech.edu. Georgia Inst of Tech, Atlanta, Georgia, United States

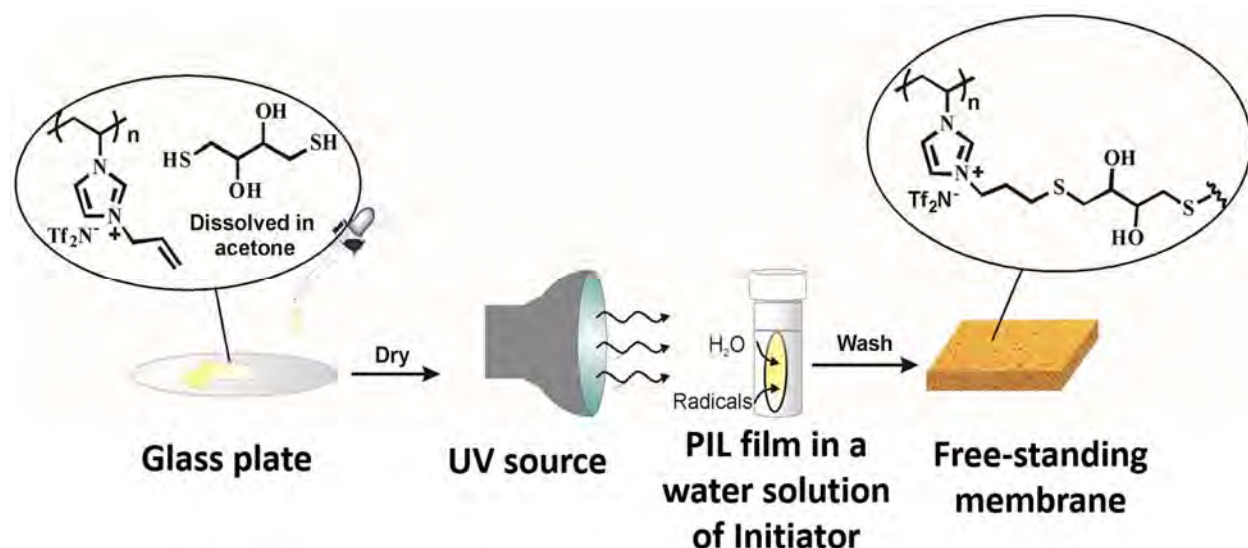
We review recent results from our research group on assembly of various polyionic compounds including traditional linear macromolecules, amphiphilic poly(ionic liquid)s, star and hyperbranched species as well thermally-responsive hyperbranched materials with end poly(N-isopropylacrylamide) (PNIPAM) blocks [1]. We study their assembling behavior in solution, within Langmuir monolayers, and within layer-by-layer multilayers at variable pH conditions, surface pressures, and temperature by combining *in situ* light scattering, atomic force microscopy, neutron reflectivity, and small-angle neutron scattering. We discuss the resulting molecular assemblies, mesoscale aggregation, organized micellar structures, and gradient interfacial morphologies, as driven by amphiphilic balance, ion pairing, ionized state of different fragments, limited aggregation, and LCST transition [2-4].



POLY 248: Stable covalently photo-cross-linked porous poly(ionic liquid) membrane with gradient pore size

Alessandro Dani³, Karoline Taeuber³, Weiyi Zhang², Helmut Schlaad⁴, **Jiayin Yuan¹**, jiyuan@clarkson.edu. (1) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden (2) Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam, New York, United States (3) Max Planck Institute of Colloids and Interfaces, Potsdam, Germany (4) Universitaet Potsdam, Potsdam, Germany

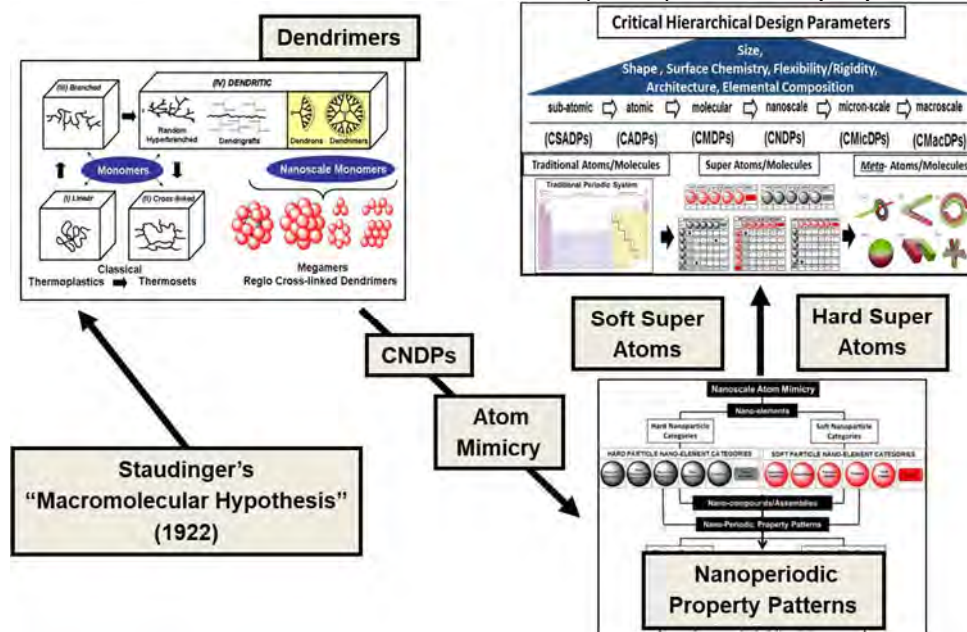
Here, we describe a direct way to obtain a porous polyelectrolyte membrane by covalent cross-linking of a single poly(ionic liquid) (PIL) polyelectrolyte, avoiding the use of inter-polyelectrolyte complexation. The covalent cross-links among the PIL chains were synthesized by a thiol-ene photo-induced reaction in a non-solvent to the PIL, resulting in phase separation that induces porosity in the as-formed membrane. Furthermore, this cross-linking method leads to a pore size gradient along the membrane cross section, producing a stable, asymmetric, covalently cross-linked PIL membrane in a single step procedure.



POLY 249: Engineering CNDPs of soft superatoms to produce new emerging properties such as terahertz radiation generators or non-traditional intrinsic fluorescence (NTIF)

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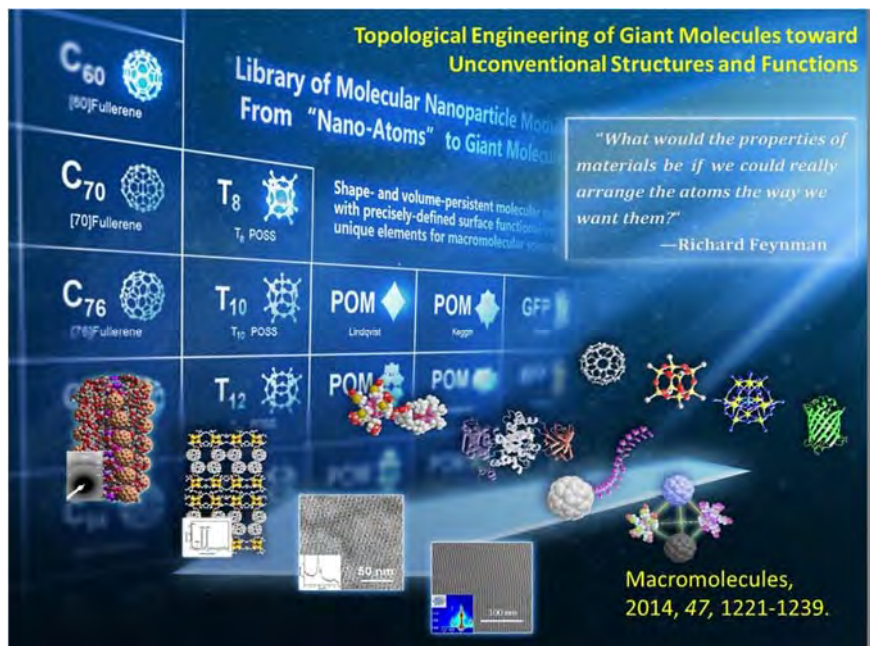
In 1922, Staudinger's *macromolecular hypothesis* demonstrated that large assemblies of covalently linked monomers produced a wide range of new emerging properties based on their new *sizes, shapes, surface chemistries, rigidity/flexibility and elemental compositions*. After Staudinger's introduction of linear polymers, a total of four major polymer architectures have now been recognized and unarguably *architecture* is equally valued for its dramatic influence on emerging new properties. These six parameters above are referred to as *critical nanoscale design parameters* (CNDPs) and are analogous to *critical atomic design parameters* (CADPs) that define atoms at the picoscale level.¹⁻² Based on extraordinary CNDP control, atom mimicry and nanoperic property patterns observed for *proteins, DNA/RNA, viral capsids, polymeric micelles and dendrimers*, these entities have been accepted by both chemists and physicists as quantized nanoscale building blocks and referred to as *soft superatoms*.¹ The most compelling evidence and validation of a prevailing systematic nanoperic concept based on hard/soft superatoms resides with predictive Mendeleev-like nanoperic tables reported by Percec, et al.¹⁻³ for amphiphilic dendrons/dendrimers, as well as recently published nanoperic tables for proteins.⁴ This lecture will overview the CNDP engineering of soft superatoms (i.e., dendrimers) to produce new emerging optoelectronic properties suitable for the generation of terahertz radiation. Furthermore, it will describe the CNDP manipulation of non-emissive *hetero-atomic sub-fluorophores* (HASFs) in soft superatoms such as dendrimers or proteins to produce new *non-traditional intrinsic fluorescence* (NTIF) emission properties.



POLY 250: Topological engineering of giant molecules toward unconventional structures and functions

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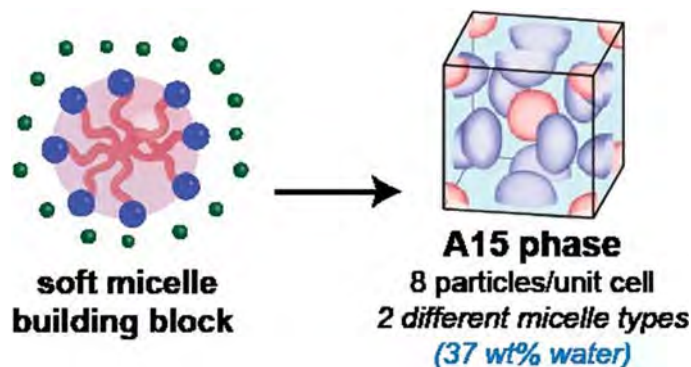
Inverse design and inverse thinking are critical steps in the materials genome approach. When we design materials with specific functional properties, we often start with independent building blocks which possess well-defined molecular functions and precise chemical structures. Using “Lego” type of modules, we can then assemble such elemental building blocks together in preferred secondary structures (or packing schemes) to construct materials possessing topologically mandated hierarchical structures with desired functions. In this talk, a unique approach along this design and thinking path will be presented. Various “giant molecules” based on “nano-atoms” are designed and synthesized. “Nano-atoms” refer to shape-persistent molecular nanoparticles (MNPs) such as fullerenes, polyhedral oligomeric silsesquioxanes, polyoxometalates, and folded globular proteins. These “nano-atoms” possess precisely-defined chemical structures, surface functionalities and molecular shapes, serving as elemental units for the precision synthesis of “giant molecules” by methods such as click chemistry and other efficient chemical transformations. These “giant molecules” include, but are not limited to, giant surfactants, giant shape amphiphiles, and giant polyhedra. These “giant molecules” can assemble into diverse higher order building blocks to further construct the thermodynamically stable and metastable hierarchical structures in the bulk, thin-film, and solution. Unconventional nanostructures can be obtained in various environments via sequence/topology mandated assemblies to exhibit specifically desired properties. This approach has provided a versatile platform for engineering nanostructures that are not only scientifically intriguing, but also technologically relevant.



POLY 251: Frustration-induced self-assembly of simple molecular amphiphiles into complex liquid crystalline Frank-Kasper phases

Mahesh K. Mahanthappa, maheshkm@umn.edu. Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, Minnesota, United States

Water drives the self-assembly of minimally hydrated amphiphiles into lyotropic liquid crystals (LLCs) with nanoperiodic aqueous and hydrophobic domains. Well-known LLC morphologies include lamellae, columnar phases, polycontinuous networks, and high symmetry sphere packings such as body-centered cubic (BCC), face-centered cubic (FCC), and hexagonally close-packed (HCP) structures. However, we recently discovered that ionic surfactant micelles can also spontaneously form low symmetry, tetrahedrally close-packed Frank-Kasper σ and A15 phases, and related Laves phases, that mirror the structures of well-known intermetallic compounds. These new, low symmetry phases arise from a frustrated supramolecular force balance that minimizes local variations in amphiphile solvation, while optimizing global micellar cohesion. The observed morphologies sensitively depend on both the surfactant headgroup and counterion chemistries. This work suggests that molecular engineering of frustration at competing length scales drives periodic pattern formation at length scales that far exceed those of their constituent molecular and supramolecular building blocks.

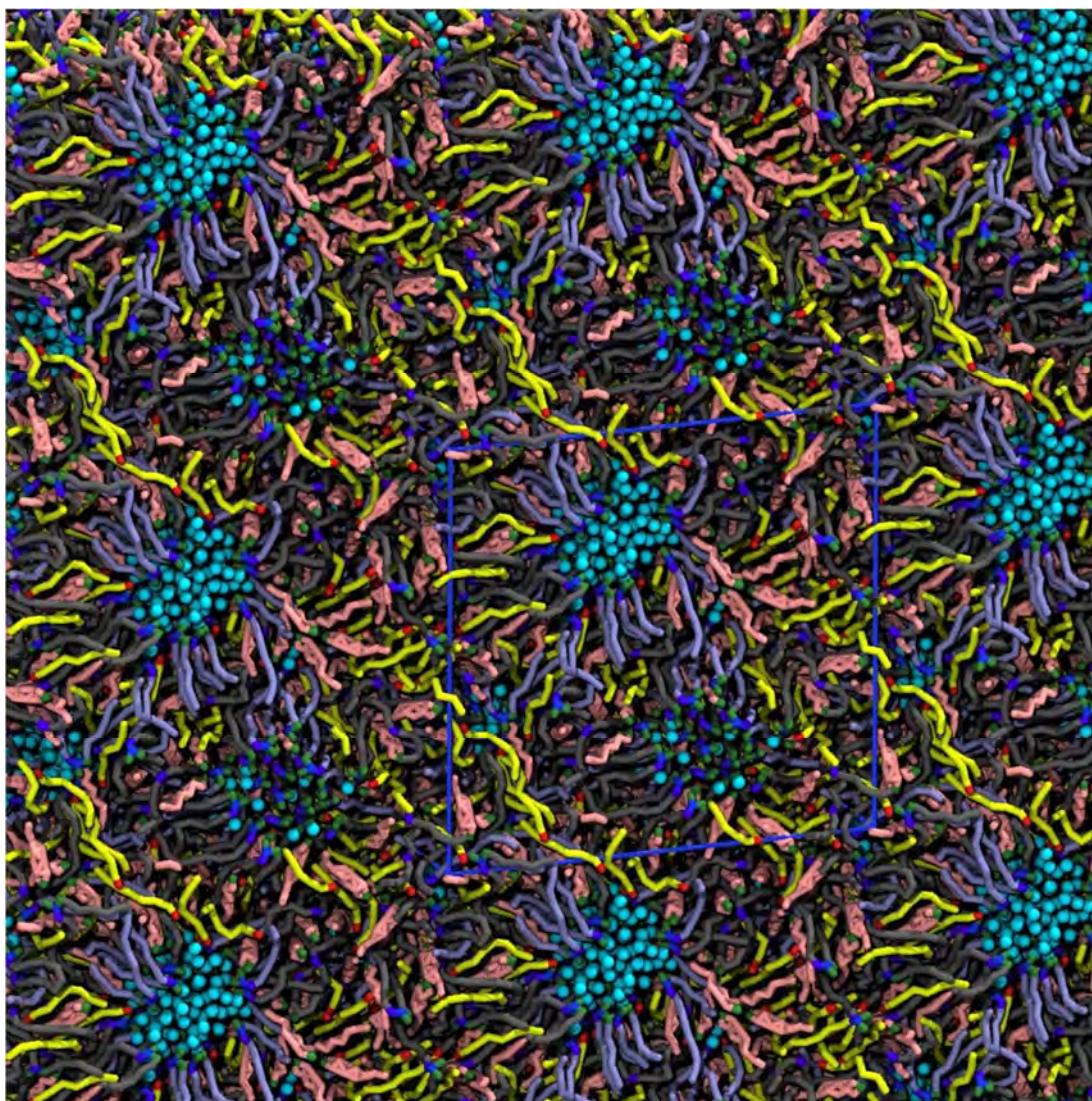


POLY 252: Crystals, liquid crystals, plastic crystals, & more...

Michael L. Klein, mklein@temple.edu. Inst Comp Molecular Science, Temple University, Philadelphia, Pennsylvania, United States

My talk will first review the states of matter accessible to condensed phase systems. Atomic solids typically exhibit three phases: long-range center-of-mass order (conventional solid), plus disordered liquid or glass phases. Molecular systems, on the other hand, have orientational degrees of freedom, which introduce additional possibilities, even for small molecules.

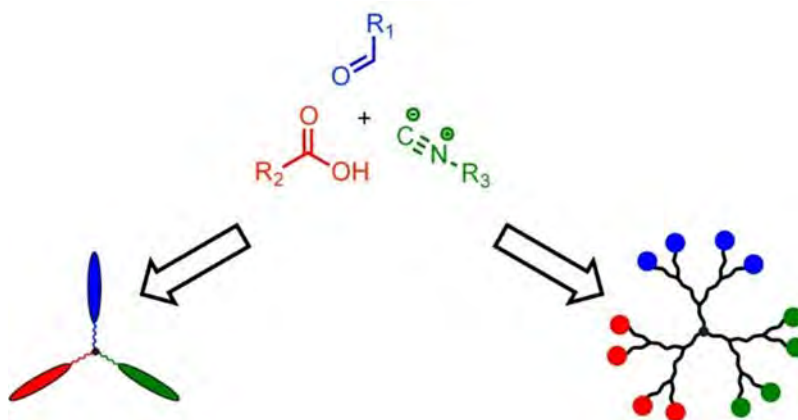
Molecules with internal degrees of freedom and/or flexibility, such as, surfactants, lipids, dendrimers, block copolymers, peptides, or even proteins, self-assemble into an array of distinct (Frank-Kasper) condensed phases. Using selective examples, the talk will survey some of the intriguing phases exhibited by Nature.



POLY 253: Precision synthesis of supramolecular materials using multicomponent reactions

Jonathan G. Rudick, *jon.rudick@stonybrook.edu*. Department of Chemistry, Stony Brook University, Stony Brook, New York, United States

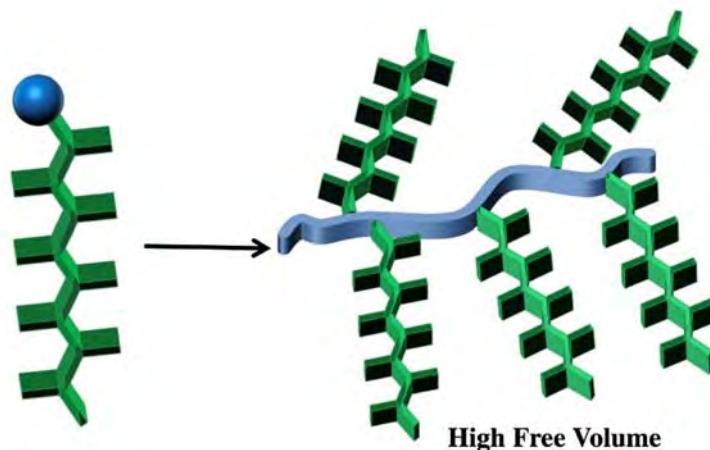
Sequence-defined multifunctional polymers provide control over structural features and functional properties in hierarchically organized materials. A wide range of robust chemistries have been adopted in iterative synthesis strategies to prepare sequence-defined and high molecular weight oligomers. Nonetheless, linear, iterative synthesis strategies are limited by diminishing yields as the sequences become larger and the eventual limits in the maximum length of a sequence. We have been exploring non-iterative synthesis strategies to complement linear, iterative synthesis for the assembly of structurally perfect multifunctional macromolecules. The presentation will focus on multicomponent reactions as well as their application to hierarchically organized liquid crystalline materials.



POLY 254: Bottom up design of materials: The utility of bicyclic ring structures

Timothy M. Swager, tswager@mit.edu. MIT, Cambridge, Massachusetts, United States

Organic chemists have long been fascinated with bicyclic ring systems and these structures were central in classical physical organic studies of carbocations and hyperconjugation. We introduced the concept of these ring structures having the ability to create polymers with intrinsic free volume for size selective gas/molecular permeability (JACS 1998, 120, 5321), low dielectric constants (JACS 2003, 125, 14113), liquid crystal alignment (Macromolecules 2007, 40, 19-25) and high strength interlocking structures (Macromolecules 2006, 39, 3350). The versatility of these materials to create functional materials continues and is widely practiced in gas separation. This presentation will summarize the general design principles and highlight our recent results in the creation of new materials for gas separation and ion exchange membranes. As will be demonstrated the bicyclic ring systems are extremely versatile and can be integrated into polymer sidechains as well as mainchains. Materials with record high ionic conductivities and gas permeability will be detailed.

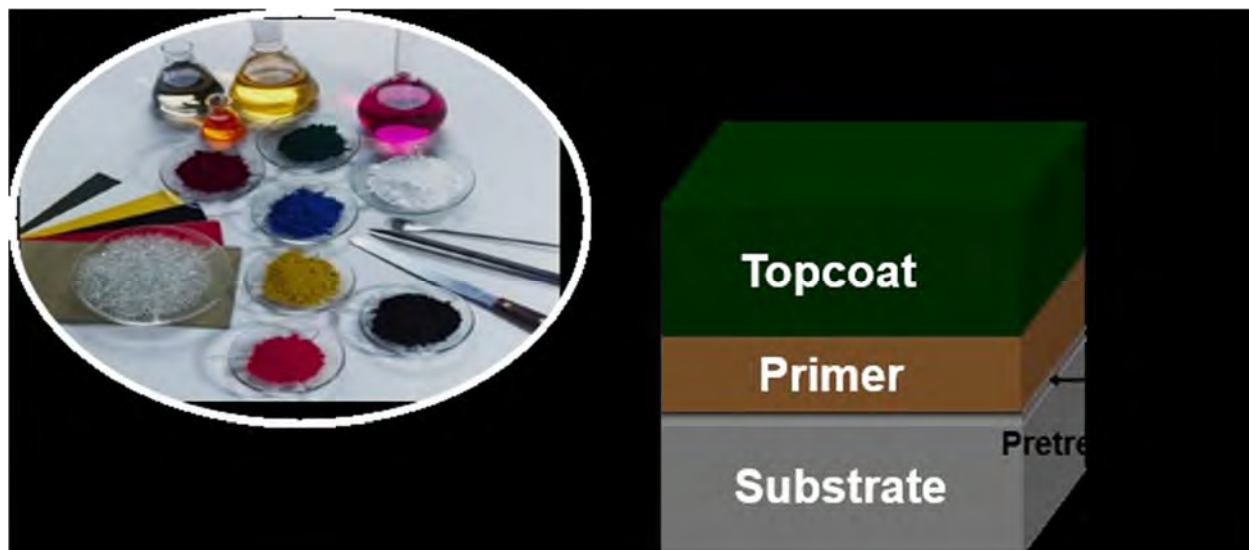


Macromonomers having pendant rigid side chains with [2.2.1] and [2.2.2] ring systems can be polymerized to produce materials with high intrinsic porosity with utility as gas separation materials.

POLY 255: Next generation coatings for DOD

John A. Escarsega, john.a.escarsega.civ@mail.mil. US Army Research Lab, Aberdeen Proving Ground, Maryland, United States

The US Army Research Laboratory (ARL) has the lead research and development responsibility for chemical agent resistant coatings (CARC) and manages the respective specifications that govern the topcoats, primers and key pretreatments for the CARC systems. In striving to optimize coating durability, embrace pollution prevention principles and to extend life cycles of vehicle and weapon platforms using CARC materials, ARL has evaluated numerous CARC systems in variety of exposures. This effort has implemented both accelerated outdoor exposures and laboratory weathering chambers to determine basic weathering properties for current and new urea and urethane technologies. This presentation will highlight the respective chemistries used, key formulation parameters and detail findings of the formulation evaluated. Additionally, ARL will also update the community with regard to its CARC program and its progress in supporting the DOD for next generation of coatings technology.

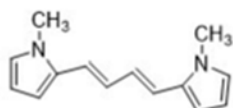


POLY 256: Smart corrosion-inhibiting coatings for department of navy applications

Peter Zarras¹, *peter.zarras@navy.mil*, John D. Stenger-Smith¹, Paul A. Goodman¹, Alfred Baca¹, Roxanne Quintana¹, Lee Cambrea¹, Lawrence Baldwin¹, Todd M. Dames¹, Alicia M. Hughes¹, Quynh-Vy Nguyen¹, Jacob Lechter¹, Andrew Chafin¹, Daniel T. Connor², James C. Amato³. (1) NAWCWD (Code 4F0000D), China Lake, California, United States (2) NAWCWD (Code 434000D), China Lake, California, United States (3) NAWCWD (Code 434100D), China Lake, California, United States

Conductive polymers (CPs) have been investigated for several decades as corrosion-inhibiting coatings. Our efforts have focused on using two novel bis-heterocyclic butadiene compounds with significant differences in their oxidation potentials. This difference can be exploited to prepare a “smart coating” capable of on-demand release of a monomer which can polymerize forming a conductive polymer film. This would be achieved without encapsulation of the active CP monomer. The synthesis of the (1E, 3E)-1,4-bis(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene, which is a novel compound, was prepared via a Wittig reaction. The compound obtained was a brilliant yellow powder in 51% yield. The synthesis of the (1E, 3E)-1,4-di(thiophene-2-yl)buta-1,3-diene monomer was obtained via a literature procedure. These two compounds will be incorporated into a smart corrosion-inhibiting coatings containing the poly [1,4-di(thiophene-2-yl)buta-1,3-diene] as the host and the (1E, 3E)-1,4-bis(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene monomer as the guest. The resulting polymer system will be fully characterized and its properties measured for potential applications as smart coatings on DON alloys, specifically 1008 steel.

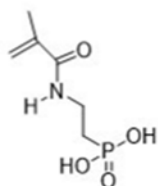
In addition, (2-methacrylamidoethyl)phosphonic acid has been polymerized via solution polymerization to very high molecular weight ($M_w \sim 1,400$ kDa). This polymer is soluble in DI water and has been spin coated onto HY80 steel coupons. This polymer is being tested as a flash rust inhibiting coating.



(1E,3E)-1,4-bis(1-methyl-1H-pyrrol-2-yl)buta-1,3-diene



(1E,3E)-1,4-di(thiophen-2-yl)buta-1,3-diene

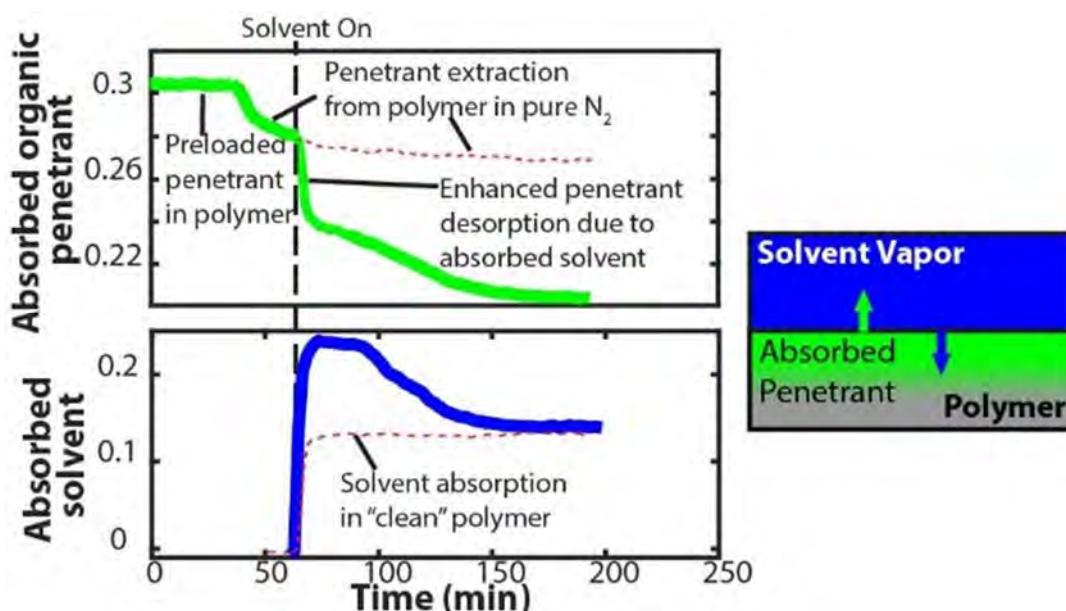


(2-methacrylamidoethyl)phosphonic acid

POLY 257: Multicomponent transport and extraction of chemical species in polyurethane

Devon Boyne^{4,1}, dboyne@udel.edu, Mark Varady¹, Robert H. Lambeth², Janlyn H. Eikenberg¹, Stefan Bringuier^{5,1}, Thomas P. Pear^{5,1}, Brent A. Mantooth³. (1) Edgewood Chemical Biological Center, APG, Maryland, United States (2) US Army Research Lab, Aberdeen Proving Ground, Maryland, United States (3) Attn: RDCB-DRP-D (Dr. Brent Mantooth), Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland, United States (4) Leidos, Reston, Virginia, United States (5) DCS Corporation, Abingdon, Maryland, United States

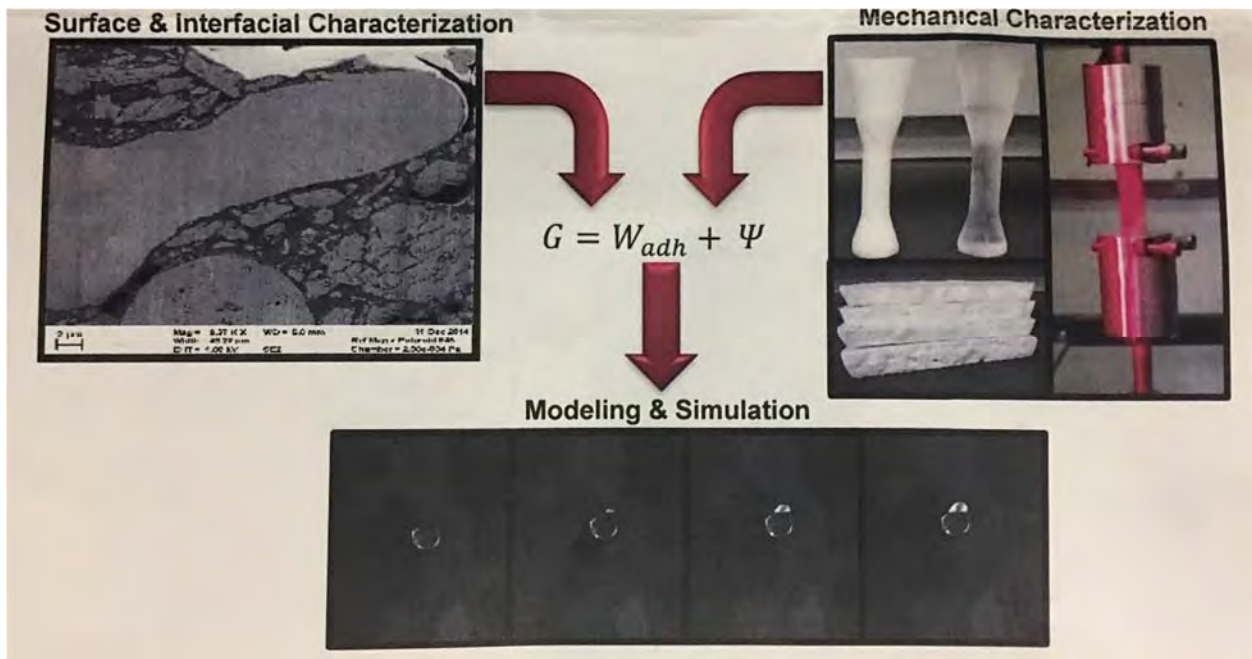
Polyurethanes (PU) are widely used in defense applications such as high performance coatings and other engineered materials due to their versatility and durability. In situations where chemical contamination is a concern, a fundamental understanding of the chemical interactions that result from chemical species absorption into PU plays a key role in the development and optimization of decontamination formulations as well as coatings materials for increased chemical resistance. In this contribution, we explore the chemical mechanisms responsible for the enhanced extraction of a hydrogen bonding penetrant (2,5-lutidine) from PU films using aprotic and protic solvents. The chemical interaction between the solvent, penetrant, and polymer functional groups are characterized via time-resolved FTIR spectroscopy. Inspection of the FTIR spectra reveals two potential mechanisms that facilitate the enhanced desorption rate: (1) penetrant/solvent competition for hydrogen donor groups on the polymer backbone and (2) disruption of the self-interaction (cohesive forces) between neighboring polymer chains. Finally, the aprotic solvent is found to generate an order of magnitude greater desorption rate of the penetrant, which is attributed to a greater disruption of the self-interaction during penetrant desorption in comparison to the protic solvent and the inability for an aprotic solvent to form larger and potentially slower penetrant-solvent complexes.



POLY 258: Surface and interfacial influences on the bulk mechanical responses of polymeric composites

Stacy M. Manni¹, stacymanni@icloud.com, **Elizabeth Carbone²**, **Tomislav Kosta¹**, **Stephen Pemberton¹**. (1) Energetic Materials Branch, Air Force Research Lab, Magnolia Springs, Alabama, United States (2) University of Dayton Research Institute, Eglin AFB, Florida, United States

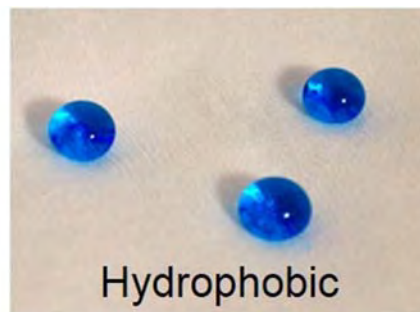
An advanced understanding of how internal surface and interfacial characteristics affect bulk mechanical properties will enable cogent design decisions and improved materials for future heterogeneous composite needs. This is being achieved through the development of improved methods of material surface characterization, correlation of interface vs. bulk properties with heterogeneous conglomerates and a statistics-based empirical model that links surface and bulk properties in composite materials. The complexities of modern polymeric composite materials require that surface and bulk properties be measured and understood with higher fidelity than traditional testing techniques have achieved. These challenges are addressed through the development of advanced surface characterization through inverse gas chromatography, the use of hyper-engineered heterogeneous composite materials to separate and clarify the independent contributions of surface and bulk properties, and the leveraging of current microstructure characterization projects to build highly-advanced, statistics-based models for composite properties that properly combine the separate contributions.



POLY 259: Roll-to-roll deposition of functional polymers onto fibers

Christine Cheng, **Malancha Gupta**, malanchg@usc.edu. University of Southern California, Los Angeles, California, United States

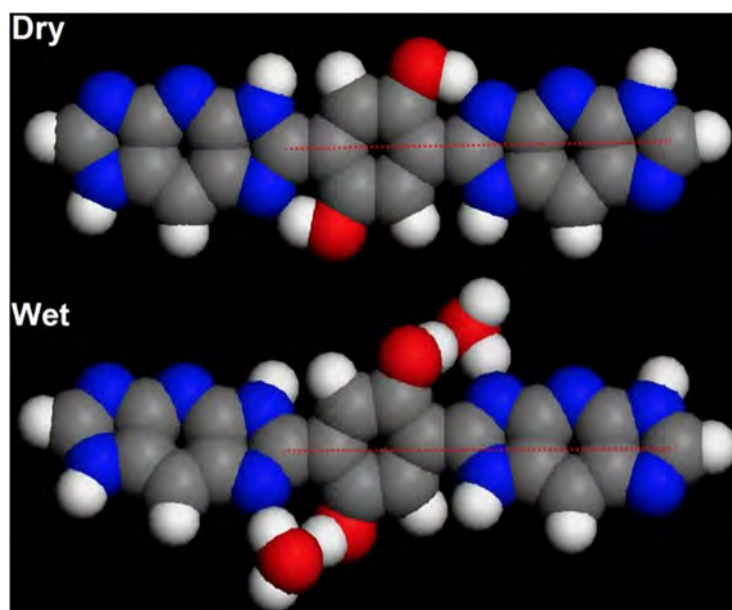
This talk will discuss roll-to-roll deposition of functional polymers onto fibers. Initiated chemical vapor deposition (iCVD) is used to deposit hydrophobic, hydrophilic, and light-responsive polymers. In the iCVD process, the monomer and initiator molecules are introduced in the gas phase. A hot filament array is used to cleave the initiator molecules to begin free-radical polymerization. Polymerization occurs on the surface of the fibers. There are no surface tension effects or clogging, therefore the breathability of the fabric is maintained before and after coating.



POLY 260: Mechanistic impact of water on M5 structure and properties

Steven Lustig, *s.lustig@northeastern.edu*. Chemical Engineering, Northeastern University, Boston, Massachusetts, United States

The hydrophilicity of polypyridobisimidazole challenges the development of M5 fiber for high-tensile modulus applications. The material's intractability makes it practically impossible to determine whether the observed loss of stiffness upon water sorption is due to either chemical hydrolysis or physical softening or subtle changes in post-spin structure. This work quantitatively characterizes the mechanisms by which water is challenging the technical development of M5 fiber. M5 fibers with different heat and humidity treatments are characterized by two-dimensional, high resolution X-ray scattering. Molecular modeling elucidates the detailed structure and identifies where molecular water resides in the M5 crystal. Water interrupts both intermolecular and intramolecular hydrogen bonding as well as changes the larger-range, morphological order within the fiber crystallites. Molecular modeling suggests a specific mechanism how water molecules interrupt intramolecular hydrogen bonding. This single mechanism predicts the tensile modulus softening between heat-treated and subsequently moistened fiber that agrees quantitatively with experimental data. These preliminary results support the contention that M5 modulus softening with water ingression can be explained by purely-physical conversion of the inherent intrachain molecular hydrogen bonding to intermolecular hydrogen bonding with water, without having to invoke an additional chemical hydrolysis contribution. Quantum molecular dynamics simulations suggest that the polypyridobisimidazole molecule actually exists in two keto-enol tautomeric forms, which interconvert dynamically. Current results indicate that neither form is particularly sensitive to chemical hydrolysis. We currently hypothesize that the post-spinning, heat-treatment provides a structure that resists chemical hydrolysis.

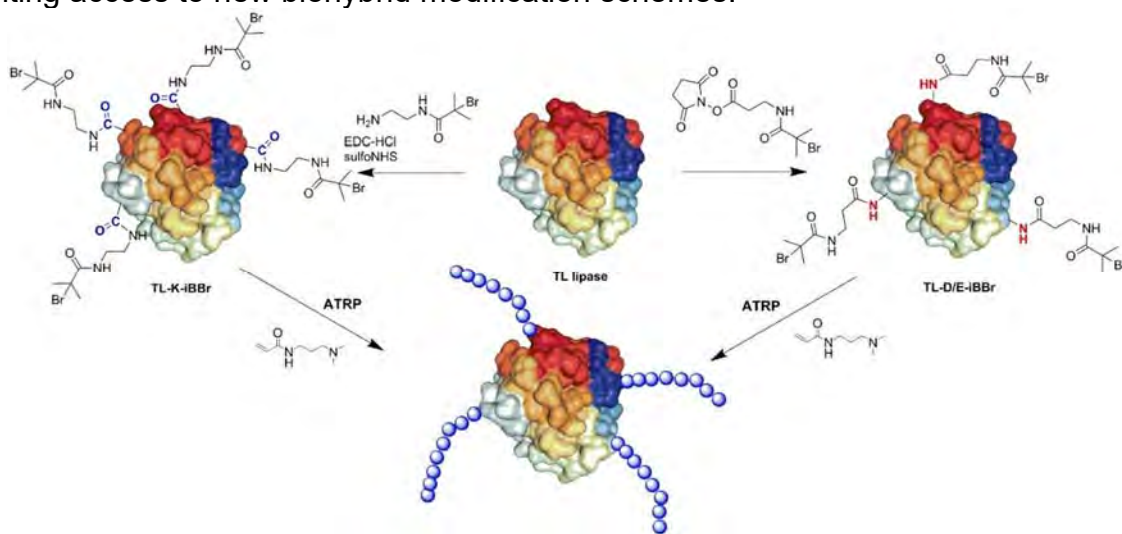


Physical conversion of the inherent intrachain hydrogen bonding to intermolecular hydrogen bonding with water accounts for modulus softening.

POLY 261: Impact of amino acid residue on biohybrid activity: Asp/Glu Vs Lys

Saadyah Averick¹, saadyah.averick@ahn.org, Marina Kovaliov². (1) Neuroscience Institute, Allegheny Singer Research Institute, Pittsburgh, Pennsylvania, United States (2) Neuroscience Research Institute, Allegheny Health Network, Pittsburgh, Pennsylvania, United States

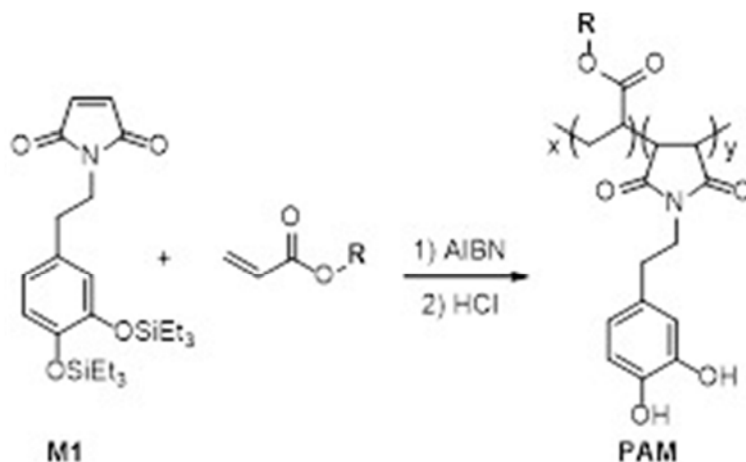
The use of enzymes as catalysts has become increasingly important in many industrial applications such as food processing, detergents, textiles and organic synthesis. However, a limiting factor for the industrial application of enzymes is their poor operational or long-term stability when exposed to environmental challenges, such as elevated temperatures and pH extremes. Recent advances in atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) enable the polymerization of acrylates and acrylamides from proteins. In both cases amino acid residues are modified with chain-transfer agents or ATRP initiators and polymers grafted-from in situ. In the literature the primary residues modified are lysine, due to this residues relative surface abundance and ease of preparing activated ester CTA/ATRP initiators. Cysteine residues, although less abundant on protein surfaces can be readily reacted with alkene bearing CTA/ATRP initiators such as maleimide or acrylate. Less common residues modified include the N or C terminal or the genetic introduction of non-canonical amino acid moieties. We were interested in studying the impact of residue modification using grafting from of another common surface residue aspartic (D) or glutamic acid (E). ATRP was selected as the grafting-from strategy due to the inherent instability of an amine containing RAFT agent required for acid residue ligation. Lipase TL was modified at either lysine (K) or acid (D/E) residues and *N*-[3-(Dimethylamino)propyl]acrylamide (DMAc) was grafted from using ICAR ATRP. Protein activity was assessed using a colorimetric based hydrolysis assay under normal and elevated temperature. We found that the grafted TL-D/E-pDMAc had a significantly higher activity than TL-K-pDMAc more importantly our results indicate that this new amino acid modification strategy may be employable in other enzymes granting access to new biohybrid modification schemes.



POLY 262: Catechol-functionalized bioinspired synthetic adhesives: Effect of comonomer composition on adhesive properties

Scott Radzinski¹, *scr014@bucknell.edu*, **Matthew Bartucci**¹, **David P. Flanagan**¹, **Joseph Lenhart**¹, **Joshua A. Orlick**². (1) U.S. Army Research Laboratory, Bel Air, Maryland, United States (2) Army Research Laboratory, Aber Prov Grd, Maryland, United States

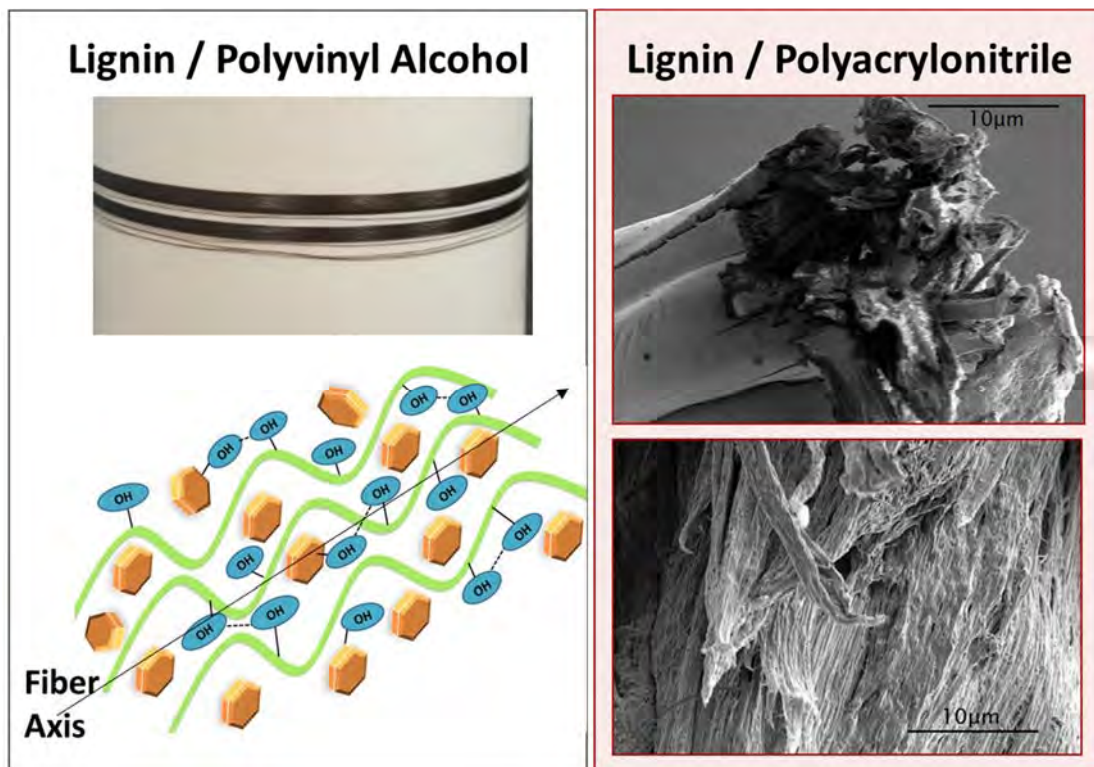
Most commercial adhesive performance degrades under wet and dirty environments, while mussel foot proteins have been optimized for these conditions. Sequencing of the interfacial protein residues has revealed that nearly a third of the repeat units consist of 3,4-dihydroxyphenylalanine (DOPA) which have pendent catechols. The versatile chemistry exhibited by catechols (e.g. covalent cross-linking, metal chelating) has led to a number of groups exploring the incorporation of catechol functionality into synthetic backbones. We have synthesized a library of poly(meth)acrylate-co-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimides (**PAMs**) that vary in their aliphatic side-chain length and comonomer composition on a common polymer backbone, allowing for control over T_g and backbone polarity. It is expected that the modest adhesive performance garnered by the library will provide fundamental insight for the coupling of established adhesive chemistries with novel bioinspired approaches, allowing for the rational design of improved interfacial adhesion in adverse environments.



POLY 263: Revisiting lignin-based fibers: Understanding gel-fiber spinning, structure and property relationships

Ericka Ford, enford@ncsu.edu, Chunhong Lu, Charles Blackwell. NC State University, Raleigh, North Carolina, United States

The next frontier of sustainable, soft armor yarns and carbon fiber precursors for military applications must eventually come from natural resources that are indigenous to the United States. In this talk, we discuss the coupling of an abundant, low cost raw material and best practices in the fibers spinning community to achieve mechanically strong fibers. This work revives the discourse on lignin (aromatic biopolymers that develop between the cell walls of vegetable matter), having renewed hopes of achieving mechanical performance that is competitive with current, more expensive high-performance fiber technologies. Gel-spinning, the same technology that has rendered cut resistance and ballistic protection from linear ultra-high molecular weight polyethylene fibers, is applied to lignin-based fiber production. The dope of dissolved lignin/vinyl polymer, liquid to gel conversion, and post drawing conditions have intricate roles in fiber spinning for optimum performance. Higher modulus and toughness upon lignin addition- is attributed to the anti-plasticization of lignin within composite, gel-spun fibers. Anti-plasticization describes lignin's role as a plasticizer for higher spin-draw ratios and stiffening additive by its aromatic structure. In addition to enhanced toughness and modulus among fibers with lignin, we describe structure-processing relationships for aligning lignin's complex supramolecular structure.

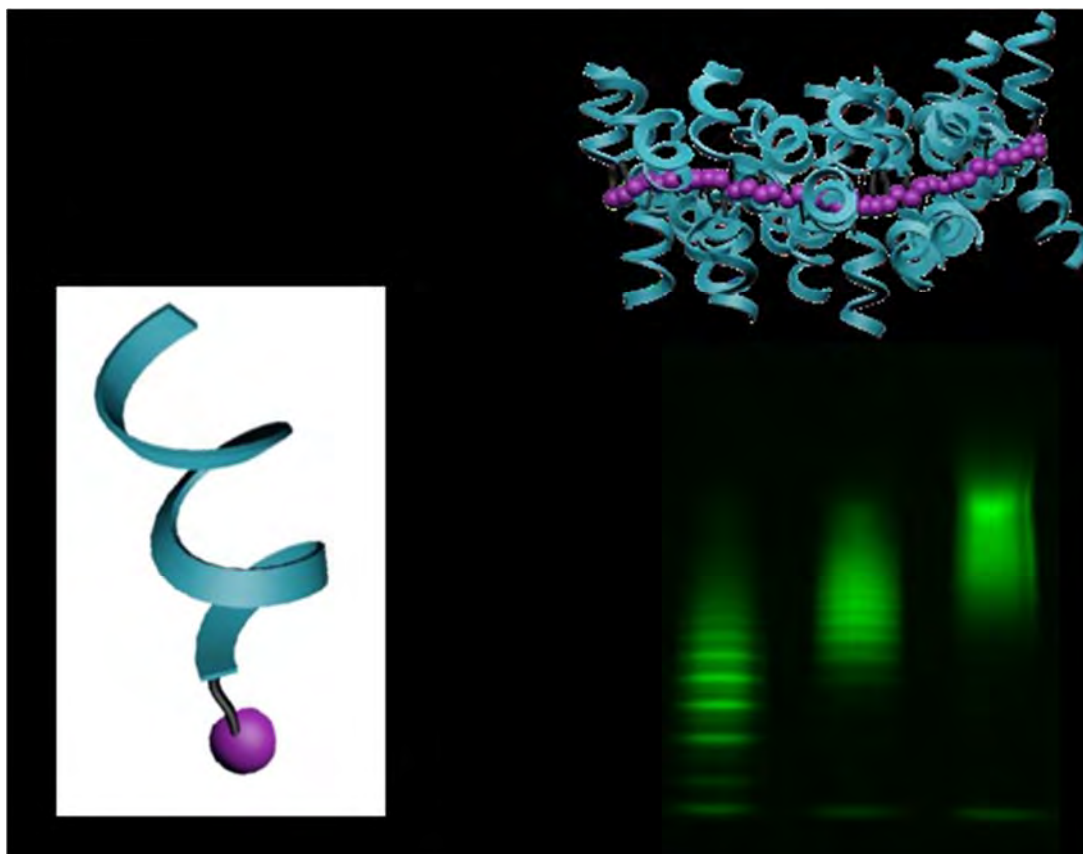


Continuous lignin/poly(vinyl alcohol) and lignin/polyacrylonitrile filaments were gel-spun.

POLY 264: Poly(oligonucleotide) - Bringing phosphodiester oligonucleotides to polymer chemistry

Ke Zhang, *k.zhang@northeastern.edu*. Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States

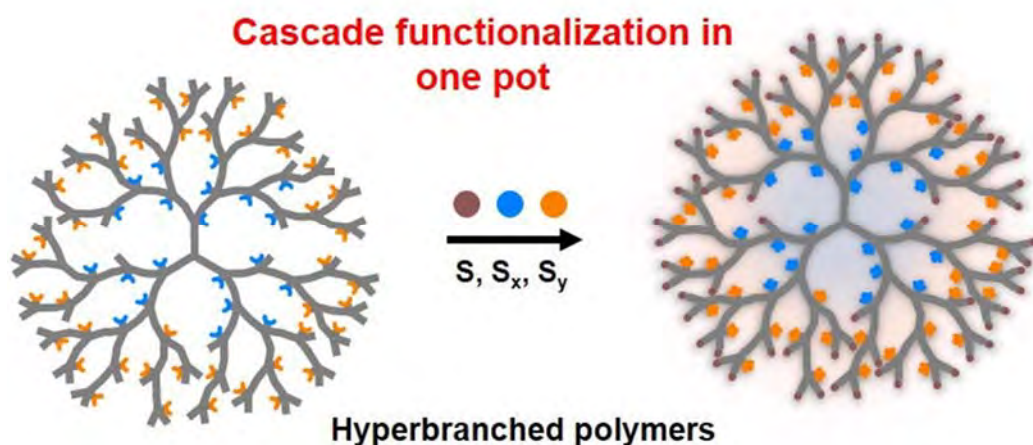
Reactions involving oligonucleotides (ON) are often carried out post-ON synthesis using bioconjugation techniques in aqueous solutions, due to the poor solubility of ON in organics and side reactivity of the exocyclic nucleophilic bases. Herein, we develop organics-soluble oligonucleotide macromonomers that can be directly polymerized using ring-opening metathesis chemistry. A range of architectures, including brushes, block copolymers, and block brushes, can be accessed. In particular, brush-architected poly(oligonucleotide) exhibit interesting physiochemical properties and biological properties, including increased binding affinity with a complementary sequence and enhanced cellular uptake.



POLY 265: Develop nanostructured hyperbranched polymers as unimolecular containers

Haifeng Gao, gaohaifeng1@gmail.com. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States

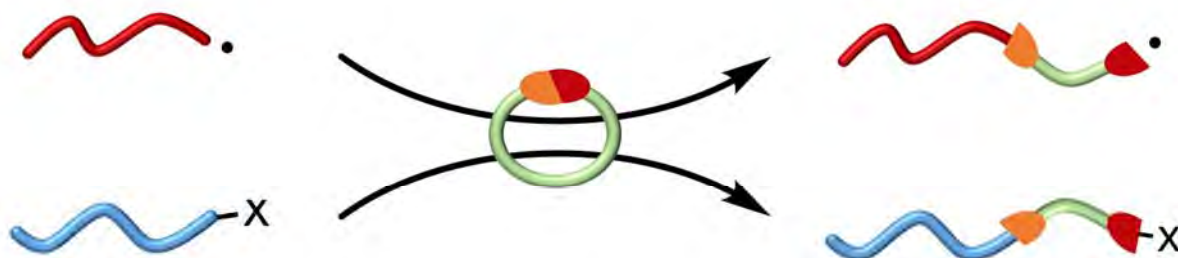
This presentation discusses our recent progress on synthesis and application of nanostructured hyperbranched polymers as unimolecular containers. The hyperbranched polymers are constructed based on chain-growth CuAAC polymerization of AB₂ monomers with defined molecular weights, low dispersity and accurate placement of reactive groups. These polymers with segmented nanostructures achieve orthogonal functionalization in different domains via cascade reactions. These polymers are successfully applied as unimolecular containers for dyes, metallic nanoclusters and biomocromolecules.



POLY 266: New chemical approaches for ring-opening polymerization

Will R. Gutekunst, willgute@gatech.edu, Guanyao Fu, Mizhi Xu. School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

Ring-opening polymerization has been a mainstay of living polymerization for decades and has been demonstrated with a variety of chemical mechanisms that range from ionic to radical to organometallic. By taking cues from known organic reactivity found in the small molecule literature, our group has been translating existing ideas to generate new concepts in how ring-opening polymerization manifolds can be revealed. Through this approach, new monomers for radical ring-opening polymerization have been devised that have rapid copolymerization with activated vinyl monomers. In addition, a new type of ionic ring-opening polymerization has been invented that relies on simple alkyl halides for initiation. These two projects will be presented with a focus on how they can be applied to generate sequence-controlled polymers and also explore polymer secondary structure.

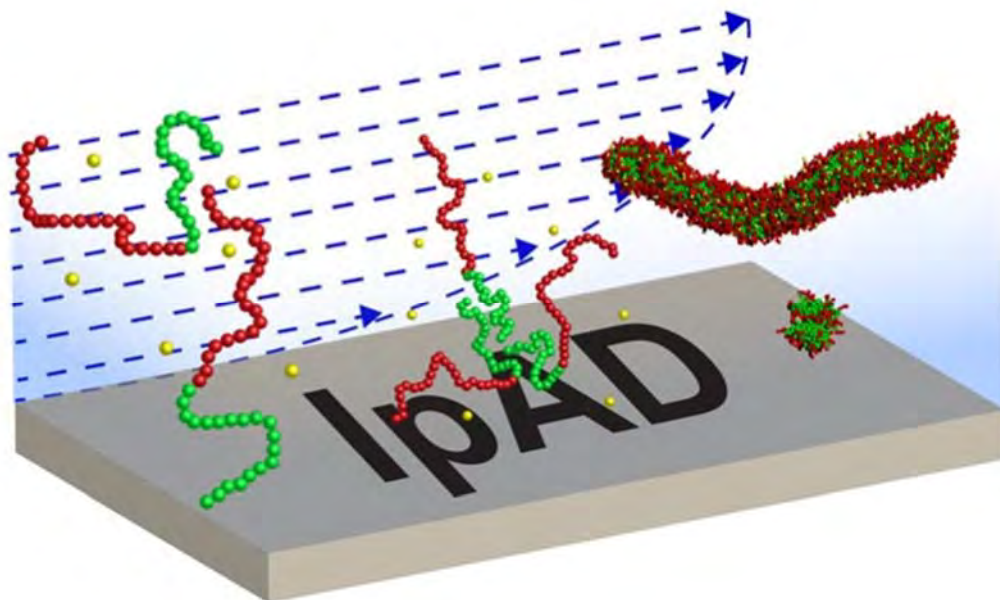


New Modes of Reactivity for Ring-Opening Polymerization

POLY 267: Interface-promoted assembly and disassembly processes for rapid manufacture and transport of complex hybrid nanomaterials

Karen L. Wooley, wooley@chem.tamu.edu. 3255 TAMU, Texas AM University, College Station, Texas, United States

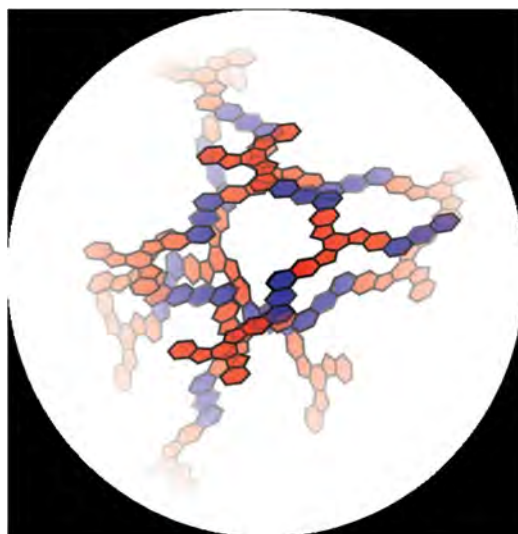
This presentation will highlight collaborative research that aims to develop approaches to rapidly discover and manufacture hybrid inorganic-organic nanostructured objects (HIONs) possessing complex compositions, structures, properties and functions. Theory and simulation tools are being developed in the laboratory of Arthi Jayaraman at the University of Delaware, and applied to block polymers and block bottlebrush polymers to inform experimental synthetic, assembly and characterization studies in the Wooley laboratory at Texas A&M University. The assembly and characterization efforts are further enhanced by activities in the laboratory of Darrin Pochan at the University of Delaware. Finally, computational and experimental efforts in the William Johnson laboratory at the University of Utah are investigating nanostructure-substrate interactions and nanostructure transport through porous media. By leveraging interface-driven synthesis and dynamic assembly/disassembly of organic polymers and inorganic nanoparticles under flow, our goal is to expedite and drive intermolecular and interparticle assembly that is inefficient or impossible in the absence of such interfacial interactions.



POLY 268: Hyperbranched polymer nanoparticles featuring ladder-type conjugated backbones

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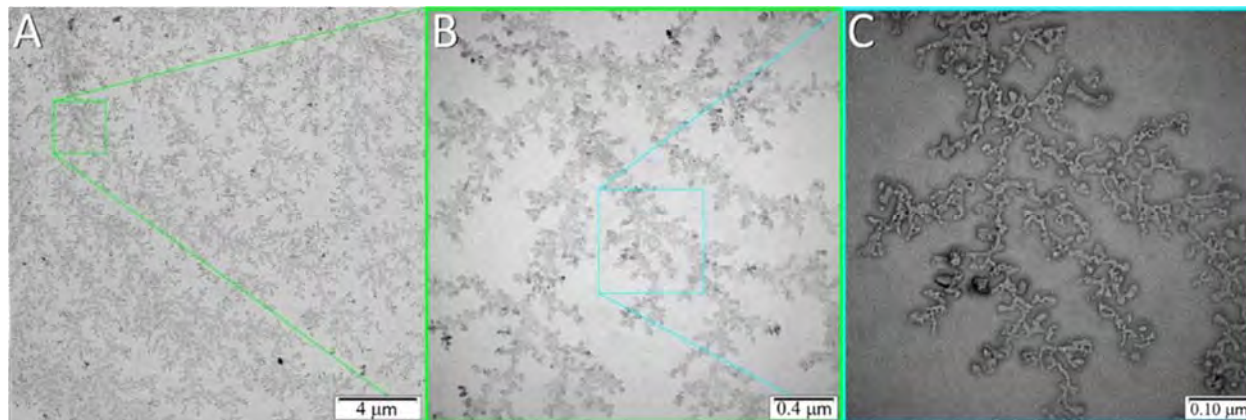
Hyperbranched conjugated polymer nanoparticles represent a promising subset of nanoparticulated polymer materials, in which the solubility and processability of nanoparticles, the optical properties of conjugated polymers, and the porosity of microporous polymers are integrated. Exploitation of the optical, electronic, and stimuli-responsive functions of these materials, however, is impeded by the challenges associated with torsional disorders and optical stability. By introducing fused-ring ladder-type constitution along the entire hyperbranched backbone, the optical properties, stability, sensing performance and other properties undergoes significant improvements, opening the door to a promising new class of functional polymeric materials with brighter fluorescence, better stability, improved porosity, and simple processability.



POLY 269: Peptide-based star and triblock copolymers: Dynamics of hierarchical assembly and responsiveness

*Ian Smith, Brooke Barnes, Craig Machado, **Daniel A. Savin**, dsavin1973@gmail.com.
Chemistry, University of Florida, Gainesville, Florida, United States*

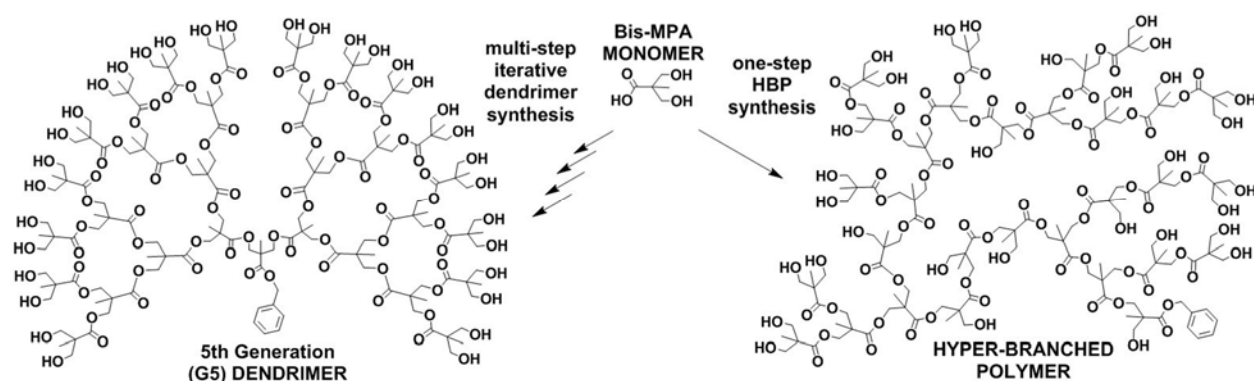
This study involves the bottom-up design and tunability of responsive, peptide-based block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic triblock and star copolymers containing poly(lysine) (PK), poly(leucine) (PL) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. The peptide block in these structures can serve to introduce pH responsiveness (in the case of PK and PE), or can facilitate the formation of elongated, kinetically-trapped, or fractal structures (in the case of PL.) This talk will present some recent studies in solution morphology transitions that occur in these materials as a result of the helix-coil transition and associated charge-charge interactions. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.



POLY 270: Preparation and application of polyesters with controlled branching

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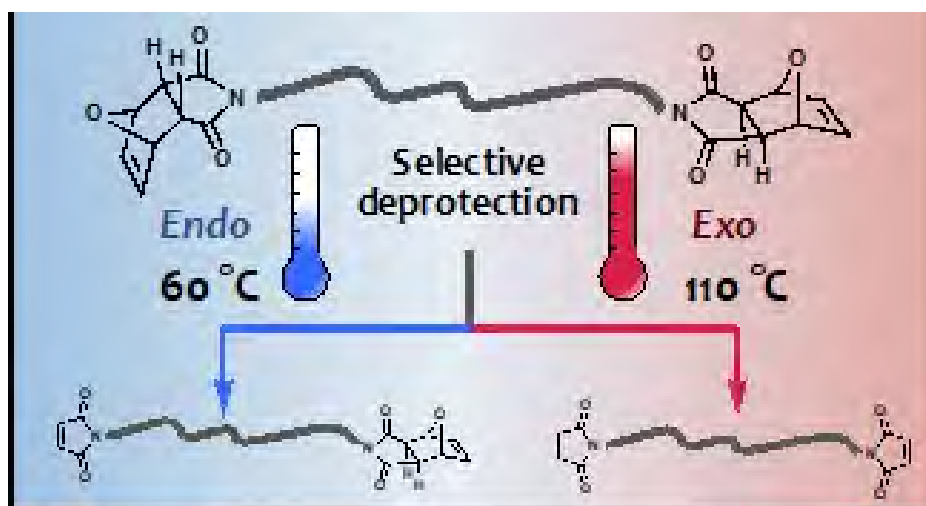
The importance of branching in polymers is well-documented, from classical examples of light branching in polyethylene to more the modern hyperbranched polymers Boltorn® and Hybrane®. However, the understanding of the exact roll that branching plays in determining a material's properties remains incomplete. For example, how does local branching effect reactivity of adjacent sites, or how does the location of branching effect the self-assembly of amphiphilic polymers? Of the branched materials available, bis-MPA-based polyesters remain the most appealing platform for systematic study, as both their dendrimers and their hyperbranched polymers have been synthesized and previously studied in detail. Architectural effects will be explored by making well-defined dendritic materials and carrying out detailed studies of their architecture-dependent behavior.



POLY 271: Combining organic synthesis and polymer chemistry for new functional macromolecular architectures

Craig J. Hawker, hawker@mrl.ucsb.edu. Univ of California, Santa Barbara, California, United States

The interface of organic method development and polymer synthesis opens numerous opportunities for the controlled introduction of reactive functional groups to a wide variety of polymeric platforms. To illustrate the power of this approach, the development and application of a novel *endo* furan-protected maleimide building block will be discussed. The *endo* isomer undergoes deprotection at temperatures ~ 50 °C below the *exo* derivative. This enables a simple and powerful approach to quantitatively and selectively introduce functional maleimide groups via temperature modulation which allows for efficient chain end coupling, backbone modification and star synthesis.



POLY 272: RAFT/MADIX approaches to new cryoprotective polymers

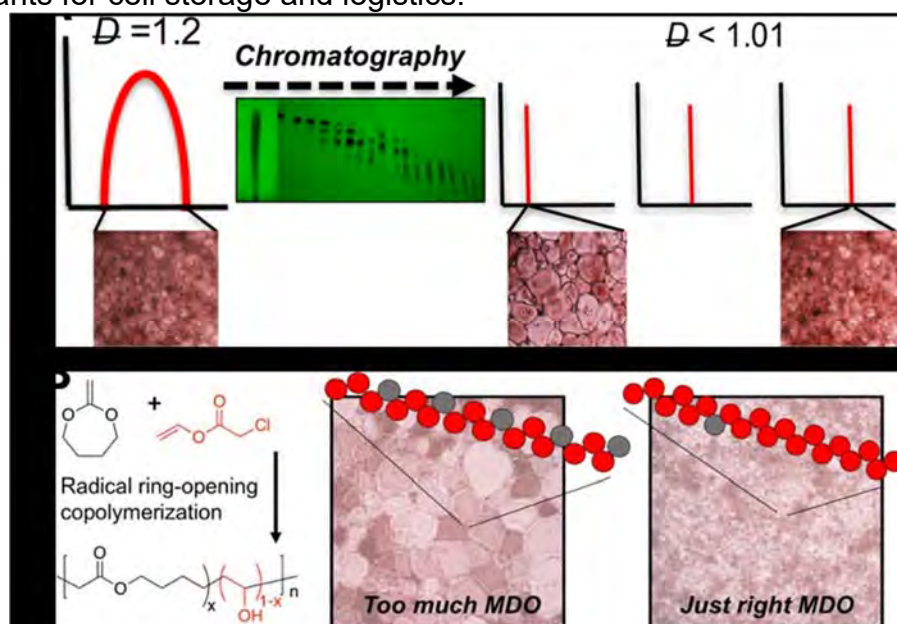
Christopher Stubbs¹, *c.stubbs@warwick.ac.uk*, **Guillaume Hedir**¹, **Nicholas Vail**¹, **Matthew I. Gibson**², **Andrew P. Dove**³. (1) Department of Chemistry, University of Warwick, Warrington, Cheshire, United Kingdom (2) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom (3) Univ of Warwick, Coventry, United Kingdom

Antifreeze (glyco) proteins (AF(G)Ps) are highly active ice recrystallization inhibitors (IRI), which makes them desirable for a range of applications from frozen food to cell cryopreservation. We have a large research interest in designing new biomimetic polymers which can reproduce this activity, but taking advantage of the scalability, tuneability, and versatility of synthetic polymers.

Poly(vinyl alcohol) is the most active IRI polymer reported to date, despite its remarkably simple structure, and is desirable due to its excellent toxicity profile. However, the exact mode of action is not understood, and PVA itself is not degradable in the body. Here I will discuss our progress in this area.

Firstly, I will report the use of column-chromatography to enable us to isolate near-discrete (dispersity < 1.01) oligomers of PVA to enable us to identify the critical chain length for activity to help guide us in understanding its function and to help design new more complex materials with 'triggerable' IRI activity. Secondly, I will describe the use of radical ring-opening copolymerization of vinyl chloroacetate with 2-methylene-1,3-dioxepane (MDO) to obtain PVA's with ester groups in the main chain, introducing degradability into the polymer. We crucially show there is a sweet spot for MDO incorporation, with too much leading to no activity, and too little limiting the degradability.

These results are helping to guide us in developing new and more effective cryoprotectants for cell storage and logistics.

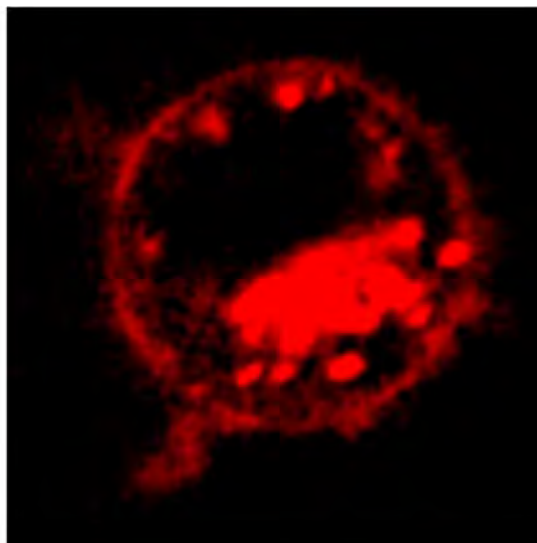
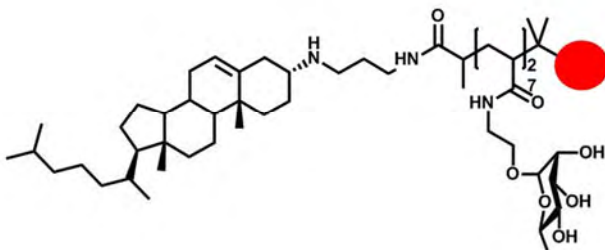


A: IRI activity of ultralow dispersity poly(vinyl alcohol). B: Synthesis of degradable PVA and corresponding IRI activity.

POLY 273: Antibody-recruiting polymers

Bruno De Geest, *br.degeest@ugent.be*, Ruben De Coen, Annemiek Uvyn. Ghent University, Ghent, Belgium

Therapeutic strategies based on easy-to-access synthetic compounds that recruit endogenous antibodies (i.e. antibodies present in large amounts in every human being) towards the tumor cell membrane to exert subsequent antibody-mediated cell killing effects might be of value of cancer immunotherapy. Here we report on a novel class of materials called antibody recruiting polymers (ARPs). ARPs consist of polymeric copies of rhamnose or dinitrophenol which binds to endogenous antibodies present in human serum. As a proof-of-concept we have designed ARPs with a lipophilic end-group that efficiently inserts into cell surface membranes or ARPs that bear multiple cyclooctyne copies that can bind to azide moieties introduced on a cancer cell surface through metabolic cell labeling. We validate the specificity of rhamnose/dinitrophenol to attract antibodies from human serum to the target cell surface and demonstrate that ARPs outperform an analogous small molecule compound containing only one single rhamnose/dinitrophenol motif. This class of materials opens avenues for the design of potent immunotherapeutics that mark target cells for destruction by the immune system through antibody-mediated effects.

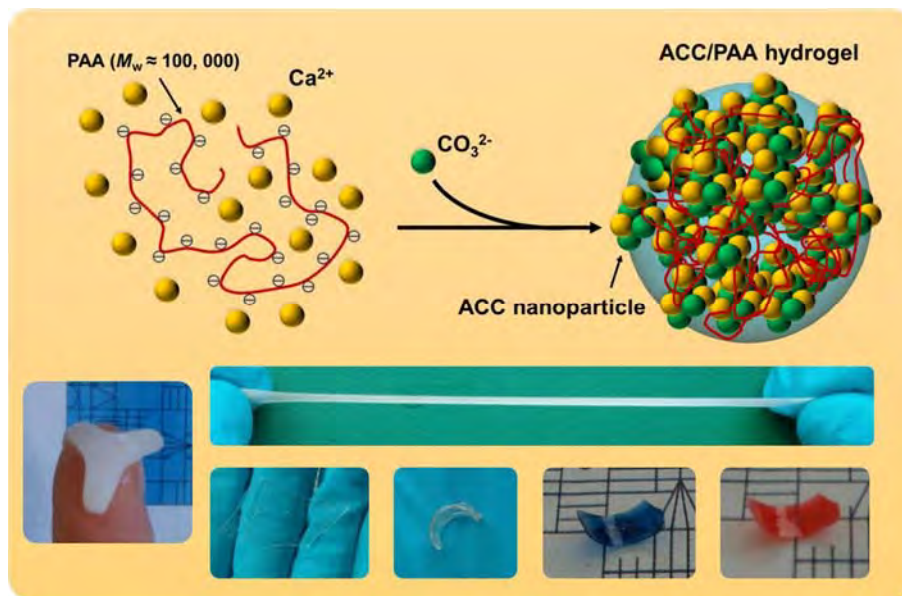


POLY 274: Hydrogels from amorphous calcium carbonate and polyacrylic acid: bio-inspired materials for "mineral plastics"

Shengtong Sun, *shengtongsun@dhu.edu.cn*. Donghua University, Shanghai, China

Given increasing environmental issues due to the large usage of non-biodegradable plastics based on petroleum, new plastic materials, which are economic, environmentally friendly, and recyclable are in high demand. One feasible strategy is the bio-inspired synthesis of mineral-based hybrid materials. We developed a facile route for an amorphous CaCO_3 (ACC)-based hydrogel consisting of very small ACC nanoparticles physically cross-linked by poly(acrylic acid). The hydrogel is shapeable, stretchable, and self-healable. Upon drying, the hydrogel forms free-standing, rigid, and transparent objects with remarkable mechanical performance. By swelling in water, the material can completely recover the initial hydrogel state. As a matrix, thermochromism can also be easily introduced. The present hybrid hydrogel represents a new class of plastic materials, and we dubbed it "mineral plastics".

Mineral plastics have not only shown great potential in substituting conventional plastics, but also can be used in other important applications, such as bioadhesion. Underwater adhesion is crucial to many marine life forms living a sedentary life style. Amongst them, mussel adhesion has been mostly studied, which inspires numerous investigations of 3,4-dihydroxyphenylalanine (DOPA)-based organic adhesives. In contrast, reef-building oysters represent another important "inorganic" strategy of marine molluscs for adhesion by generating biomineralized organic-inorganic adhesives, which is still rarely studied and no synthetic analogues have ever been reported so far. We found that mineral plastic hydrogel can be a novel oyster-inspired, injectable, reusable, and optically clear adhesive. The hydrogel shows comparable adhesion performance to DOPA-based adhesives in both dry and wet conditions, which can also be further enhanced by incorporating negatively charged nanoparticles.

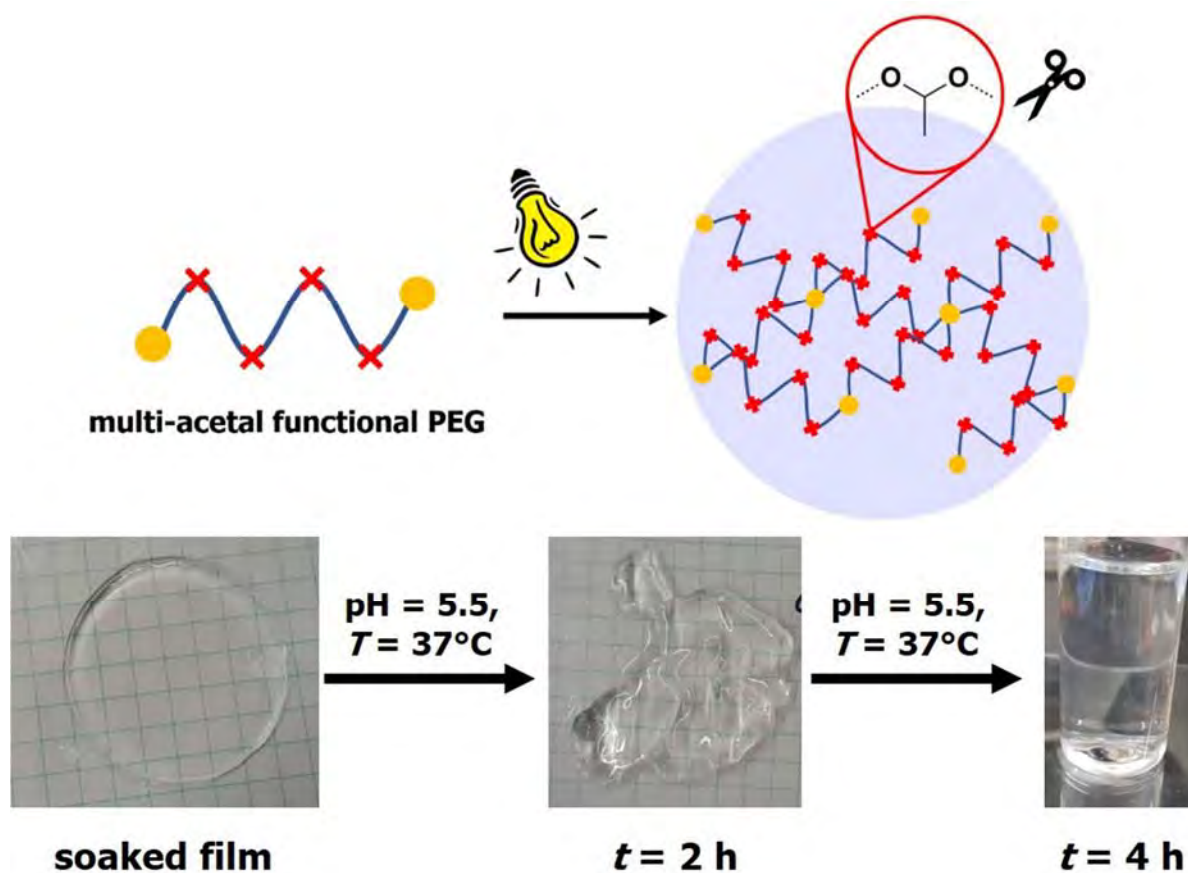


Mineral Plastic

POLY 275: Acid-cleavable polyethylene glycol hydrogels for on-demand release of active molecules

Jana Herzberger, herzberger.jana@gmail.com, James R. Brown, Chixia Tian, Emily Wilts, Timothy E. Long. Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

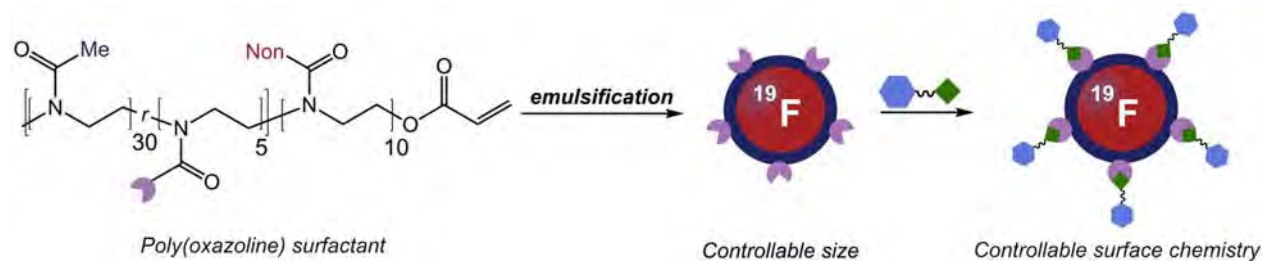
Since the 1980s, acetal groups have attracted much attention as cleavable moieties for biomedical applications. They are stable at basic pH but readily cleave at slightly acidic pH, e.g. at the pH of cancer or inflamed tissue (pH = 5.5 to 6.5). Here, we present a one-pot synthesis of multi-acetal functional polyethylene glycols (PEGs) bearing UV-curable end-groups using step-growth polymerization. UV-crosslinking and subsequent soaking in aqueous solution yielded PEG hydrogels. The incorporated acetal-groups enabled fast hydrogel degradation at slightly acidic pH. The degradation time was easily tailored by varying the number of acetal-units in the gel, while the use of PEG ensured biocompatibility. We believe that these structures are promising candidates for implantation into tumor tissue, providing controlled release of anti-tumor drugs.



POLY 276: Custom poly(oxazoline)s for the stabilization and functionalization of PFC nanoemulsions

Daniel Estabrook, destabrook@g.ucla.edu, Ellen M. Sletten. Chemistry and Biochemistry, UCLA, Los Angeles, California, United States

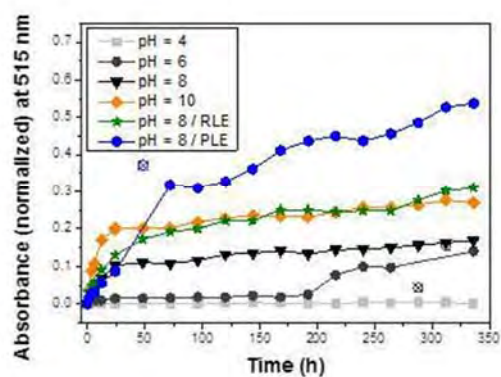
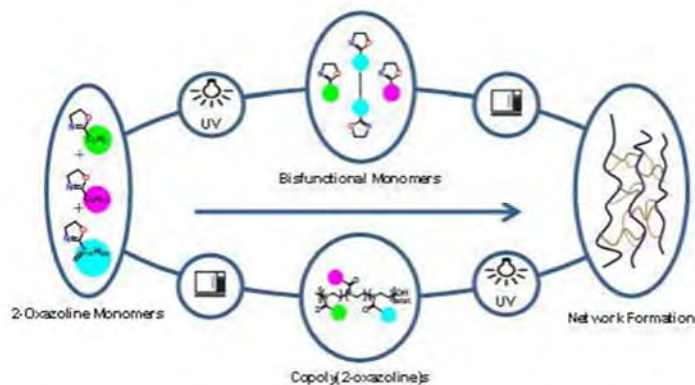
Perfluorocarbon (PFC) emulsions are non-toxic, dynamic nanomaterials that have been employed as oxygen carriers and contrast agents. Their use has historically been limited by nonfunctional poloxamer surfactants that result in size heterogeneity, instability, and multi-dose toxicity. The development of a biocompatible, functionalizable polymer surfactant would expand the versatility and utility of PFC emulsions, enabling surface modification of the droplets. We have synthesized a panel of novel amphiphilic poly(oxazoline)s derived from hydrophilic, hydrophobic and fluoros 2-substituted-2-oxazoline monomers. These polymer surfactants stabilize a series of readily accessible PFC nanoemulsions that span a wide range of surface charges and size distributions with adequate stability and modular loading capabilities. Selective placement of “clickable” alkyne and alkene comonomers allows for spatial control over emulsion functionalization. We demonstrate the use of multifunctional poly(oxazoline) surfactants to control the biodistribution and cellular uptake of these nanomaterials. Importantly, this study illustrates the role of charge in the cellular uptake of PFC nanoemulsions within healthy, cancerous, and macrophage cell lines, informing techniques for targeting and avoiding macrophage uptake.



POLY 277: Enzyme-degradable hydrogels based on copoly(2-oxazoline) networks

Frank Wiesbrock¹, frank.wiesbrock@pccl.at, Klaus P. Luef¹, Bettina Ottersböck¹, Gernot Oreski¹, Charlotte Petit², Bruno Grassl², Stephanie Reynaud³. (1) Polymer Competence Center Leoben, Leoben, Austria (2) Universite de Pau et des Pays de l'Adour, Pau, France (3) IPREM (UPPA/CNRS), Pau cedex 9, France

UV-induced click-reactions such as the thiol-ene reaction are a straight-forward strategy for the synthesis of crosslinked polymers. In this study, copoly(2-oxazoline)s composed of (monofunctional) 2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline as well as a (bisfunctional) 2-oxazolines containing either ether or ester bonds were synthesized by cationic ring-opening polymerizations; the bisfunctional 2-oxazolines were prepared from the thiol-ene reaction of glycol dimeracetoacetate or 2,2'-(ethylenedioxy)diethanethiol and 2-but-3'-enyl-2-oxazoline or 2-dec-9'-enyl-2-oxazoline. Crosslinked networks were synthesized either in-situ or by performing the polymeranalogous thiol-ene click reaction of copoly(2-oxazoline)s and glycol dimeracetoacetate. By variation of the repetition units and the degree of crosslinking, 80 gels were synthesized, of which 13 derivatives exhibited glass-transition temperatures in the narrow range from 20 to 30 °C, which renders them stiff below and flexible at body temperature. Only the gels that did not contain any 2-nonyl-2-oxazoline acted as hydrogels; all other gels were lipo- or amphigels. Maximum swelling degrees of 6 in water were observed. Polymer discs loaded with the tracer dye Eosin B were subjected to degradation, in the course of which highest release rates were found for the porcine liver esterase-mediated degradation at pH = 8.



Schematic representation of the in-situ as well as the polymeranalogous preparation of copoly(2-oxazoline) networks (left); UV-VIS monitored degradation of loaded gels (right; RLE/PLE: rabbit/porcine liver esterase).

POLY 278: Block copolymers in confinement

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The self-assembly of block copolymer in solution has brought about a large variety of functional nanoparticles. While most of the self-assembly processes are in diluted conditions, more recent reports in concentrated solution describe block copolymers to result in porous inverse morphologies and compartmentalized microparticles. This presentation discusses the self-assembly of block copolymers in the spherical confinement in nanoemulsion droplets (**Fig. 1**). During evaporation of the water-immiscible low-boiling solvent, the block copolymers concentrate and microphase separate, yet, the interfacial energy of the water/polymer interface dominates microphase separation behaviour into unprecedented morphologies. We study the confinement assembly of triblock terpolymers that give access to a large variety of multicompartiment microparticles, which in turn serve as templates the synthesis unusual Janus nanoparticles including nanotoroids, nanocups, perforated and patchy discs. The formation of a lamella-cylinder morphology in spherical confinement further poses interesting topological problems. Depending on the surfactant, we either obtain cylinders sandwiched between axially stacked discs (2D problem) or cylinders wrapped to cover concentric lamellae (3D problem). The synthesis of both types of microparticles is scalable, and the complex inner structure might be suitable for capture and release, actuation, energy storage and conversion, or applications that require high surface area.

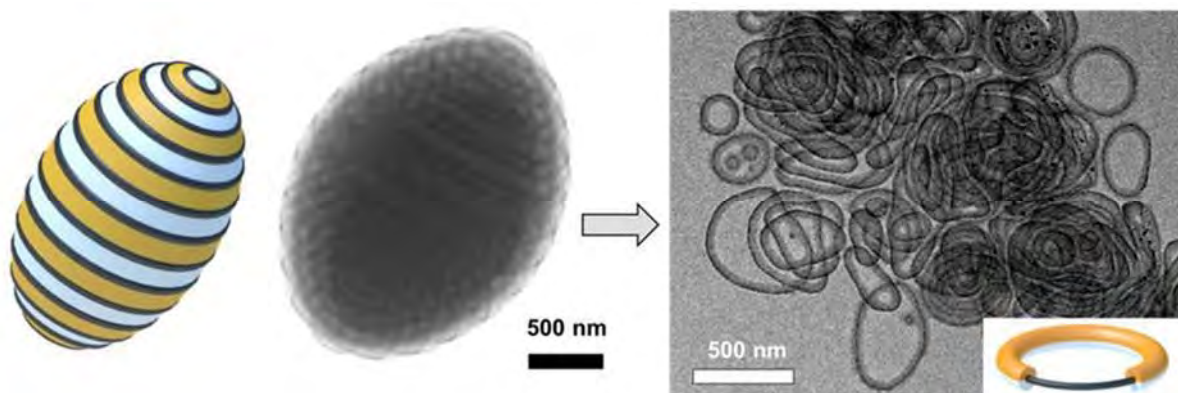
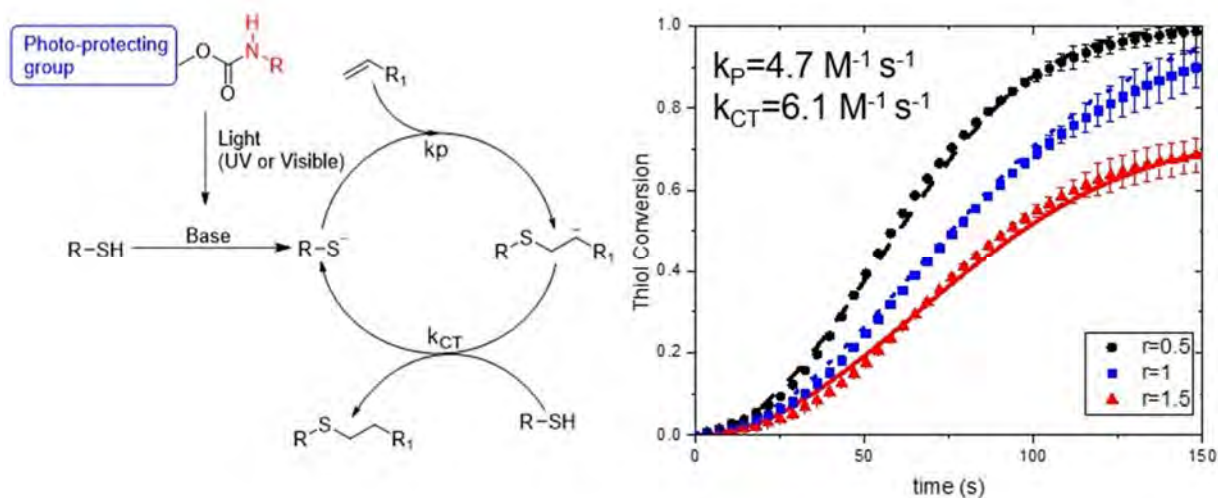


Figure 1. Self-assembly of block copolymers in concentrated solution and spherical confinement.

POLY 279: Mechanistic kinetic modeling of thiol-Michael addition reactions: Structural effects of thiol and vinyl monomers

Sijia Huang¹, *sihu1492@colorado.edu*, **Jasmine Sinha**¹, **Maciej Podgorski**¹, **Xinpeng Zhang**², **Christopher Bowman**³. (1) Chemical and Biological engineering, University of Colorado, Boulder, Colorado, United States (2) Chemistry, University of Colorado, BOULDER, Colorado, United States (3) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

Kinetic parameters and their influence on the overall rates of base-initiated thiol-Michael reactions proceeding via alternating propagation and chain transfer cycle were evaluated. A kinetic model was developed that enables the determination and accurate prediction of the reaction kinetic paths for thiol-Michael addition reaction and polymerization. Individual kinetic parameters for propagation and chain transfer steps were evaluated for three commonly used thiol and vinyl functional monomers, for example 1-hexanethiol and ethyl vinyl sulfone. The resultant reaction order showed strong dependency on the established kinetic parameters. Further, the kinetic model was tested in eight ternary thiol-Michael systems comprising of thiol-acrylate-vinyl sulfone and thiol 1-thiol 2-vinyl, wherein it clearly demonstrated that the kinetic parameters achieved from two-component reactions can facilitate accurate prediction of the reactivity and selectivity in multicomponent systems. Finally, the calculated kinetic parameters were utilized in network-forming polymerizations indicating the suitability of the model to predict network development at its initial stages. Hence, these results can serve as a useful guide towards the monomer selection for designing thiol-Michael-based polymers with desired kinetic characteristics and properties.



POLY 280: Direct synthesis of nanoparticles with spatial heterogeneity for tailored cellular interactions

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Forming patterned nanoparticles targeting a fine level of control at the nano- and bio-interface is of increasing interest for personalised, targeted and combinatorial disease therapy.

A synthetic strategy to generate branched polymer building blocks for the rapid construction of nanoparticles with pre-determined distributions of surface functional groups is presented. Hyperbranched polydendrons (HPDs) with a controlled mixture of PEG and dendron chain ends of different generation (G0 and G3), and different peripheral functionality (xanthate-, benzyl- and dimethylamino-functional), were synthesised and nanoprecipitated (50-70 nm). The patchy isolation of surface functional groups was confirmed through the *in situ* generation of thiol groups from xanthate-functional HPDs under mild basic conditions, binding of 4 nm gold nanoparticles (GNPs) and the quantification of clustering at the nanoprecipitate surface using TEM imaging. Direct cellular accumulation comparisons of nanoparticles with patchy and statistical distributions of surface functional groups (benzyl- and dimethylamino-groups) showed significantly-enhanced accumulation of patchy particles in phagocytic and non-phagocytic cells.

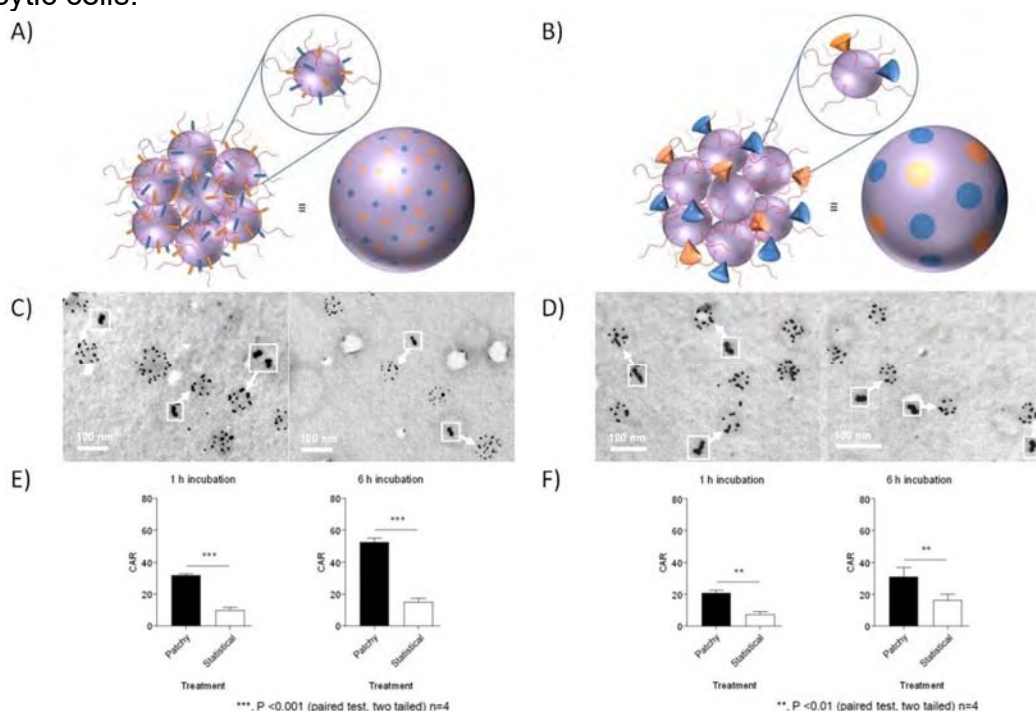


Figure 1. Schematic representation of nanoprecipitates with; A) statistical, and B) patchy distributions of surface functional groups. TEM-imaging of surface clustered GNPs on nanoprecipitates of; C) G0-containing HPDs (statistical), and D) G3-containing HPDs (patchy). Cellular accumulation ratios (CAR) for patchy (black bar) and statistically (white bar) multifunctional nanoparticles at 1 hour and 6 hours incubation with; E) ATHP-1 cells and F) undifferentiated THP-1 cells.

POLY 281: Radiopaque stents based on electrospun iodixanol/polycaprolactone nanofibrous composites

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Biodegradable stents made up of polymers are used to widen arteries and has the potential to scaffold these arteries to allow natural healing to take place, and then biodegrade. However, although biodegradable stents were shown to be effective, these polymers are radiolucent and monitoring its location and integrity over time is a challenge. In this study, we infused polycaprolactone (PCL) with different concentrations of iodixanol and electrospun to create a radiopaque, biodegradable stent. Using scanning electron microscopy, we determined the morphology and calculated the porosity of the polymeric material. Young's modulus was calculated using atomic force microscopy, while the amount of iodine was quantified using atomic absorption spectroscopy. Radiopacity was examined using x-ray and micro-CT imaging systems. In vitro cytotoxicity was tested against RF24 immortalized human vascular endothelial cells. Results show that the morphology, porosity, and Young's Modulus of PCL was not changed when iodixanol was incorporated within the polymer. Figure 1 shows that there is an increased signal enhancement in iodixanol-infused PCL compared to PCL alone. Cytotoxicity was observed in a concentration-dependent manner. In conclusion, we were able to develop a radiopaque, biodegradable stent that might have the potential for monitoring the position and integrity of the stent over time. Successful development of imaging enhancers for stents may also lead to widespread use of biodegradable devices in other cardiovascular and orthopedic applications.

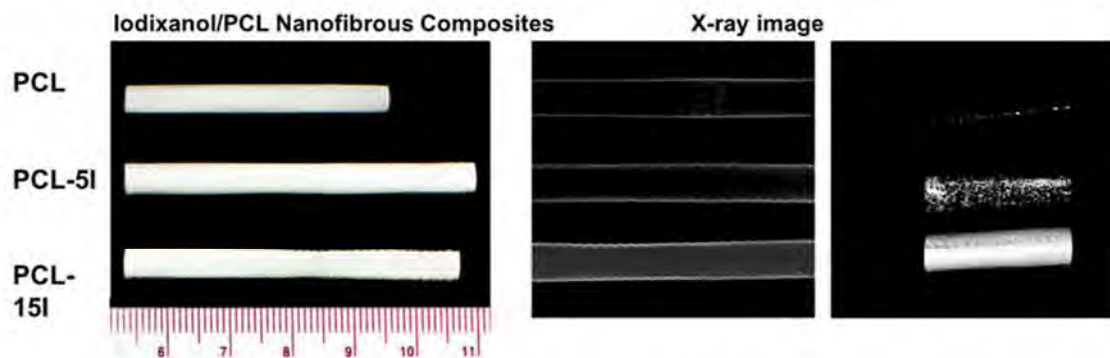


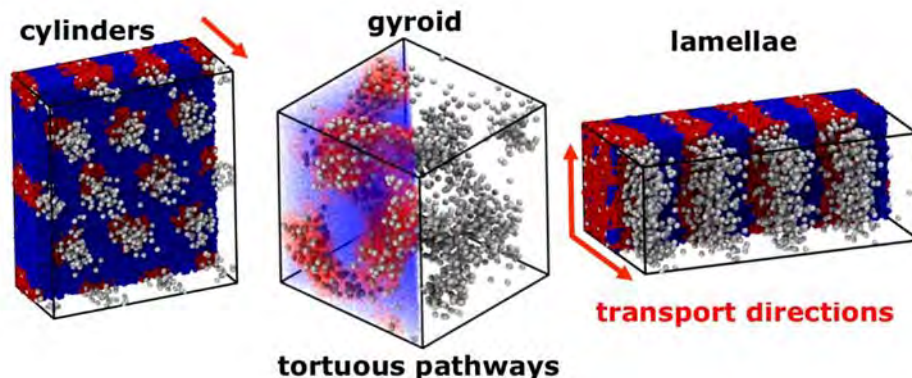
Figure 1. Radiopacity of iodine-incorporated PCL. PCL: polycaprolactone; PCL-5I: PCL infused with 5 mg of iodine; PCL-15I: PCL with 15 mg of iodine

POLY 282: Effects of morphology on diffusion through block copolymers from coarse-grained modeling

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Microphase separating copolymers are attractive for transport applications because one microphase can carry ions or small molecule penetrants, while another provides mechanical strength or other desired properties. Here, we use coarse-grained modeling to understand transport of selective small molecule penetrants in AB diblock copolymers. These copolymers are known to form a variety of microphases including lamellae, bicontinuous network morphologies such as the double gyroid phase, and hexagonally packed cylinders, depending on the segregation strength and composition. Being bicontinuous, the double gyroid phase intuitively seems advantageous for transport applications, though many authors have noted that randomly oriented grains of lamellae can also allow for transport in three dimensions, and the transport pathways are tortuous in either of these structures. Unfortunately, the gyroid phase is harder to access as it is favored in a narrow composition window, and it has been relatively less studied than the lamellar phase for ion conduction applications.

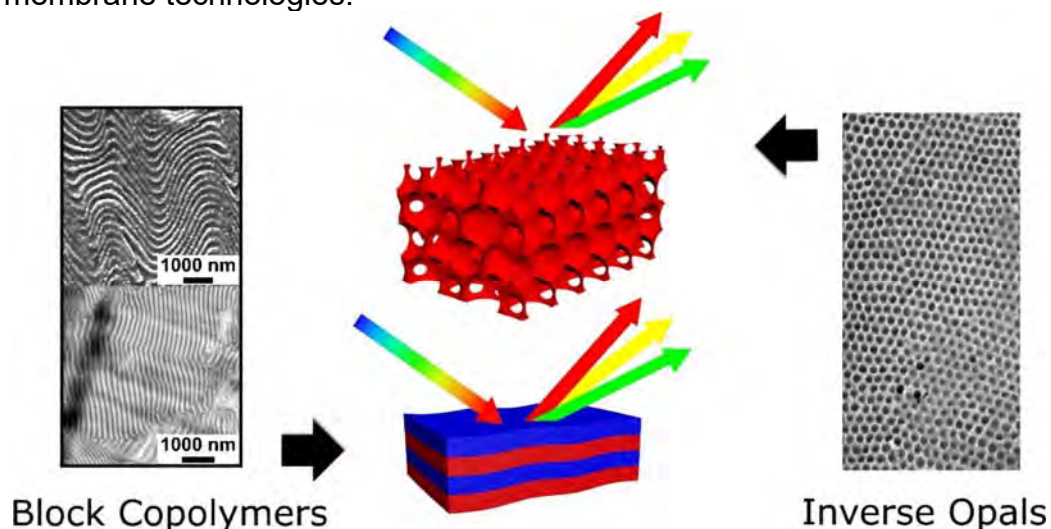
At moderate segregation strengths, our modeling yields the expected result that penetrants diffuse through aligned lamellae or hexagonally packed cylinders with a similar diffusion constant as in the analogous homopolymer (meaning that the overall diffusion constant would be approximately $1/3$ for randomly oriented cylinders and $2/3$ for randomly oriented lamellae). This result is constant across the composition range over which we find stable cylinders and lamellae. However, diffusion through the gyroid phase is reduced versus the homopolymer by an amount that depends on volume fraction. When the conductive polymer makes up the minority of the double gyroid phase, we predict the overall diffusion constant is always lower than that of the analogous lamellar system.



POLY 283: Self-assembly of stimuli-responsive polymers for optical sensing materials and smart porous membranes

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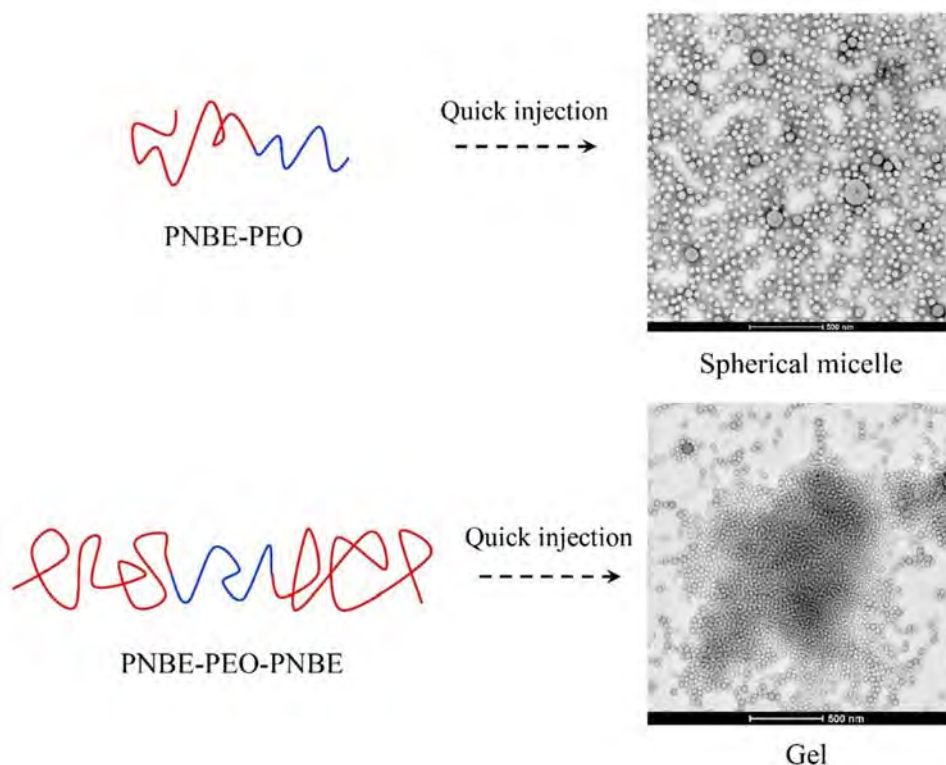
In the last decade stimuli-responsive block copolymers (BCPs) have proven their utility for a range of important applications. These polymers are capable of changing their conformation, solubility, or even of breaking or forming covalent bonds upon, for instance, a change of temperature or pH value, light irradiation, electrochemical stimuli or the presence of an electrical or magnetic field. The presentation will focus on materials, which contain at least one selectively addressable segment, either chemically or physically. Porous nano structures based on functional BCPs as well as recent advances in inverse opal films prepared by using the so-called melt-shear organization technique will be highlighted and discussed in more detail. As another highlight, ultra-high molecular weight (UHMW) BCPs were prepared via an innovative synthetic concept using anionic copolymerization and it will also be demonstrated that despite the one-step approach, strongly segregated materials with highly ordered lamellae on the order of 100-200 nm were obtained. Optical properties, *i.e.*, intense structural colors resulting from Bragg scattering at these thick lamella (or spherical domains) will be demonstrated for these self-assembled BCPs. In the case of soft colloidal crystal and inverted structures, which are also referred to as *polymeric opals*, applied external triggers lead to a remarkably fast and reversible change of their intriguing optical properties. A great benefit of opal structures by the melt-shear organization is their inexpensive and convenient preparation giving a good optical performance with iridescent reflection colours caused by Bragg diffraction. The talk will give some recent examples for the rational design of functional pure organic as well as hybrid porous materials with hierarchical architectures. Some of the presented polymer or polymer-templated structures can be advantageously used for direct conversion into ordered ceramic or carbonaceous materials. Herein presented functional materials are interesting candidates for a manifold of applications in the field of optical sensing and robust membrane technologies.



POLY 284: Synthesis and colloidal self-assembly of PNBE-PEO amphiphilic block polymers

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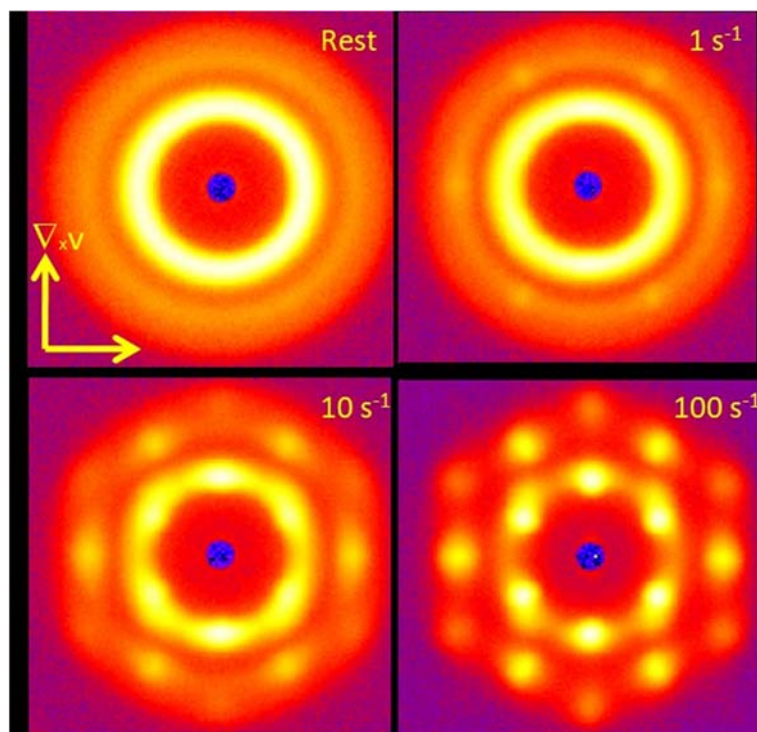
Block polymers are becoming widely used in biomedical applications. They have been used as drug carriers, prosthetic materials, tissue engineering substrates, medical membranes, and other biomedical materials. In this study, we have developed a new class of amphiphilic block copolymers combining two different controlled polymerization methods: ROMP (ring-opening metathesis polymerization) and living anionic polymerization. Using this newly developed synthetic strategy, we were able to synthesize poly(norbornene)-block-poly(ethylene oxide) (PNBE-PEO) diblock copolymers and poly(norbornene)-block-poly(ethylene oxide)-block-poly(norbornene) (PNBE-PEO-PNBE) triblock copolymers. These polymers have precisely controlled molecular weights and polymer block fractions, which is crucial for self-assembling desired colloidal nanostructures. We found that the diblock copolymer undergoes self-assembly in water to form a range of nanostructures including spherical micelle, worm-like micelle and vesicles at different concentrations. The triblock copolymer forms physically crosslinked gel structures. The nanostructured material presented may be further used in applications related to drug delivery, templated synthesis, or membrane separations.



POLY 285: Impact of external fields on structural transitions in diblock and triblock copolymer aqueous solutions

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Low molecular weight diblock and triblock polymers in selective solvents form disordered micellar phases at low concentration and liquid crystal phases at high concentration (or low solvent to amphiphile molar ratio in the case of water). The energetic barriers between different lyotropic states and structures are large enough for systems to become kinetically trapped, but low enough for weak external fields to alter the nanoscale structure. We have been able to align ordered structures and anneal out defect texture in polycrystalline materials. Results for two different block copolymers in aqueous solution will be shown and rheological features correlated with structural measurements (through SANS and SAXS). The use of weak shear fields to align lyotropic structures and then transition to other low and high symmetry structures will be demonstrated.

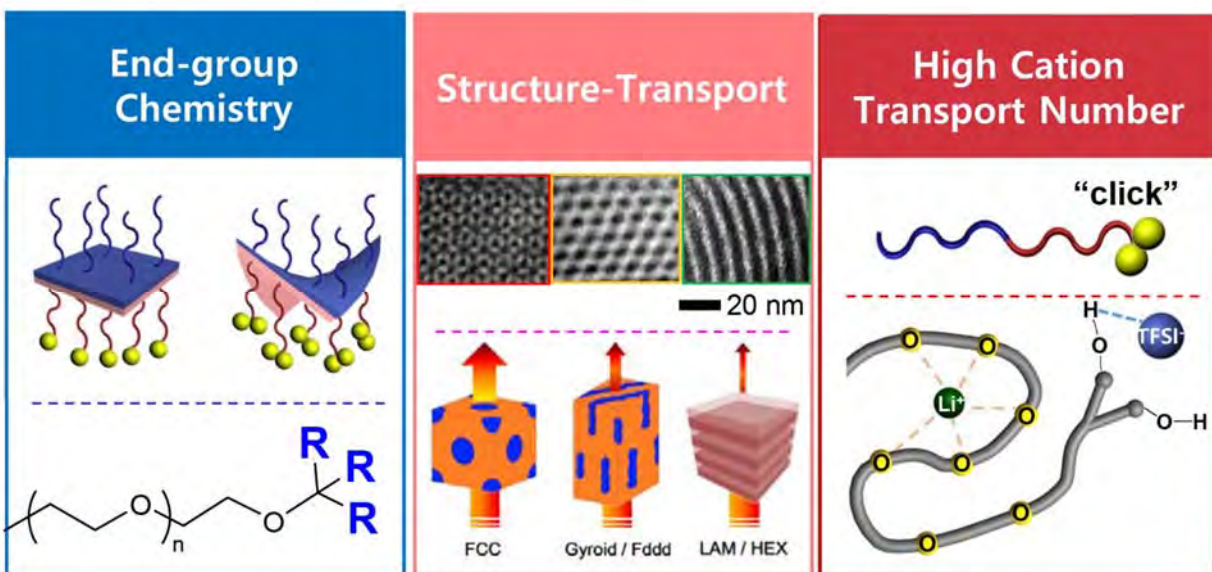


Shear alignment of nanostructured solutions of block copolymer micelles. Micelles form a cubic phase with defect texture; this texture can be annealed to a near single crystal with simple shear.

POLY 286: Design rules of efficient ion conducting polymers: From block copolymers to single-ion polymers

Moon Jeong Park, moonpark@postech.ac.kr. Chemistry, Pohang Univ. of Sci. & Tech., Albany, California, United States

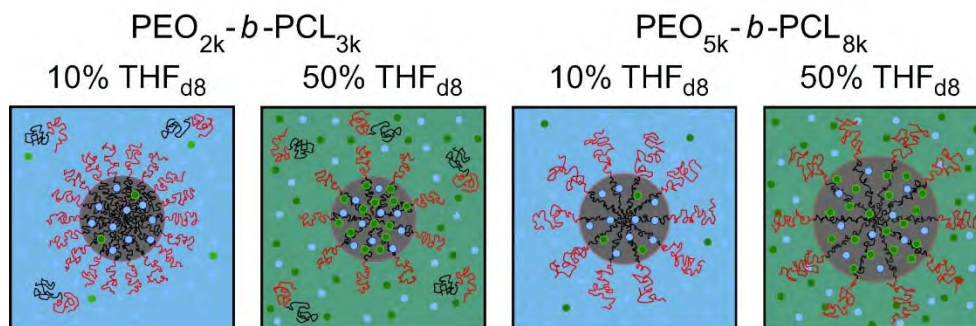
Over the past few decades, extensive research efforts have been devoted to various ion conducting materials. Although the substance of interest is different, the goal is the same as the achievement of high ionic conductivity via the creation of well-defined, less tortuous ionic channels in mechanically stable supports. In addition to that, the suppression of anion diffusion in such materials becomes increasingly important in recent years as it is connected to the device polarization with applied dc voltages. In this talk, I would like to present various strategies of enhancing ion transport efficiency in polymer electrolytes. First, the achievement of well-defined self-assembled morphologies with three-dimensional symmetries has proven to facilitate fast ion transport by constructing less tortuous ion-conducting pathways. Second, the inclusion of terminal ionic units was an effective means to control the nanoscale morphologies and conductivities of block copolymer electrolytes. Third, the addition of zwitterions selectively into nanoscale ionic domains offered a polar medium close to water, and accordingly increased the charge density and ionic conductivity. Fourth, the development of crystalline ionic channels in amorphous polymer matrix enabled us to fine-tune the dipolar interactions among ionic moieties as well as facilitated fast ion transport with low potential barrier. Our work should build up a new platform for highly efficient ion conducting materials and can find applications in various electrochemical devices.



POLY 287: Tunable structural properties of block copolymer micelles

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Block copolymer micelles enable the formation of widely tunable self-assembled structures in liquid phases, with applications ranging from drug delivery to personal care products to nanoreactors. In order to understand fundamental aspects of micelle assembly and dynamics, the structural properties and solvent uptake of biocompatible poly(ethylene oxide-*b*- ϵ -caprolactone) (PEO-PCL) diblock copolymers in deuterated water (D₂O) / tetrahydrofuran (THF_{d8}) mixtures were investigated with a combination of small-angle neutron scattering, nuclear magnetic resonance, and transmission electron microscopy. PEO-PCL block copolymers, of varying molecular weight yet constant block ratio, formed spherical micelles through a wide range of solvent compositions. Varying the solvent composition from 10 to 60 % by volume THF_{d8} in D₂O / THF_{d8} mixtures was a convenient means of varying the core-corona interfacial tension in the micelle system. An increase in THF_{d8} content in the bulk solvent increased the solvent uptake within the micelle core, which was comparable for the two series, irrespective of the polymer molecular weight. Whereas the smaller molecular weight micelle series exhibited a decrease in aggregation number with increasing THF_{d8} content in the bulk solvent, as anticipated due to changes in the core-corona interfacial tension, the aggregation number of the larger molecular weight series was surprisingly invariant with bulk solvent composition. Differences in the dependencies of the micelle size parameters (core radius and overall micelle radius) on the solvent composition originated from the differing trends in aggregation number for the two micelle series. In summary, the two micelle series showed similar solvent uptake that was independent of the polymer molecular weight, yet significantly different dependencies of their aggregation number and size parameters on the solvent composition.

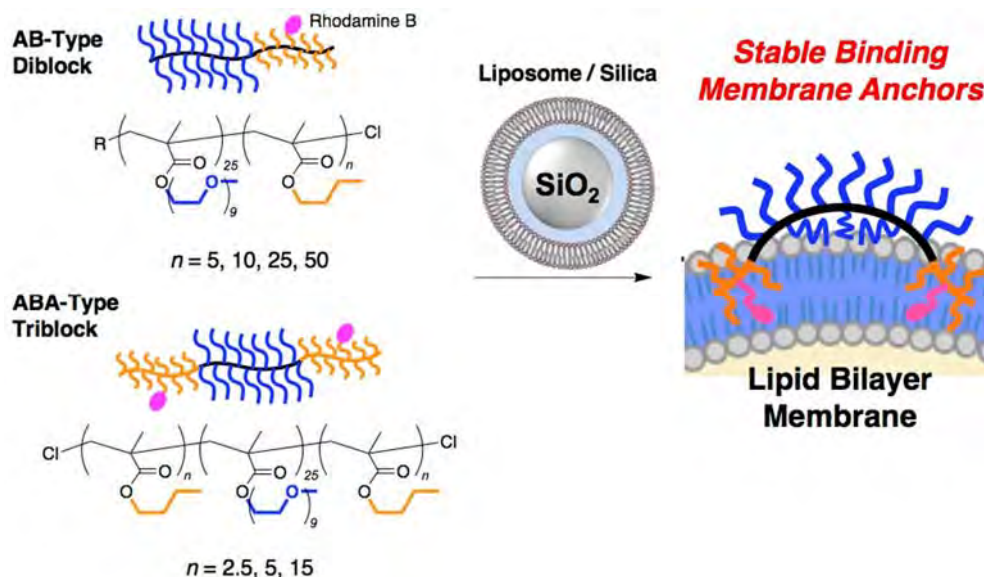


Structural changes in block copolymers micelles with varying solvent composition and polymer molecular weight.

POLY 288: PEGylated amphiphilic block copolymers as membrane anchors for controlled affinity to lipid bilayer membranes

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Cell surface engineering has promise to develop biomedical applications such as cell therapy, drug delivery system, bio-imaging and tissue engineering if decorating living cells by artificial functional molecules is possible. Artificially to functionalize cell surface toward those applications, synthetic molecules as membrane anchors need to be designed, and the synthetic molecules must stably bind onto lipid bilayer membrane of cell surfaces. To design such synthetic molecules, amphiphilic block copolymers were prepared via living radical polymerization, and were applied to membrane anchors on liposomal lipid bilayer membrane as the model of cell surface [figure1]. AB- and ABA-type amphiphilic di- and triblock copolymers were synthesized with poly(ethylene glycol) and butyl methacrylates (PEGMA, BMA) by ruthenium-catalyzed living radical polymerization. Owing to the high controllability, the amphiphilic block copolymers with narrow molecular distribution were gained ($M_n = 14000 - 20000$ g/mol, $M_w/M_n = 1.09 - 1.28$). Those block copolymers were soluble in water to form spherical self-assembled structures ($R_H = 2.7 - 26$ nm). To clear the affinity between those copolymers and lipid bilayer membrane, the effect of the primary structure on the affinity was investigated with liposome/silica nanoparticle composites as the model of cell surface. As the result, ABA-type triblock copolymers efficiently bound onto the liposomal surface, compared to the AB-type diblock copolymers. Therefore, the affinity of amphiphilic block copolymers to liposomal lipid membrane, and our investigation would contribute to the development of stable binding membrane anchors for cell surface engineering.

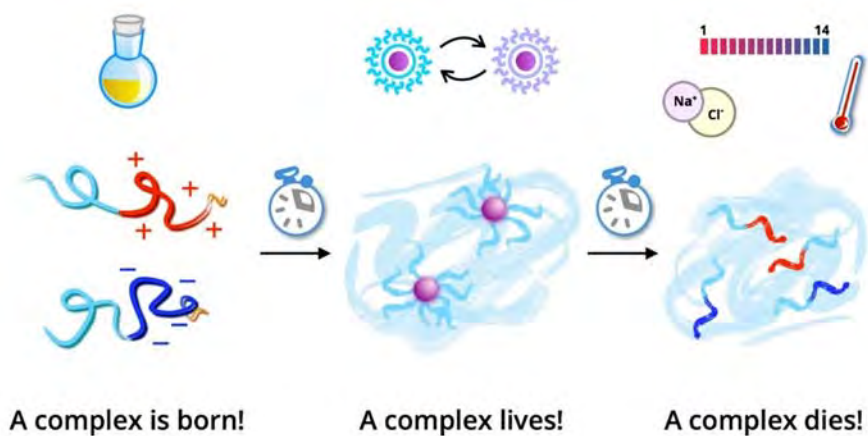


PEGylated Amphiphilic Block Copolymers as Membrane Anchors to Liposomal Lipid Bilayer Membranes

POLY 289: Life of the polyelectrolyte: Complexation, evolution, and disassembly

Jeffrey Ting, *tingx030@umn.edu*, Hao Wu, Matthew V. Tirrell. Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Polyelectrolytes are macromolecules with a substantial fraction of ionizable monomeric building blocks. When constructed into blocky architectures, oppositely-charged polyelectrolyte chains can self-assemble into micellar nanoparticles in water and respond to environmental changes in pH, salt, and temperature; these tunable features have motivated concerted efforts to integrate such materials into a diverse host of bioapplications, ranging from therapeutic polyplexes for delivering genetic payloads to soft underwater adhesives for repairing tissues between skin and bones. However, understanding how to balance the chemical and electrostatic interactions in charged structures has proven to be a longstanding unresolved problem for functional utility, where stable assemblies must be (1) produced with consistent repeatability, and (2) capable of exhibiting controlled storage/release. In pursuit of these goals, we report detailed insight into the fundamentals of solution complexation, evolution, and disassembly from a molecular engineering perspective. In a carousel parallel synthesizer, libraries of well-defined block polycations and polyanions were prepared at various neutral-to-charge chain lengths using aqueous reversible-addition fragmentation chain transfer (RAFT) polymerization. The structural assembly and ordering of model diblock and triblock systems were investigated using complementary small angle X-ray/neutron scattering and rheology; we further labeled individual polyelectrolyte chains with fluorescent tags to study the solution dynamics of complexation. At low concentrations, kinetically-trapped nanoaggregates were observed in certain systems, which enabled the opportunity to explore the role of salt in processing charged micelles. The temporal breakup of equilibrating micelles was monitored with time-resolved light scattering and cryogenic transmission electron microscopy, elucidating characteristic relaxation times of different pairings of polyelectrolytes. This fusion/fission phenomenon of complex-core micelles in response to salt evokes interesting, analogous comparisons to how temperature anneals non-equilibrium amphiphilic micelles.

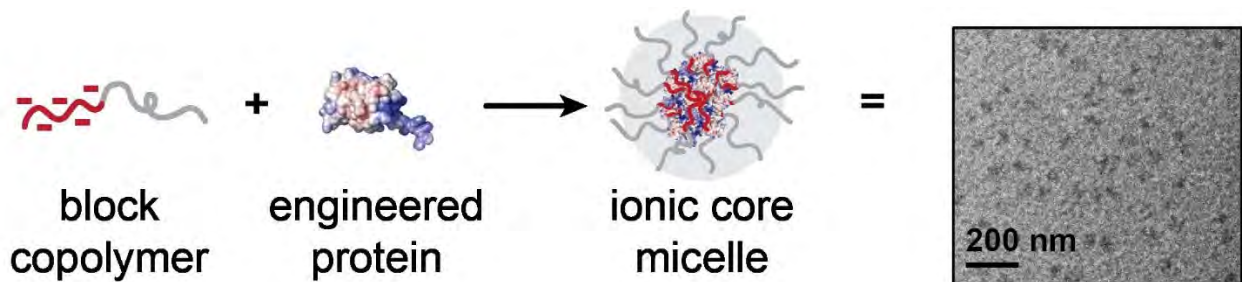


POLY 290: Ionic core micelles from block copolymers and engineered proteins

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Chemical Engineering, Columbia University, New York, New York, United States*

Encapsulation of proteins in micelles formed via liquid-liquid phase separation (LLPS) is a promising method to stabilize proteins of interest, from enzymes to therapeutics. The liquid-liquid phase separation of a globular protein with an ionic block copolymer results in a high density of proteins in the core of the resulting micelle. This highly ionic, hydrated environment stabilizes the protein component during storage, but upon a change in solution pH or ionic strength can release the unmodified protein.

We have evaluated the formation and stability of ionic core micelles with a panel of engineered proteins and neutral-ionic block copolymers. The micelles were characterized by dynamic light scattering and electron microscopy. The impact of polymer properties on protein encapsulation and stability in the micelles has been investigated to determine the optimal design parameters for protein formulation in ionic core micelles.

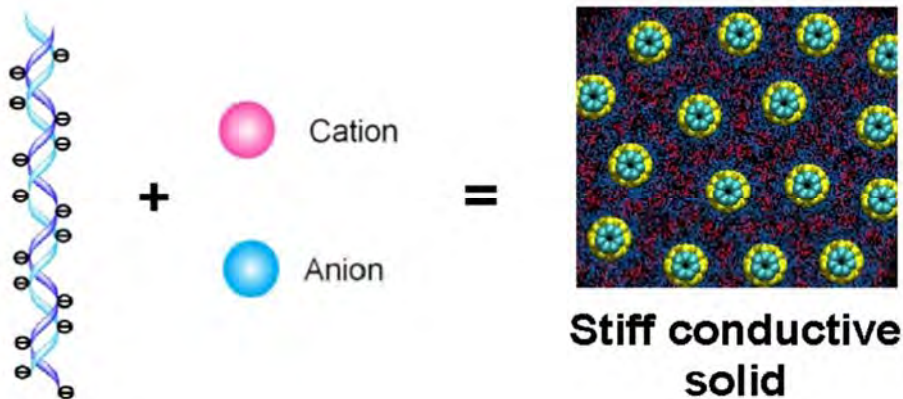


POLY 291: Double helix polyanion plus ionic liquid: Molecular ionic composites

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The collective summation of many non-covalent interactions can enable emergent bulk material properties. I will describe a solid material that simultaneously possesses high mechanical stiffness as well as free (liquid-like) ion motions. We build this material from a rigid ionic polymer and an ionic liquid. We call this new class of materials “molecular ionic composites” (MICs).

In a MIC, the sulfonated aramid polyanion (figure, left) forms a double helix that provides extreme axial rigidity (persistence length > 100 nanometers). Combining this polymer with an ionic liquid (figure, center) yields a stiff solid that can be called an ion gel. However, this solid ionic material relies on a new mechanism for mechanical cohesion – a collective electrostatic network (figure, right). Each double helix polyanion is held firmly relative to its neighbors by thousands of weak inter-ionic interactions. MICs possess high stiffness (E' up to 3 GPa), high thermal stability (up to 300 deg. C), and high conductivity (up to 8 mS/cm). This talk will overview our attempts to understand and design the behaviors of MICs from atomic to bulk length scales. I will also discuss promising results that point toward safe and high energy density alkali-metal batteries in which we have incorporated > 3 M Li^+ or Na^+ into MICs. In addition to battery applications, this new class of materials promises to facilitate optimization of properties for a host of other molecular separations applications.



POLY 292: Nanoscale resolution of electric-field induced motion in ionic copolymer films

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Understanding the mechanisms of electromechanical response on the nanoscale would greatly benefit the development of electroresponsive polymers for energy storage, actuation, and biomedical applications. In order to better design electroresponsive polymeric systems, the characterization of a material's response to an electric field *in situ* with subnanometer resolution is needed. Such a characterization provides a deeper understanding of how nanoscale interactions contribute to the electromechanical response. This talk will highlight the use of in situ voltage modulated atomic force microscopy (VM-AFM), neutron reflectometry measurements collected under applied electric fields and complementary coarse grained molecular dynamics simulations to provide nanoscale resolution of polymer and counter-anion motion in thin films. As a model system, a polymerized ionic liquid based diblock copolymer (PIL-BCP) containing a cationic, imidazolium block and a deuterated styrene block was synthesized. The relative contributions of each block and the counter anion on film deformation were observed and analyzed. These results emphasize the potential of coupling in situ techniques that can achieve nanoscale resolution in investigating the electromechanical response of polymeric systems in thin film geometries. These developments have exciting applications in the development of energy storage systems as well as the fabrication of actuating devices, where counter ion size and its polarizability can be used to tune electromechanical properties.

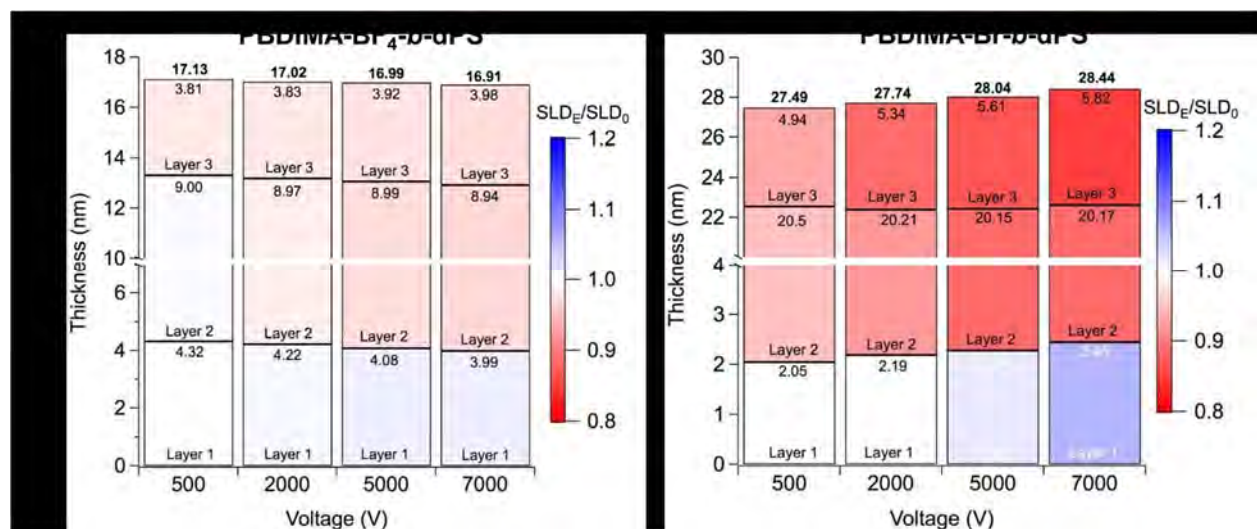
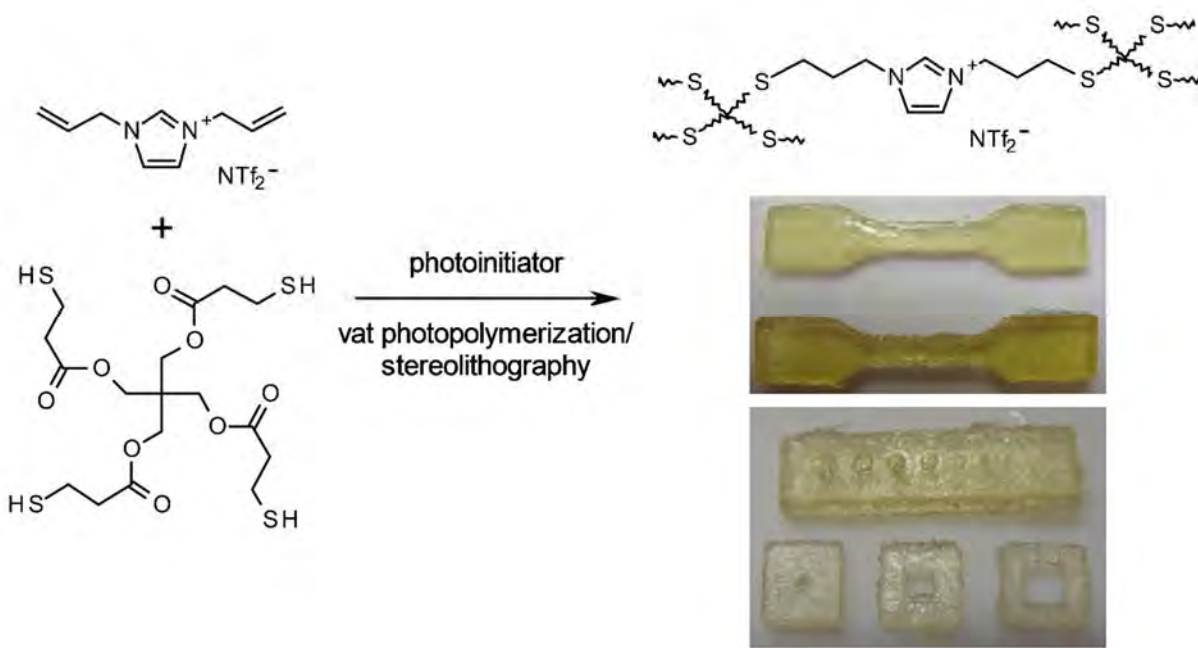


Figure 1. Changes in thickness and scattering length density for PIL-BCP with BF₄ (left) or Br (right) counter ions as a function of applied electric field strength.

POLY 293: 3D-printed imidazolium-containing thiol-ene poly(ionic liquid) networks

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The application of polymerized ionic liquids has been explored across a number of areas due to their tunable thermomechanical and conductive properties. 3D printing offers a way to manufacture such polymeric materials into complex geometric designs suited to applications including from batteries, ion/gas separation devices, and microfluidics. To that end, our research group is reporting thiol-ene 'click' photochemistry as a route to such fabrication using a commercially-available stereolithographic 3D printer (Formlabs Form 1+). In short, a basic "neat" resin was prepared from ion-containing ene monomers (bisallylimidazolium [NTf₂]⁻ and others), a commercially-available thiol-containing crosslinker, and a suitable photoinitiator. Parts of various geometries and sizes were successfully printed and their thermal, mechanical and conductive properties were measured in comparison with analogous materials made from non-3D printing UV curing. Furthermore, the overall print quality as specified by resolution and dimensional tolerances were also determined. Based on initial results from the "neat" resin, variables such as resin viscosity, monomer ratio, print/cure speed, and the inclusion of light-blocking additives were investigated to determine how they impact both the printing process and end-material properties. While thiol-ene photochemistry has been utilized to prepare non-ionic materials via 3D printing and stereolithographic techniques, the technology has not been applied, to the best of our knowledge, to the printing of electroactive materials.



POLY 294: Beyond spherical assemblies of hyperbranched poly(ionic liquid)s

Volodymyr Korolovych¹, volodymyr.korolovych@mse.gatech.edu, Andrew J. Erwin¹, Hansol Lee¹, Alexandr Stryutsky³, William Heller², Valery Shevchenko³, Leonid Bulavin⁴, Vladimir V. Tsukruk¹. (1) Materials Science and Engineering, Georgia Institute of Technology, Knoxville, Tennessee, United States (2) Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine (4) Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

Hierarchically structured assemblies of poly(ionic liquid)s with different morphology, arrangement of ionic liquid groups and response to external stimuli are the critical to energy storage, electrochemistry, catalysis and development of programmable interfaces. In this study, we analyzed the assembly of a new library of amphiphilic poly(ionic liquid)s with linear and hyperbranched architectures based on hydrophobic polyester fragments and peripheral hydrophilic ammonium carboxylates in aqueous media. The novel thermally responsive poly(ionic liquid)s were synthesized by neutralization of terminal carboxyl groups of polycarboxylic acids by amine terminated poly(N-isopropylacrylamide) (PNIPAM) to create temperature-sensitive shells. The low critical solution temperature (LCST) of poly(ionic liquid)s with linear and hyperbranched architecture increased for compounds with greater NIPAM content but is consistently lower than that for linear counterparts. We found that the poly(ionic liquid)s with linear architecture form micellar assemblies with a variety morphologies, such as unimolecular micelles and micelle aggregates at the variation content of outer PNIPAM macrocations. At the same time, hyperbranched poly(ionic liquid)s form smaller micelle aggregates. Moreover, we found network-like or spherical aggregates, vesicles and spherical particles and suggested multi-length scale hierarchical model and corresponding assembly transformations during phase transitions associated with abrupt changes in hydrophobic-hydrophilic balance of thermoresponsive polyionic liquids.

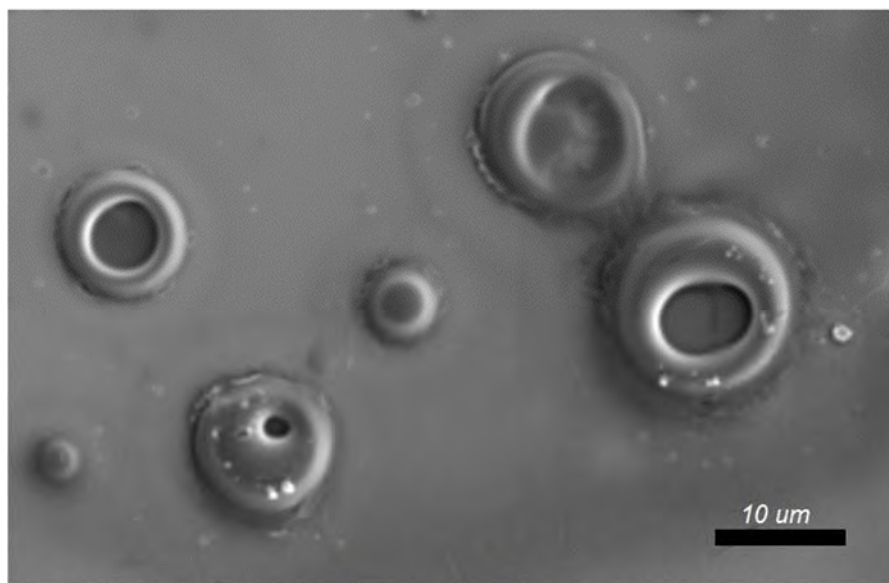
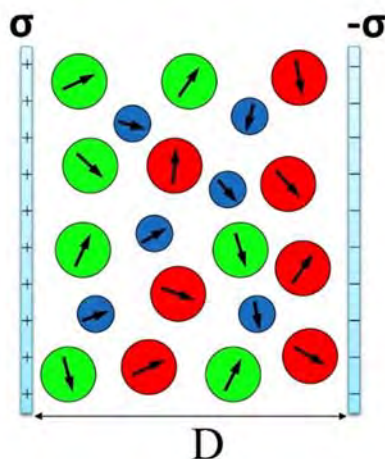


Figure. SEM images of poly(ionic liquid)s solution drops deposited on silicon wafer.

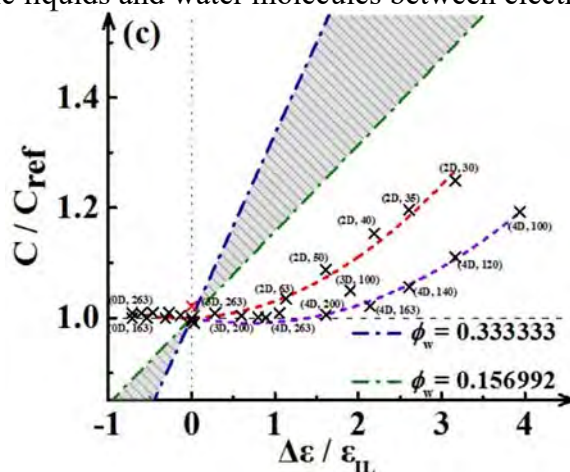
POLY 295: Water dissolution in ionic liquids between electrodes: Effects of dielectric inhomogeneity and electrostatic correlation

Issei Nakamura¹, inakamur@mtu.edu, Hongbo Chen^{1,2}, Lijia An². (1) Physics, Michigan Technological University, Houghton, Michigan, United States (2) Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Jilin, China

A recent atomistic molecular dynamics simulation suggested that water molecules in ionic liquids are significantly adsorbed onto electrodes, but an understanding of this mechanism is limited. To clarify the simulation data, we highlight the effects of the dielectric contrast among the species by developing the mean-field theory that accounts for molecular polarization. We then demonstrate that polar molecules such as water may be enriched in the vicinity of electrodes and even markedly bound onto the charged surfaces when the electrostatic correlations are combined. Furthermore, we show that the energy efficiency may be improved through tuning the dielectric contrast within a certain range of the applied voltage.



Ionic liquids and water molecules between electrodes



Capacitance vs. the dielectric contrast between the water and ionic liquid (Hongbo Chen, Lijia An, and Issei Nakamura, *Mol. Syst. Des. Eng.*, 2018: <http://dx.doi.org/10.1039/C7ME00119C>)

POLY 296: Self-propelled motion of ion gel at surfaces and interfaces

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We recently reported that a gel composed of an ionic liquid and a polymer (ion gel) shows a powerful and durable self-propelled motion at air-water interface.¹⁾ This is a new characteristic of an ion gel, in addition to its known applications as gate insulators and solid electrolytes. The combination of ionic liquid and polymer is diverse. Their self-propelled properties, however, have not been investigated. The ion gel we reported is composed of 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) and poly(vinylidene fluoride-co-hexafluoropropylene). Based on this knowledge, we study self-propelled properties of ion gels with different alkyl-chain length on the cation, RMIM (R = C₂H₅:**1**, C₆H₁₃:**2**, C₁₀H₂₁:**3**, C₁₂H₂₅:**4**, C₁₆H₃₃:**5**).

The ion gel (iG) **1-5** are cut into long rectangular pieces which are then placed on various surfaces and interfaces. In most cases, they exhibit rotational self-propelled motion. The edge velocities are summarized in Table 1.

On H₂O surface, self-propelled motion is observed for iG**1** and **2**, but not for iG**4** and **5**. The motion is driven by Marangoni effect caused by the elution of the ionic liquid (IL) from the iGs. Thus the tendency at H₂O surface is correlated to the solubility of IL**1-5** in H₂O. Next we test on CHCl₃, in which all ILs are well soluble. However, no iG in this study shows self-propelled motion on CHCl₃ surface.

At H₂O/CHCl₃ interface, iG**5** shows powerful self-propelled motion, although it moves neither on H₂O nor CHCl₃. We think IL**5** eluted to the H₂O/CHCl₃ interface plays a critical role: IL**5** molecules eluted to CHCl₃ at the interface interact with H₂O in close proximity to generate a difference in surface tension in H₂O side. To support our idea, we observe self-propelled motion at interface between C₆H₁₄, a solvent all ILs are insoluble, and H₂O. The results show that iG**5** no longer shows the motion: only the iGs containing IL soluble in H₂O show the motion.

Surface/Interface \ Ion gel	1	2	3	4	5
Air/H ₂ O	160	54*	-	×	×
Air/CHCl ₃	×	×	×	×	×
H ₂ O/CHCl ₃	130	64	57	63	93
C ₆ H ₁₄ /H ₂ O	120	58	6	×	×
Solubility in H ₂ O (wt%)	1.8	0.2	0.1	0.0	0.0

*: translational motion

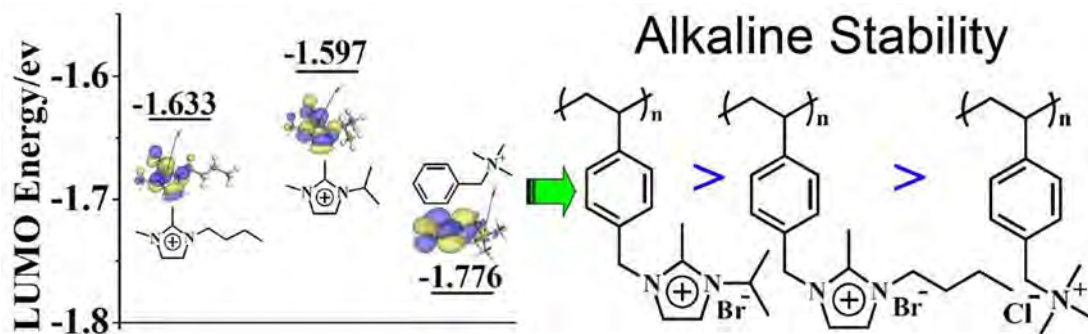
Table 1. Edge velocity (mms⁻¹) in self-propelled rotation motion of ion gel at surfaces and interfaces with solubility of ionic liquid in H₂O.

POLY 297: Poly(ionic liquid) membranes: Synthesis & applications

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ABSTRACT

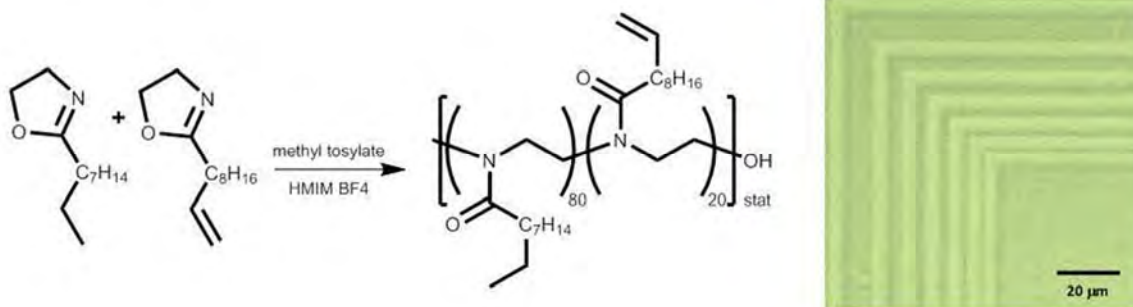
Ionic liquids (ILs) are attracting significant attention in many fields of chemistry and industry because of their unique physicochemical properties, such as negligible vapor pressure, low volatility, high thermal stability and ionic conductivity. Recently, the number of polymerizable ILs is steadily increasing, and ionic polymers of polymerizable ionic liquid monomers have been produced as exotic polyelectrolytes.¹⁻³ This talk will report our recent results on the poly(Ionic Liquid) membranes for anion-exchange membrane, stimulus-responsive functional material and antibacterial applications.



POLY 298: Ionic liquids as (recyclable) reaction media for the synthesis of poly(2-oxazoline)-based photoresists from renewable resources

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Photoresists have a broad range of applications in particular in the semiconductor industries. Preceded by the formulation of a water-developable poly(2-oxazoline)-based photoresist, this study addressed the synthesis of a copoly(2-oxazoline)-based photoresist derived from renewable resources. The corresponding 2-oxazoline monomers were synthesized from the reaction of undecenoic acid (derived from castor oil) and decanoic acid (derived from coconut oil), respectively, with ethanol amine. The copolymerization itself was performed at a scale of 250 g under microwave irradiation in the ionic liquid n-hexyl methylimidazolium tetrafluoroborate, in the course of which the IL acted as prime absorber of microwave irradiation. While both types of 2-oxazoline monomers are soluble in the IL, the copolymer precipitated from the IL upon cooling, enabling the straight-forward recovery and purification of the copolymer and the IL. Both, the copoly(2-oxazoline) as well as the IL, were recovered in quantities of 95%; the weight dispersity of the polymer was 1.34. The photoresist could be formulated (and developed) in ethyl lactate. Crosslinking of the copolymer was realized by UV-induced thiol-ene reactions of the polymer and the tetrathiol pentaerythritol-tetra-(3-mercaptopropionate), providing resolutions of the photoresist higher than 1 μm after development.



Structural formula of the copoly(2-oxazoline) (left); resist after UV-induced crosslinking of the polymer with a tetrathiol and development in ethyl lactate (right).

POLY 299: Hydrogen bonded silicone rubber: A new additive improving self-healing

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Silicones are mainly used in the industry for their good mechanical and insulation properties at elevated temperature. Unfortunately to bring rigidity to these materials, a vulcanization step is occurring during the synthesis resulting in non-healable materials. The aim of this study is to reduce the impact on the environment, by saving a vulcanization step, allowing recycling and self-healable silicones.

To avoid the chemical crosslinking step we focused our work on supramolecular modified silicone compounds previously investigated by Yilgor et al and commercialized by Wacker under the name GENIOMER®. These systems (Figure 1) contain hard segment (HS) which interact by hydrogen bonding alternated by silicone soft segment (SS). The large difference of solubility parameters of both segments creates a microphase separation. These compounds exhibit good thermal and mechanical properties but no healing at room temperature.

The main challenge of this project is to manage the balance between rigidity and chains dynamics allowing self-healable materials with good mechanical properties. In this context we have synthesized and added to supramolecular silicone formulations a new additive. The addition lowers a little material rigidity (which could be compensated by addition of fillers), but brings self-healing abilities at room temperatures to those materials (Figure 2).

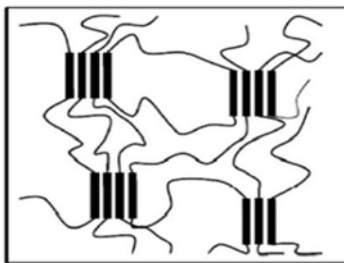


Figure 1: Schematic representation of intermolecular interaction in silicone-urea copolymers

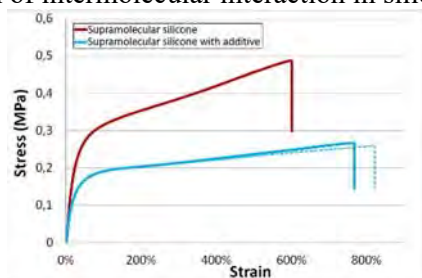
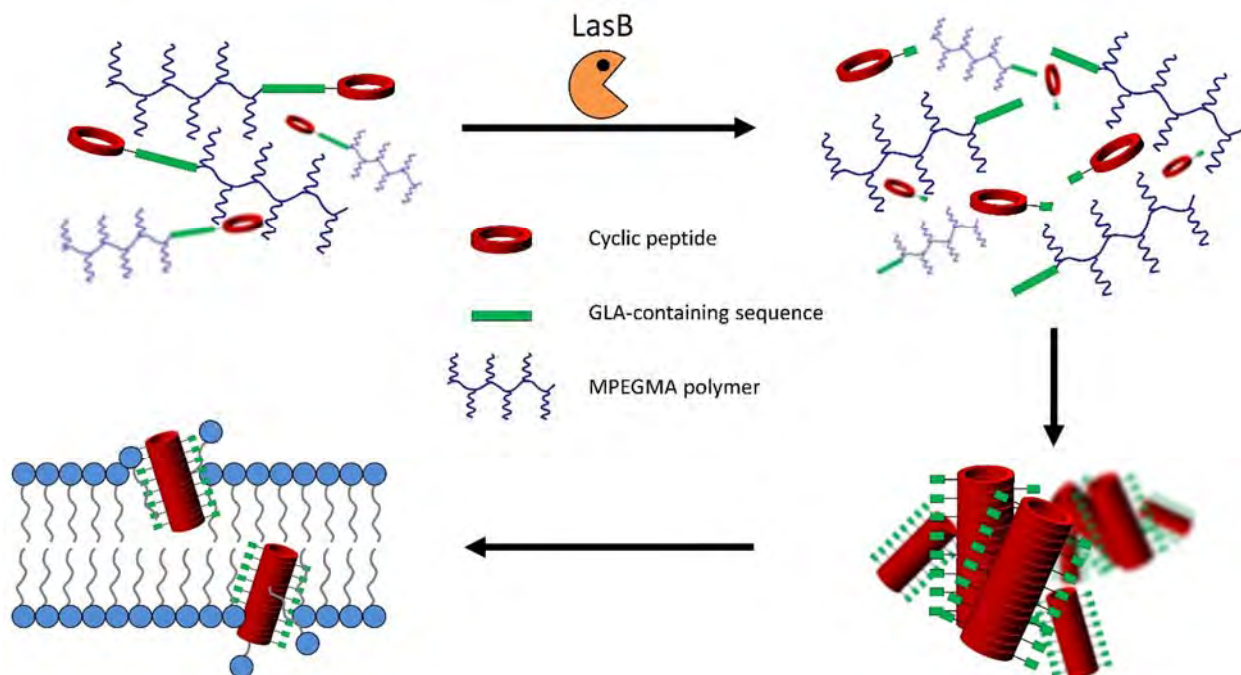


Figure 2: Stress-strain curves for a supramolecular silicone (red) and the silicone with the additive (blue). Dotted line represents the healed sample after 24 hours at room temperature

POLY 300: Synthesis of LasB-stimulus-responsive cyclic peptide-polymer-conjugates as potential antimicrobials to combat multi-drug resistant *P. aeruginosa* infections

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The rapid increase in the occurrence of multi-drug resistant bacteria emphasizes the need for therapeutic alternatives to commonly available antibiotics. Cyclic peptides (CP's) with an even number of alternating D- and L- α -amino acids can self-assemble via β -sheet stacking into rod-like nanotubes with distinct properties. These cyclic peptide nanotubes (CPNT's) appear to be a promising class of potential antimicrobials. However, a major drawback is their lack in selectivity regarding the cell membrane disruption. In this work, a bulky polymethacrylate (p(MPEGMA)) bottle brush copolymer was attached to CPs via a stimulus-responsive linker to decrease non-specific toxicity towards mammalian cells. The linker exhibits a GLA-peptide sequence which can be cleaved selectively by the virulence factor *P. aeruginosa* elastase (LasB) that is secreted in case of an infection. Hence, the selectivity is supposed to be enhanced without loss of antimicrobial activity. The brush-shaped polymer solubilizes the conjugate and prevents the nanotube formation prior to the cleavage. The targeted conjugates were synthesized and SLS measurements showed that no self-assembly occurs when the polymer is still attached. Linker sequence, as well as the final conjugate were shown to be cleavable in the presence of LasB.



POLY 301: Gas-responsive self-assemblies for mimicking the alveoli

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Alveoli are the main parts of gas exchange in human body. It is a small vesicle structure formed by the expansion and protrusion of the bronchioles at the end of the lung. Studies have shown that inflammation of the alveoli causing swelling of the alveoli is an important cause of pneumonia, tuberculosis, or emphysema. Therefore, it is important to study the regulation mechanism of alveoli formation, respiration and apoptosis. A class of amphiphilic triblock copolymers, PEG-*b*-P(DEAEMA-*co*-PFMA)-*b*-PS were synthesized and self-assembly in aqueous solution. Because of the gas response segments, self-assemblies in the air underwent the morphology transition from nanotubes to vesicles; at the same time, the vesicles can further realize the volume expansion and contraction in alternating stimulation of carbon dioxide and nitrogen, eventually rupture. The system successfully simulated the process of formation, respiration and apoptosis of alveoli in different stages on the nanometer scale, and provided an important basis for exploring the phenomena of life.

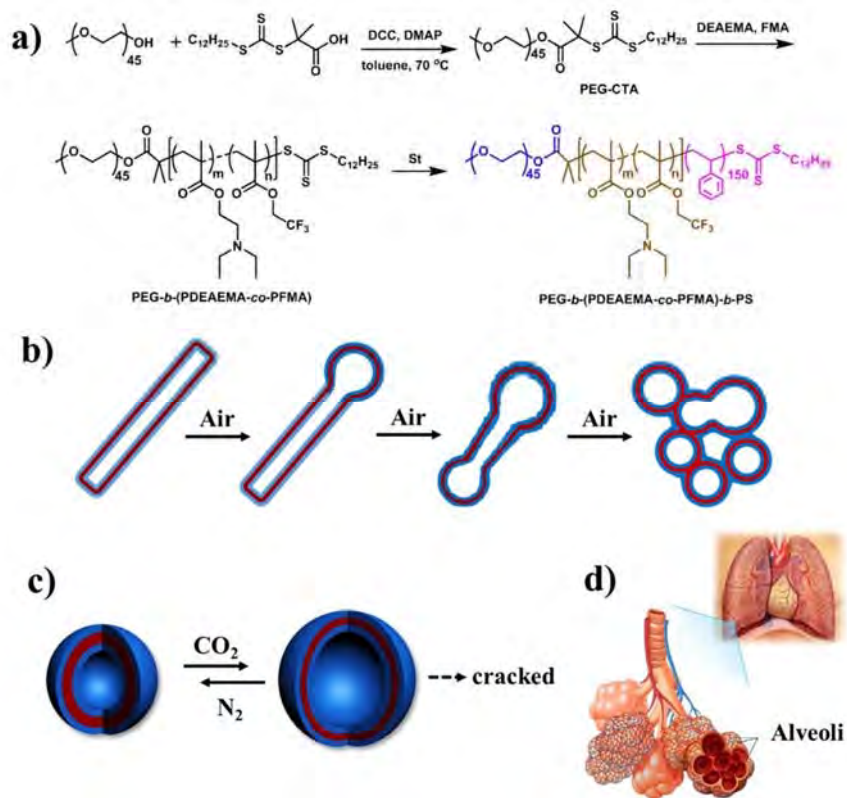


Figure 1. The synthesis of gas-responsive triblock copolymers.(a) Schematic of the shape regulation of different aggregates under air (b) and the breathing feature of vesicles under CO₂ bubbling (c). The formation of Alveoli.(d)

POLY 302: Construction and experimental validation of a dynamic kinetic model of photo-RAFT and photo-PISA

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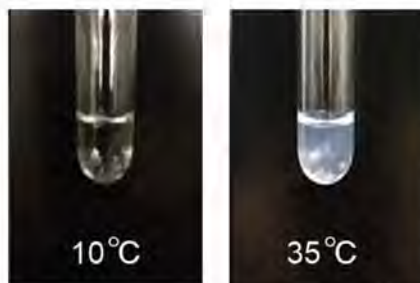
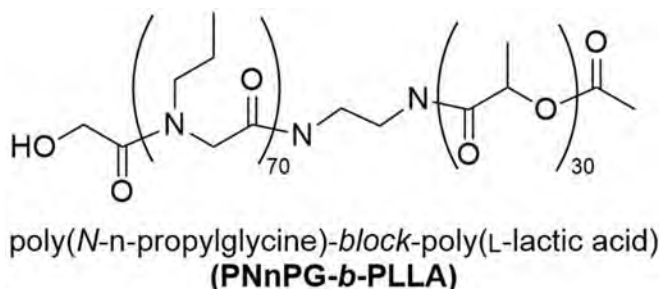
Amphiphilic block-copolymers can undergo self-assembly into a range of relevant morphologies (micelles, worms, vesicles...). Photo-RAFT and photo-PISA (polymerization-induced self-assembly) are experimentally proven technologies with convenient performance such as low operating temperature and narrow polydispersity of the resulting polymer blocks. In this work, we develop a novel dynamic model integrating photo-energy/electron-transfer kinetics with a standard model of the RAFT polymerization kinetics, as well as a convenient method for parameter estimation that only requires typically available experimental data. We have successfully validated the model and parameter identifiability methodology against experimental data for PEG-b-PHPMA block copolymer at different operation conditions. Finally, we will also discuss how the model proved useful even beyond its intended initial purpose.

Origins of Life Initiative

POLY 303: Development of thermo-sensitive polymer micelle for direct injection at the targeted tumor region

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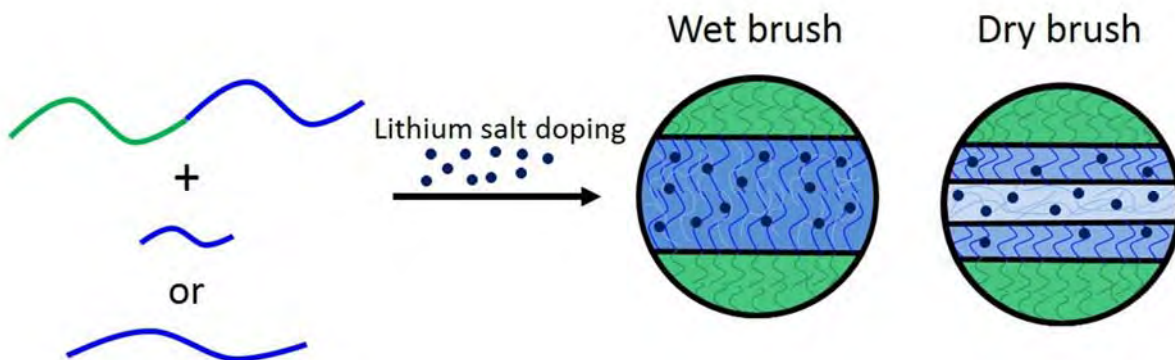
We have developed polymer micelle prepared from amphiphilic block polymer consisting from hydrophilic poly(*N*-methyl glycine) and hydrophobic poly(L-lactic acid) (PNMG-*b*-PLLA). The micelle shows better blood circulation behavior and can be used as carriers for drug delivery from intravenous injection. On the other hand, injectable thermo-sensitive hydrogels have attracted increasing attention for tumor therapies due to their long-term and effective drug levels at local sites. Depending on the purpose of the treatment, using these different two intravenous injection and local direct injection type carriers for drug delivery is important. In this study, based on the polymer micelle discussed above, a thermo-sensitive type micelle for direct injection was prepared from newly designed amphiphilic block polymer poly(*N*-*n*-propyl glycine)-*block*-poly(L-lactic acid), PNnPG-*b*-PLLA. PNnPG-*b*-PLLA was synthesized via *N*-carboxy anhydride (NCA) polymerization using PLLA as a macroinitiator, and polymer length on hydrophilic and hydrophobic chains determined by NMR were 70 mer and 30 mer, respectively. Micelle was prepared by injecting the polymer solution dissolved in acetone to the ice-cooled aqueous solution. Diameter of the micelle measured by DLS was 50-60 nm, which was almost the same size with non-thermo-sensitive micelle from PNMG-*b*-PLLA. The micelle was stable below 15 degrees, but the diameter was increased to submicron size with temperature increase. As an anti-tumor agent, docetaxel was encapsulated into the micelle, and *in vitro* anti-tumor activity of the micelle was evaluated using LNCaP human prostate adenocarcinoma cell line.



POLY 304: Enhanced ionic conductivity in homopolymer-blended block polymer electrolytes

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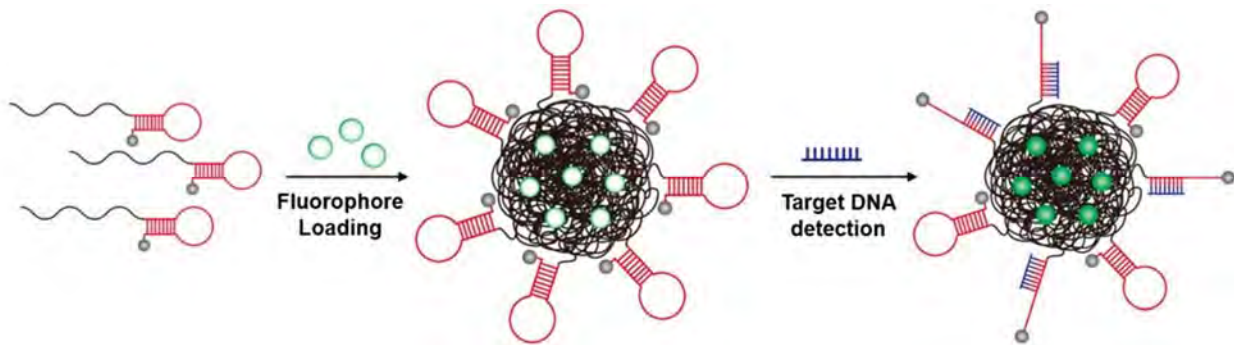
Block polymers (BPs) are attractive materials for lithium-ion battery electrolytes because they unlock the ability to independently tune multiple material properties, such as ionic conductivity and mechanical stability. However, ionic conductivity in BPs typically is reduced in comparison to that in the corresponding homopolymer, as polymeric segmental motion, the main transport mechanism of ions through amorphous electrolytes, is hampered by tethering at domain interfaces. Thus, we have investigated a strategy in which ion-conducting homopolymer is blended into a BP electrolyte such that the final material had enhanced ionic conductivity with retained ability to form desirable nanostructures. Two homopolymer molecular weights were employed to access different self-assembly regimes such as wet (homopolymer distributed throughout the corresponding block of the BP) and dry (homopolymer formed its own regime within the corresponding block of the BP) brush. These homopolymer distributions in the BP were determined via neutron reflectometry by leveraging the scattering length density contrast between deuterated homopolymer and non-deuterated BP. Conductivity (via alternating current impedance spectroscopy) and glass transition temperature (via differential scanning calorimetry) were measured to elucidate the effects of homopolymer blending and distribution on physical and transport properties. By connecting the structure of the blended BP electrolytes to their physical properties, improved designs can be developed to create safer batteries that are faster charging with higher energy densities.



POLY 305: DNA block copolymer micelles as ultra-sensitive bio-detector

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DNA-based biosensors have been developed for a wide range of both *in vitro* and *in vivo* applications. While the detection of biological targets by DNA pair hybridization is highly specific, the signal-to-background ratio for most of the available technologies is still poor. One way to improve the signal strength is to put the DNA probe in a block copolymer structure. By tethering DNA probe to hydrophobic polymer, DNA block copolymer micelles of controllable size and morphology can be made, where the micelle surface is decorated with DNA probes. In this contribution, we report a DNA block copolymer micelle system, which incorporates a modified molecular beacon to achieve enhanced detection signal strength. In our design, diblock copolymers containing one hydrophobic synthetic block and a second block composed of a hairpin shaped DNA with its free chain end connected to a quencher molecule are synthesized. During the process of micelle formation in solution, fluorophore molecules are loaded into the hydrophobic micelle core, while the DNA probes are expressed on the micelle surface. When DNA targets are present, they bind to the loop region of the hairpin shaped DNA block, resulting in a conformational change. This change causes the DNA block to be elongated and the quencher molecules removed away from the fluorophore containing micelle core, and consequently detection of fluorescent signal. This design breaks the limitation associated with traditional molecular beacon where signal intensity can only increase linearly with the number of bound molecular beacons. Furthermore, we demonstrate that the fluorescent signal can be tuned by control of micelle size, allowing the realization of high signal strength even in the limit of dilute target concentration.



Schematic for DNA Block Copolymer Based Target Detection

POLY 306: Co-nanoprecipitation of branched vinyl polymers and block co-polymers for encapsulation and delivery of poorly water soluble molecules

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Conventionally used chemotherapeutic agents often suffer with poor water-solubility. As a consequence many suffer from poor bioavailability or ability to be formulated, thus limiting their overall therapeutic effect. To compensate, high and frequent dosing may be needed with the potential to expose patients to greater levels of cytotoxicity and potentially leading to poor control of clinical outcomes. One materials strategy to overcome these issues is to encapsulate hydrophobic drugs within polymeric nanocarriers. Here, we present a nanocarrier synthesis platform utilising co-nanoprecipitation of branched vinyl polymers with varying amphiphilic A-B block co-polymers. The internal core characteristics of the particles can be varied by changing the monomer composition, the degree of polymerisation and branching of the branched vinyl polymer, whilst variation of A-B block co-polymer chemistry allows control of nanoparticle stability. These variables affect host-encapsulation and subsequent loading within the polymeric nanoparticle. The current fundamental study, using a variety of different methacrylate branched polymers, combined with polyethylene glycol methacrylate block co-polymers, with encapsulation of a dye molecule has shown the impact of the different nanoparticle building blocks.

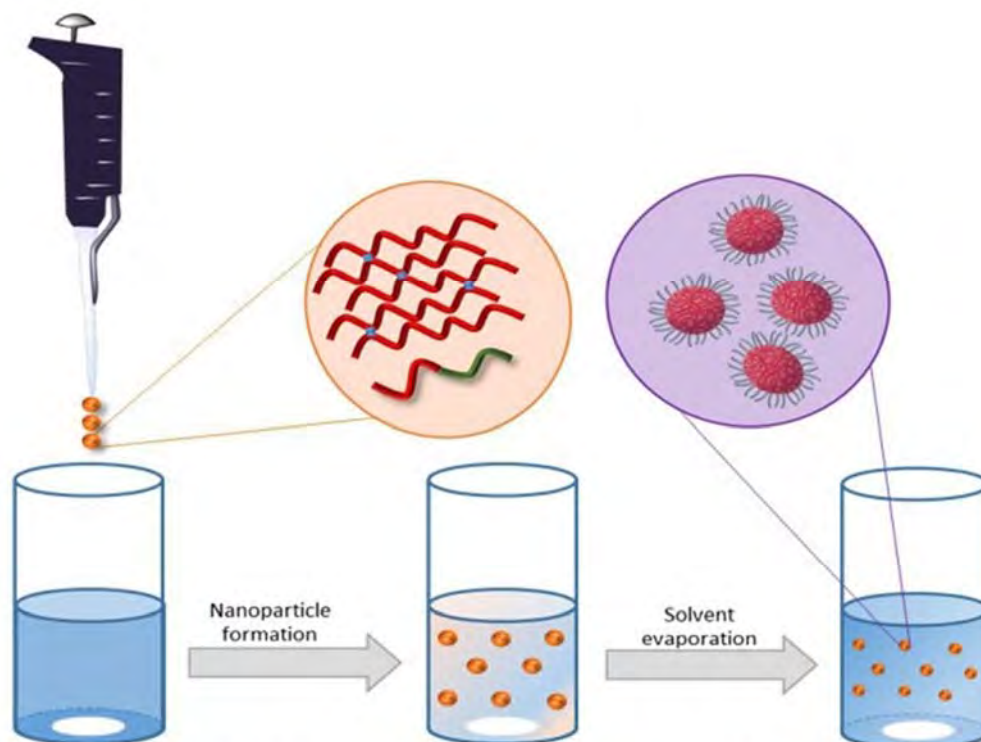
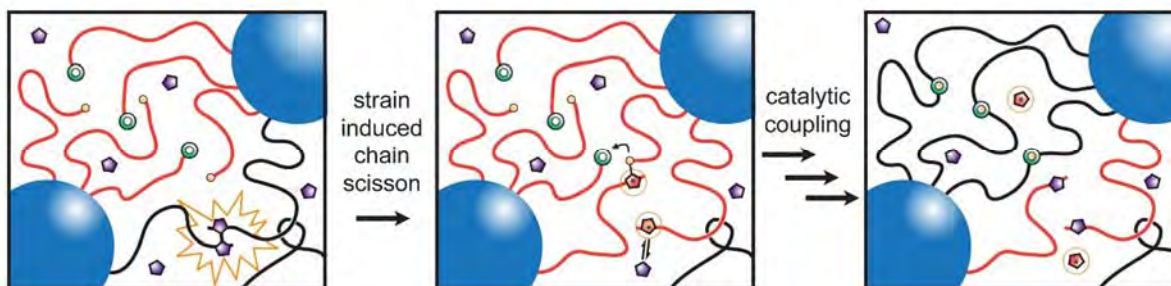


Figure 1 Schematic representation of a co-nanoprecipitation producing branched vinyl polymeric nanoparticles.

POLY 307: Development of tear-resistant block copolymer ion gels via mechano-catalyzed toughening mechanisms

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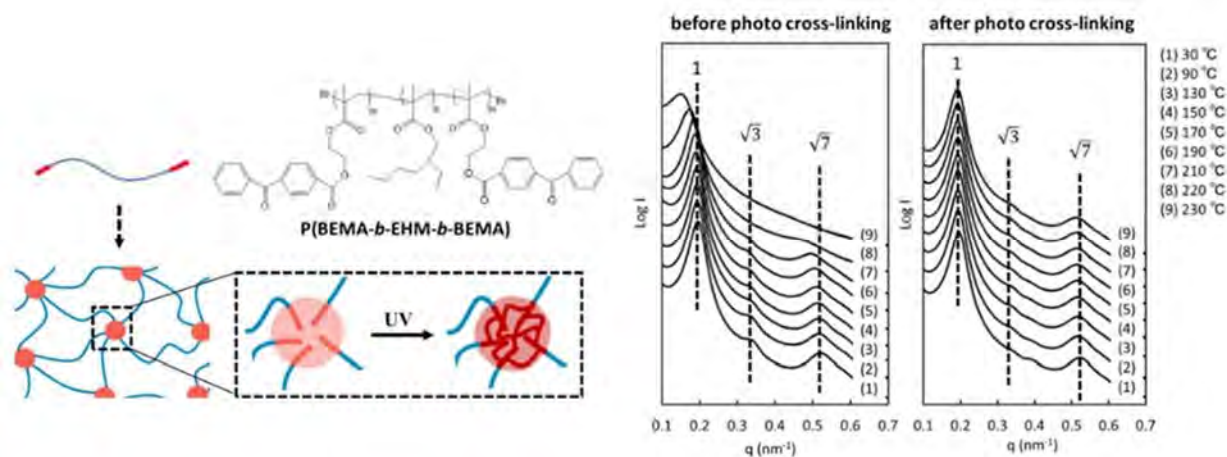
Recently, our group has investigated the use of sphere-forming AB and ABA blends of thermoplastic elastomer block copolymers as composite ionic liquid membranes. These ion gels, which employed the strategic use of vitrified, hydrophobic spherical cores (A block) and a hydrophilic and elastic coronal B block to form a highly uniform tethered micellar network, were melt processed and then swollen in room temperature ionic liquid (RTIL) to form a composite membrane with good mechanical properties and potential for gas transport applications. However, small flaws or tears in the material easily caused catastrophic failure of the membrane when a mechanical stress was applied. This study investigates the ability of prescribed fracture at metal coordination bonds inserted within the B block of the ABA tethers as a means of liberating a catalytic active site promoting the localized formation of new covalent tethers between functionalized AB chain ends. This adaptive remodeling of the network would allow for selective reinforcement of high stress regions in the hydrogel, fighting fracture and improving overall toughness.



POLY 308: Thermal stability enhancement of ABA triblock copolymers based on morphology by photo cross-linking the A blocks

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Nagoya institute of technology, Nagoya , Japan*

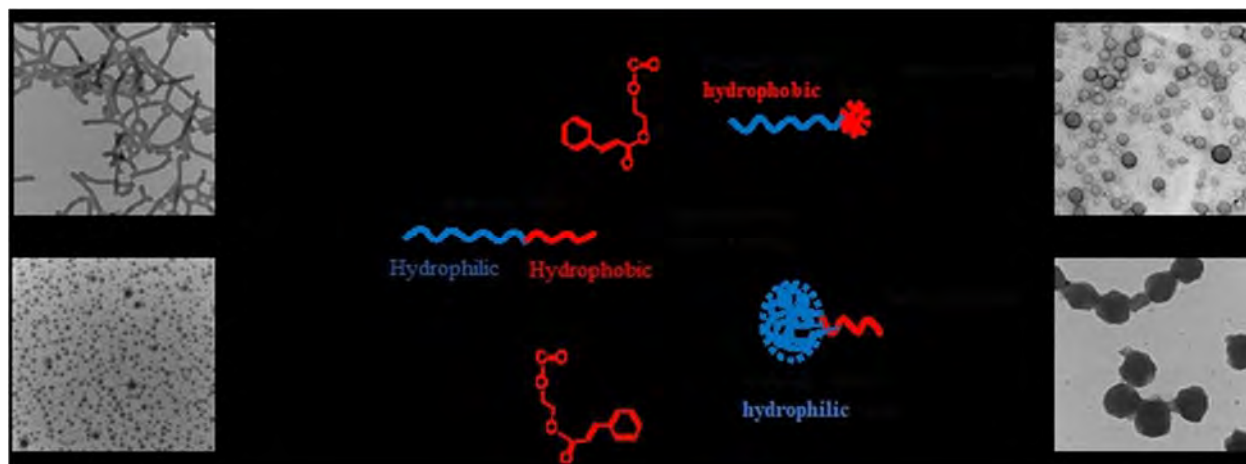
Block copolymers with incompatible components form various micro-phase separated structures. The type of micro-phase separation structure is determined according to the segregation power. Generally, the segregation power decreases with a temperature rise, which makes the morphology from the ordered state to the disordered state. Some research groups have investigated how the cross-linking influenced the thermal stability of micro-phase separated structures. These reports mostly used cross-linking such as thermal crosslinking and coordination bonding. In these past reports, the high heat or addition cross-linkers were required for the cross-linking, where the original morphology was inevitably affected by cross-linking. So, for more accurate investigation of correlation between cross-linking of domain in the microphase separated structures and the thermal-responsiveness, it is necessary to perform crosslinking without affecting original morphology. To realize this demand, we focus on photo cross-linking because crosslinking can be progressed at room temperature, and an ABA triblock copolymer with photo cross-linkable A blocks was prepared. The B chain component was poly(2-ethyl hexyl methacrylate) (PEHM), and the A chain component was poly(2-benzophenoxylethyl methacrylate) (PBEMA) with benzophenone moieties which are photo cross-linkable groups. The P(BEMA-*b*-EHM-*b*-BEMA) ($M_n = 3.2 \times 10^4$, $M_w / M_n = 1.4$, $\Phi_A = 0.11$) was prepared using two step ATRP. Subsequently, SAXS measurements were carried out to investigate the morphology. Scattering peaks of samples before and after photo cross-linking were almost same, which means photo cross-linking didn't the original affect micro-phase separated structure. In SAXS measurement for the sample before photo cross-linking at elevated temperature, collapse of the micro-phase separation structure was observed at around 220 °C. On the other hand, for the photo cross-linked sample, the micro-phase separation structure was retained even at 230 °C. We succeeded in improving the thermal stability of micro-phase separated structure by cross-linking within the A chain domains.



POLY 309: Programmable self-assembly of amphiphilic tadpole-shaped single-chain polymer nanoparticles

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We present the programmable self-assembly of tadpole-shaped single chain polymer nanoparticles (SCPNs) prepared from intramolecularly cross-linked amphiphilic di-block copolymers (di-BCPs). Two amphiphilic di-BCPs poly(N,N'-dimethyl acrylamide)-*block*-polystyrene (PDMA-*b*-PS) containing photo cross-linkable cinnamoyl groups either in hydrophobic or hydrophilic blocks were synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization. We used intramolecular cross-linking as a tool to control the collapse degree of one of the blocks of di-BCPs. Tadpole-shaped SCPNs with either hydrophobic or hydrophilic head were prepared via photo-cross-linking of cinnamoyl groups of the di-BCPs. The photo-cross-linking of cinnamoyl groups offers control over the self-collapse degree of the head-forming blocks. The self-assembly studies show a clear morphological transition from branched cylindrical micelles to spherical micelles when the cross-linking occurred in hydrophobic PS blocks at a dimerization degree of ~63%. While the photo-cross-linking was performed in the hydrophilic PDMA blocks, the micelles size increased at lower dimerization degrees due to the shift of hydrophobic-to-hydrophilic balance. At higher dimerization degrees (> 60%), tadpole-shaped SCPNs assembled into nonconventional aggregates with a non-smooth surface. Our results show the impact of chain topologies on the self-assembly of di-BCPs which will open the doors to prepare various desired nanostructures of polymer micelles by using just one parent linear BCPs.



POLY 310: Synthesis and characterization of novel gradient copolymers by a high-throughput approach

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The advances in the synthesis of sequence controlled copolymers (containing two or more monomers) have opened up a new perspective for building materials, where the properties and functionalities can be controlled on demand and cannot be achieved through homopolymerization. Within this framework, gradient copolymers may be considered to be an intermediate species between block and random copolymers whereas the comonomer composition varies continuously as a function of chain length. Gradient copolymers have shown interesting properties and applications, for instance, in shock- and noise-absorbing materials and interfacial stabilizers as compared to block copolymers. Nevertheless, the preparation of copolymers with a well-defined gradient monomer composition requires demanding synthetic procedures, including complex semi-continuous monomer feeding processes, which require constant feedback to manipulate the copolymer composition at each stage of polymerization. In this contribution, we explore, via high-throughput experimentation, facile and better-understood batch polymerization strategies to fabricate polymers with structural features of gradient copolymers. The preparation of extensive libraries of gradient copolymers with different structures and the properties of this novel class materials are investigated.

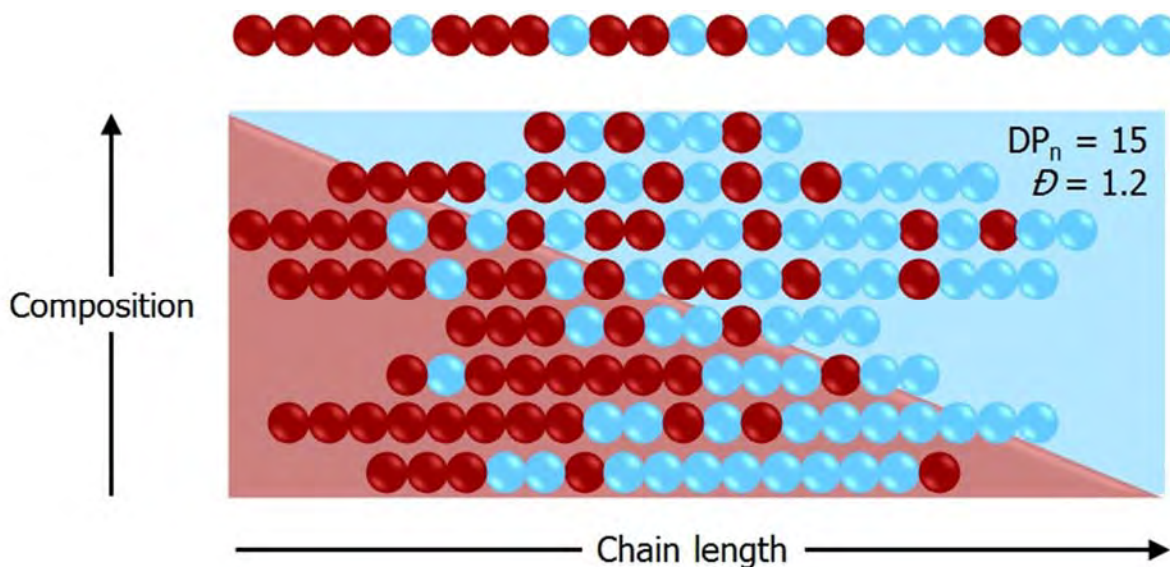


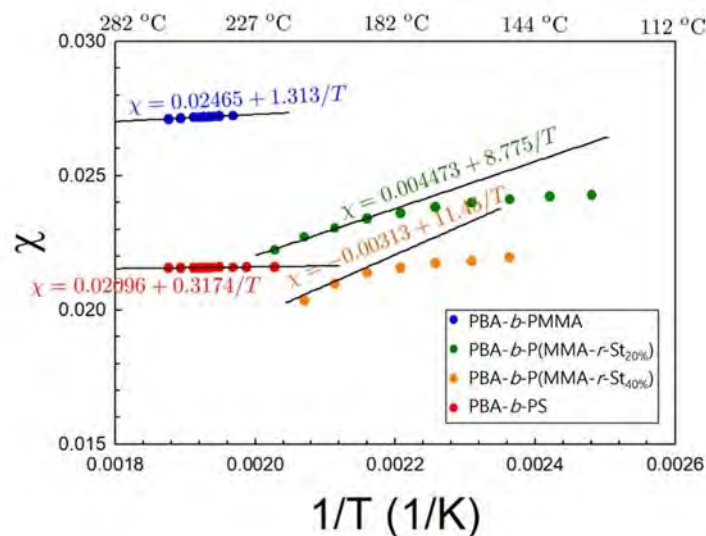
Figure 1. Representations of a gradient copolymer based on: Average composition (top) and distribution of chains (bottom).

POLY 311: Effect of comonomer composition on the segregation behaviour of poly(butyl acrylate)-*b*-poly(methyl methacrylate-*r*-styrene) prepared by atom transfer radical polymerization

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Block copolymers, composed of two or more chemically different polymer blocks connected by covalent bond, can self-assemble into periodically segregated nanostructure. The phase behavior of block copolymer is dictated by the Flory-Huggins interaction parameter between dissimilar blocks (χ), volume fraction (f), and degree of polymerization (N).

In this study, we investigated the segregation behavior of a molten diblock copolymer, poly(butyl acrylate)-*b*-poly(methyl methacrylate-*r*-styrene) (PBA-*b*-P(MMA-*r*-St)) where styrene is incorporated as a comonomer in the second block for controlling the incompatibility between two blocks. Poly(butyl acrylate)-*b*-poly(methyl methacrylate-*r*-styrene) (PBA-*b*-P(MMA-*r*-St)) was synthesized by atom transfer radical polymerization (ATRP). The PBA block has a relatively narrow molecular weight distribution (MWD: 1.06) and the P(MMA-*r*-St) block has a relatively polydisperse molecular weight distribution (MWD: 1.2 ~ 1.5). To examine the effect of styrene comonomer fraction (ϕ) on the segregation behaviors of PBA-*b*-P(MMA-*r*-St), the bulk morphologies of PBA-*b*-P(MMA-*r*-St) with different ϕ were characterized by transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS). The effective χ parameter between PBA block and P(MMA-*r*-St) block was estimated by analyzing SAXS profiles with the random phase approximation (RPA), which allows us to quantify the degree of incompatibility of PBA-*b*-P(MMA-*r*-St) diblock copolymer as a function ϕ .



The Flory-Huggins interaction parameter (χ), as a function of the reciprocal temperature for diblock copolymers

POLY 312: Effects of architecture on the co-nanoprecipitation of branched polyesters

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In recent years, biodegradable nanoparticles have gained increased interest in their application as drug delivery vehicles due to their improved ability to be cleared from the body after administration. Within this group, polyesters are a popular choice after validation in a range of clinical applications. For example, lactide-based polymers have been commonly used as tissue scaffolding, and used as the hydrophobic blocks within poly(ethylene glycol)-PLA drug delivery copolymers. Although poly(lactide) nanoparticles have been widely researched, other polyester candidates, such as poly(caprolactone), are available with similar properties but without the same depth of study. Here, we have utilised co-nanoprecipitation with a range of linear and branched homo- and co-polymers of ϵ -caprolactone, synthesised by acid-catalysed ring opening polymerisation. The effects of architecture and the hydrophilic/hydrophobic balance of the amphiphilic AB block co-polymers on the colloidal stability of the particles, has been investigated in detail. The branched architecture considerably reduced the size of the resulting nanoparticles in comparison to experiments using linear analogues. Additionally, the role of architecture and higher molecular weight in the nucleation process was further highlighted with increased stability of particles seen. Further investigations were also conducted with both mixed solvent systems and guest encapsulation being examined, allowing a deep understanding of branched poly(caprolactone) co-nanoprecipitation.

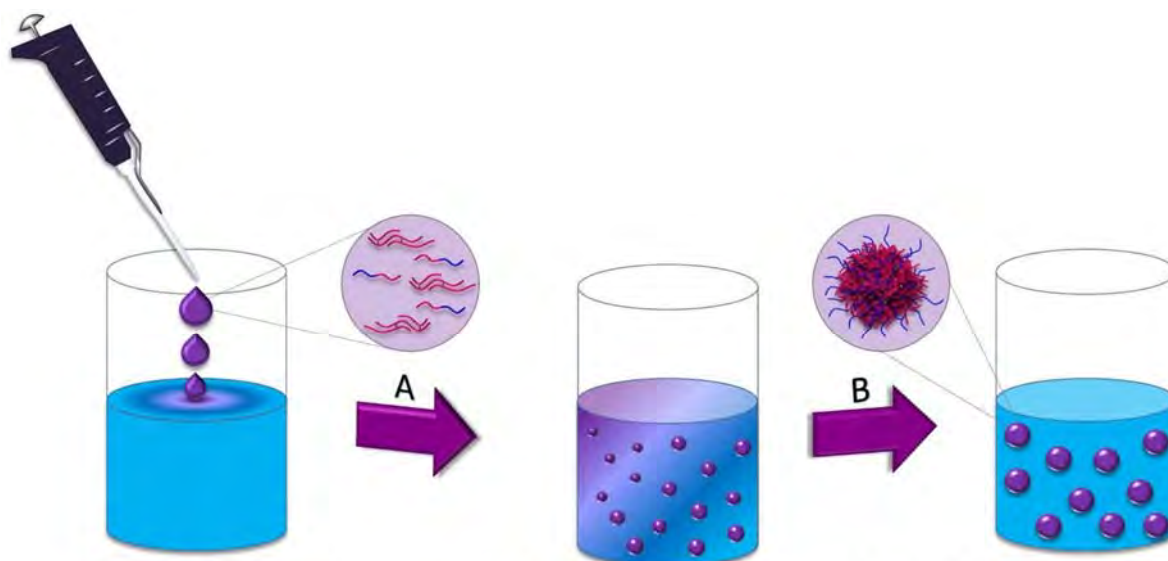


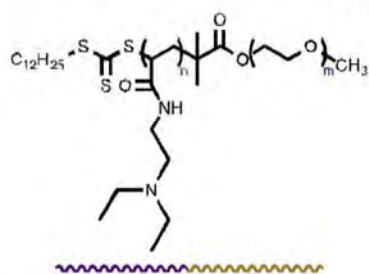
Figure 1- Scheme representing co-nanoprecipitation of polyesters and AB block co-polymers with A) stirring and B) solvent evaporation.

POLY 313: Self-assembly of pH-responsive amine-based diblock copolymers

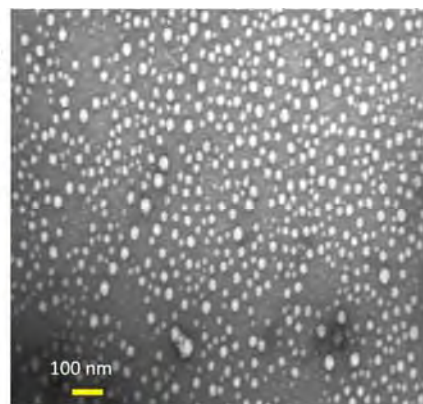
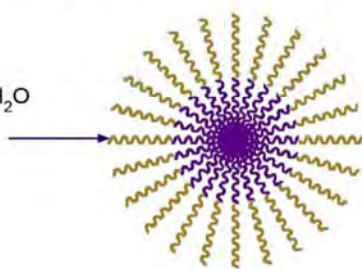
Hanson Koota, *hanson.koota@gmail.com*, Christina Chen, Nora Lee, Luke Cai, Anna Ringuette, Christopher Goh, Sarah L. Goh. Dept of Chemistry, Williams College, Williamstown, Massachusetts, United States

Nanoparticles have emerged as a promising new tool to effectively treat cancer. With the limiting factor of most chemotherapeutics being their adverse side effects, nanoparticles have the ability to encapsulate drugs and deliver them to cancerous tissue with minimal effect to normal cells. These particles can be designed to take advantage of cancer cell physiology to preferentially target cancerous tissue over normal tissue. We use RAFT polymerization to explore the versatility of poly[(*N,N*-diethylaminoethyl) acrylamide] (pDEEN) as a component of micellar delivery vehicles. Diblock polymers are composed of pDEEN, which is cationic at neutral pH, with poly(*n*-butyl acrylate) (pnBuA) or monomethoxypolyethylene glycol (mPEG) to yield p(DEEN)-*co*-p(nBuA) and p(DEEN)-*co*-mPEG. In aqueous solutions both polymers form aggregates 100-200 nm in diameter above their critical aggregate concentrations. The p(DEEN)-*co*-p(nBuA) amphiphilic diblock copolymer demonstrates resistance to pH change and the p(DEEN)-*co*-mPEG doubly hydrophilic diblock copolymer results in a change in aggregate size, a decrease in stability, and a change in morphology over the pH range of 5.8 to 8.0. These copolymers effectively bind Cu(II) and encapsulate plasmid DNA through ionic interactions, demonstrating a potential use as a non-viral DNA vector. The versatility of p(DEEN) in these diblock copolymers shows a promising start to the design of oncological treatments.

TEM of self-assembled p(DEEN)₄₅-*co*-mPEG₁₁₃ at pH 7.2



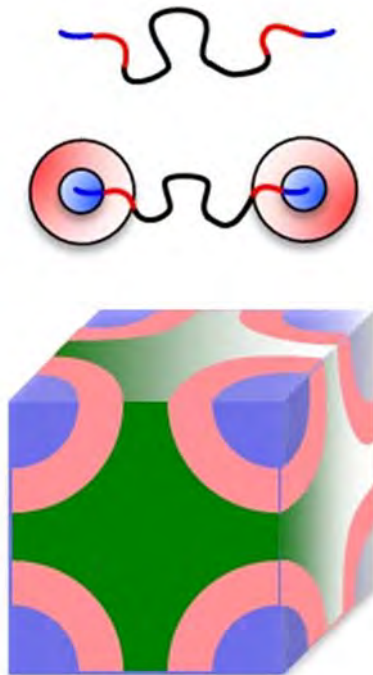
H₂O



POLY 314: Targeting core-shell-sphere block copolymer morphology for tough, fatigue-resistant hydrogels

Allee Klug¹, allee.klug@colostate.edu, Travis S. Bailey². (1) Chemistry, Colorado State University, Fort Collins, Colorado, United States (2) Colorado State University, Fort Collins, Colorado, United States

Our group has developed hydrogel systems based on AB diblock and ABA triblock copolymer blends that use nanostructure to create useful mechanical properties. These materials utilize a network of tethered vitrified spheres to provide structure, elasticity, and fatigue resistance. However, this highly elastic network does not dissipate energy efficiently and is therefore prone to failure by fracture. We have since hypothesized that introduction of an elastic, hydrophobic B block in analogous blends of sphere-forming ABC triblock and ABCBA pentablock copolymers may allow such highly elastic networks to selectively dissipate excessive strain energy in regions in which high concentrations of stress threaten microcrack formation and catastrophic failure by fracture. This presentation details the synthetic targeting of ABC core-shell-sphere morphology by changing the volume fractions of the A and B blocks and evaluation of the hydrogel mechanical properties produced in direct contrast to a non-dissipating AB/ABA system.



POLY 315: Poly-2-oxazolines block copolymers with fluorophilic blocks: New frontiers for the design of self-assembling systems

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2-Oxazolines are widely used as building blocks for the controlled synthesis of self-assembling polymer systems. The cationic ring-opening polymerization (CROP) is usually used for the synthesis of poly-2-oxazolines. In the absence of moisture and other nucleophilic impurities, the CROP proceeds in a living mode allowing the precise control of the blocks ratio and, thus, obtaining well-defined polymers.

Meanwhile, this approach is not applicable for the synthesis of fluorinated 2-oxazolines. It is known that the synthesis of fluorinated 2-oxazoline-based homo- and copolymers suffers from extremely low activity of 2-perfluoroalkyl-2-oxazolines in the CROP both in the initiation and in the propagation. Recently, we reported a detailed study of increasing the polymerization reactivity of fluorophilic 2-oxazolines by the insertion of alkyl spacers between the fluorinated substituent and the 2-oxazoline ring. This approach offers a new platform for the synthesis of various of copoly(2-oxazoline)s with fluorinated blocks.

A series of poly(2-oxazoline)-based block copolymers containing hydrophilic (2-methyl-2-oxazoline, 2-ethyl-2-oxazoline), thermo-responsive (2-*n*-propyl-2-oxazoline, 2-*i*-propyl-2-oxazoline), hydrophobic (2-*n*-octyl-2-oxazoline, 2-phenyl-2-oxazoline) and fluorophilic blocks (Figure 1) was synthesized. By combination of experimental methods including dynamic light scattering (DLS), small angle X-ray and neutron scattering (SAXS and SANS), cryo-TEM microscopy, we proved that synthesized copolymers self-assemble into the micellar-like structures in diluted aqueous solutions.

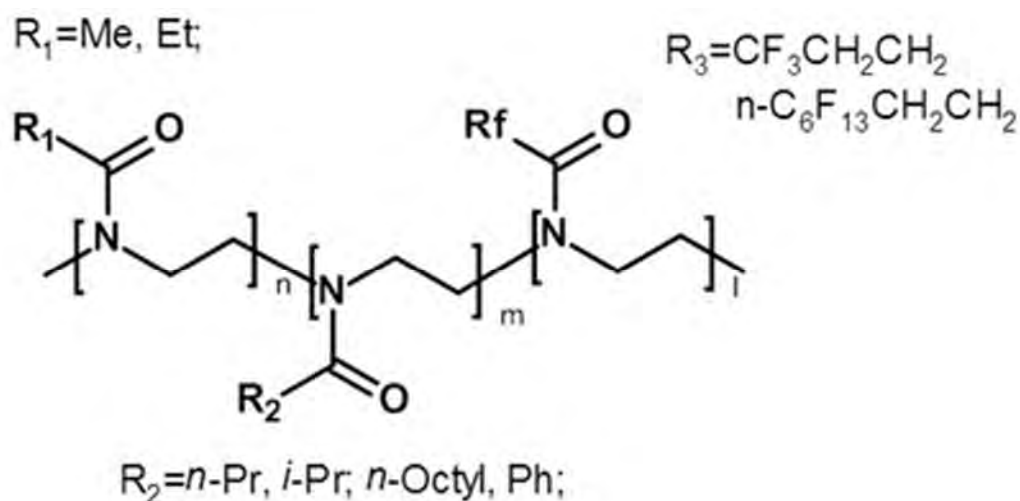


Figure 1. General structure of investigated 2-oxazoline block copolymers

POLY 316: Block and gradient copoly(2-oxazoline) micelles: Strikingly different on the inside

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Herein, we provide a direct proof for differences in the micellar structure of amphiphilic diblock and gradient copolymers, thereby unambiguously demonstrating the influence of monomer distribution along the polymer chains on the micellization behavior.[1] The internal structure of amphiphilic block and gradient copoly(2-oxazolines) based on the hydrophilic poly(2-methyl-2-oxazoline) (PMeOx) and the hydrophobic poly(2-phenyl-2-oxazoline) (PPhOx) was studied in water and water-ethanol mixtures by Small-Angle X-ray Scattering (SAXS), Small-Angle Neutron Scattering (SANS), Static and Dynamic Light Scattering (SLS/DLS), and ¹H NMR spectroscopy. Contrast matching small angle neutron scattering (SANS) experiments revealed that block copolymers form micelles with a uniform density profile of the core. In contrast to popular assumption, the outer part of the core of the gradient copolymer micelles has a distinctly higher density than the middle of the core (**Fig.1**). We attribute the latter finding to back-folding of chains resulting from hydrophilic-hydrophobic interactions, leading to a new type of micelles that we refer to as micelles with a “bitterball-core” structure (**Fig.1**).

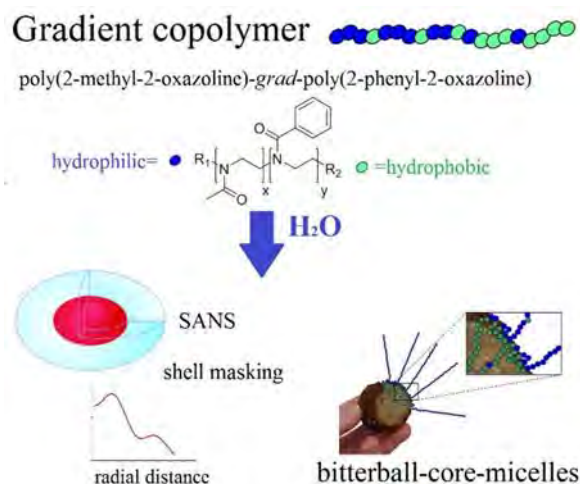
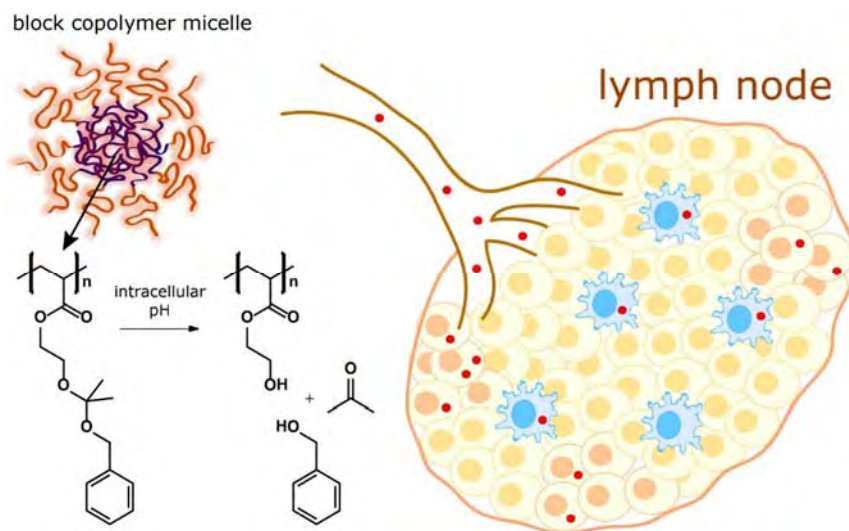


Figure 1. (Top) Chemical structure and schematic presentation of the structures of the PMeOx-PPhOx block and gradient copolymers. (Bottom, left) Contrast density profiles. (Bottom, right). The hypothetical structure of block and gradient nanoparticles and bitterball-core-micelles. Red color stands for PhOx and green on stands for MeOx blocks.

POLY 317: Lymph node targeting acid-degradable amphiphilic polymers with π - π stabilisation

Bruno De Geest¹, **Simon Van Herck**², *Simon.VanHerck@UGent.be.* (1) Ghent University, Ghent, Belgium (2) University Ghent, Gent, Belgium

From a biomedical point of view, polymer functionality relates to biodegradability, pharmacokinetics and structure-activity properties. Taken in account these aspects we report here on novel pH-degradable amphiphilic block copolymers bearing an acid-cleavable benzylic moiety and an activated ester in the hydrophobic domain synthesised by RAFT polymerisation. The use of an aromatic functionality in the hydrophobic domain promotes self-assembly into 50 nm micellar nanoparticles with increased stability due to π - π interactions. The acid-sensitive ketal spacer allows for intracellular transformation into a fully water-soluble polymer by cleaving off the benzylic moiety at lysosomal pH. Functionalisation of the polymers with either Cy3 or Cy5 dyes allows for a detailed supramolecular investigation based on the Cy3/Cy5 FRET coupling. Both *in vitro* as well as *in vivo* the concept of stable, but acid-degradable nanoparticles is proven by an increased cellular uptake and superior lymphatic drainage for self-assembling amphiphiles compared to fully water-soluble polymer. These properties were used in the development of a vaccine adjuvant formulation by covalent modification of a TLR7/8 agonist, yielding a highly potent lymph node directing vaccine formulation with a strong localised immune activation.



POLY 318: Developing protein engineered injectable hydrogels for post-traumatic osteoarthritis

Priya Katyal¹, priya.katyal@nyu.edu, Michael Meleties¹, Qingyun Tian², Chuanju Liu^{2,3}, Jin K. Montclare^{1,4}. (1) Chemical and Biomolecular Engineering, New York University, Tandon School of Engineering, Brooklyn, New York, United States (2) Department of Cell Biology, New York University Langone Health, New York, New York, United States (3) Department of Orthopaedic Surgery, New York University Langone Health, New York, New York, United States (4) Department of Chemistry, New York University, New York, New York, United States

Protein based biomaterials offer several advantages over synthetic materials, owing to their unique stimuli-responsive properties, biocompatibility and modular nature. Our lab has successfully developed protein block polymers engineered by combining the coiled-coil domain of the Cartilage Oligomeric Matrix Protein (C) with an elastin-like polypeptide (E). Our protein block polymer, EC demonstrates the formation of micelle-like particles as characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The dynamic association of these micelles leads to hydrogel formation with EC exhibiting smart sol-gel response at physiological temperature (Figure 1). This approach combines syringeability of sol and *in situ* gelling properties of a gel, making it an excellent candidate for injectable biomaterials. Here, we expand the versatility of EC, and explore its potential in storing and delivering progranulin (PGRN), a chondroprotective protein therapeutic, providing a sustained effect of the drug in post-traumatic osteoarthritis (PTOA) patients. PGRN has been shown to enhance cartilage repair in animal models of PTOA effectively delaying osteoarthritis onset and progression. Overall, we will discuss: 1) the synthesis and mechanism of hydrogel formation; and 2) the effects of PGRN-loaded EC hydrogel on chondrocyte migration, proliferation and metabolism.

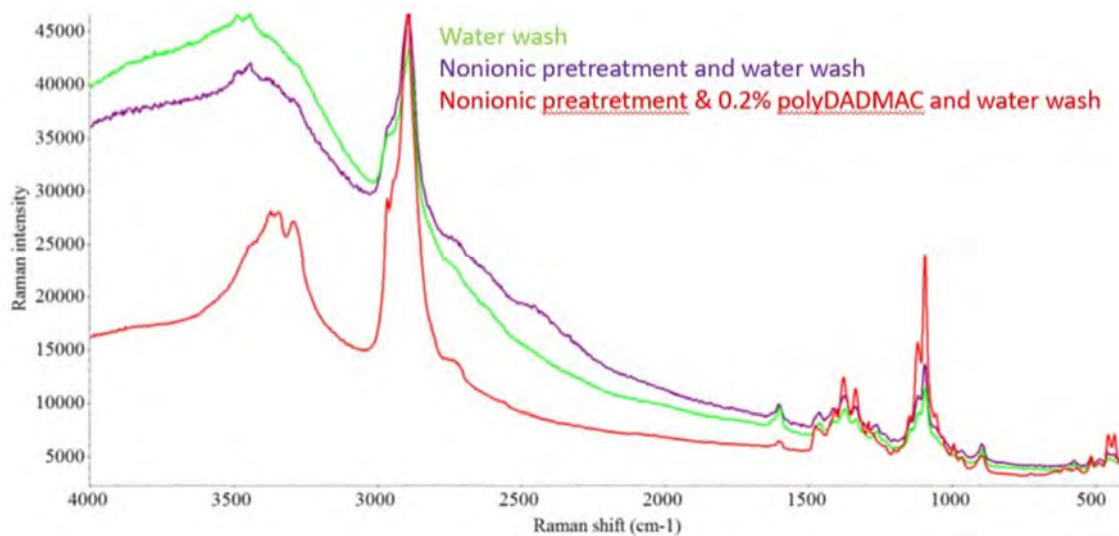


Figure 1. Schematic of gel formation; EC exists as solution (sol) at lower temperature and solid gel at 37°C. The approach combines syringeability of sol and *in situ* gelling properties of gel. Lower panel: Inversion test showing sol-gel transition using EC in 1x PBS at pH 7.4.

POLY 319: Poly(diallyldimethylammonium chloride) treatment of cotton surfaces: A Raman study

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Confocal Raman Spectroscopy was utilized to examine interactions between poly(diallyldimethylammonium chloride) and cotton. Based on the unique structural probe associated with Raman spectroscopy, we identified transition peak shifts and peak shape changes associated with cotton after treatment with poly(diallyldimethylammonium chloride) consistent with complex formation. These changes are absent if other treatments are applied to the cotton surface. The poly(diallyldimethylammonium chloride) association with cotton results in a fixative characteristic for stained and dyed materials.

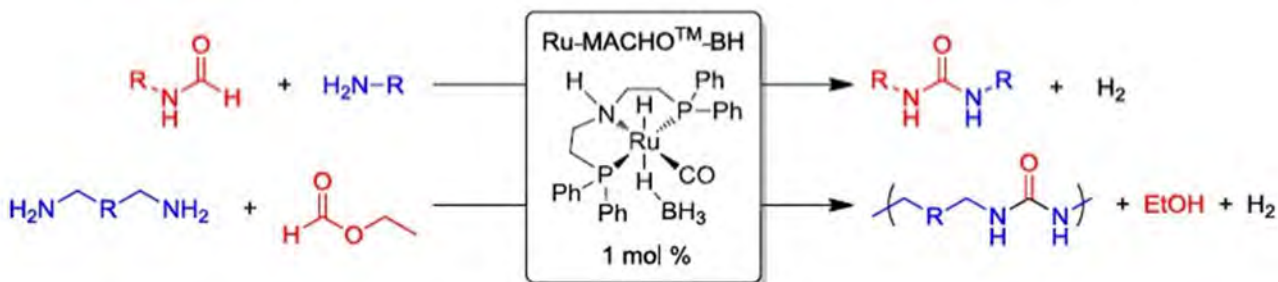


Raman spectra of cotton with varying treatments

POLY 320: Isocyanate-free syntheses of ureas and polyureas via ruthenium-catalyzed dehydrogenation of amines and formamides

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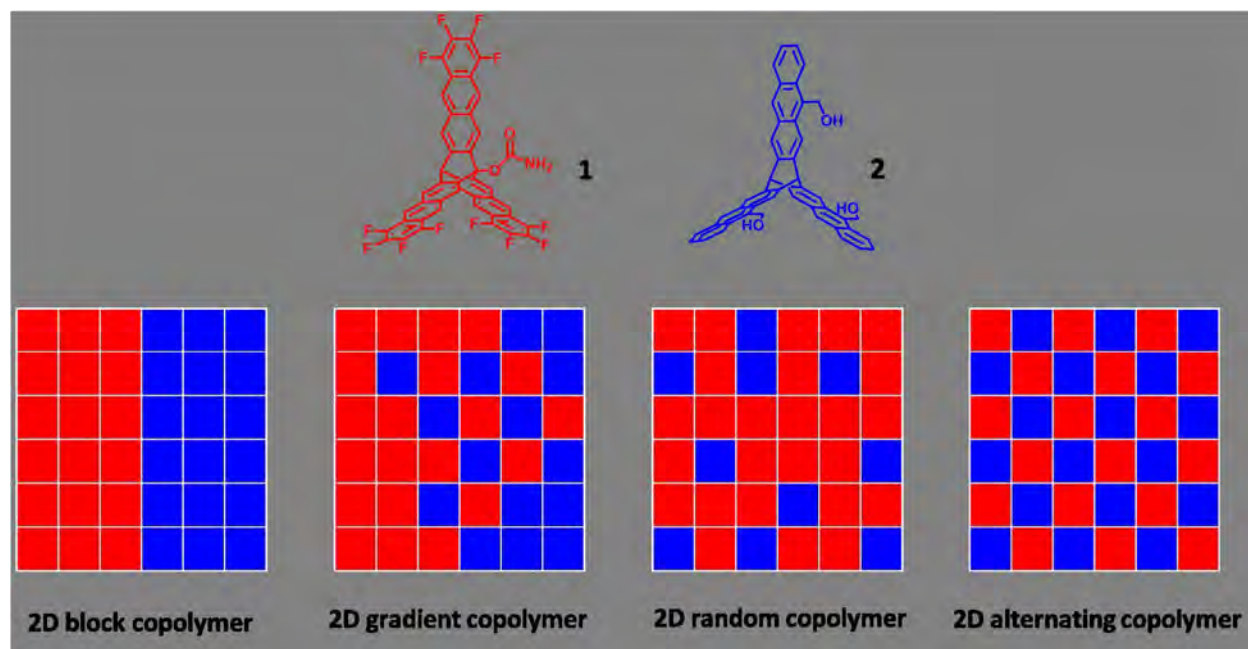
Ureas (and polyureas) are commonly prepared by reacting an amine (or diamine) with an isocyanate (or diisocyanate). While this method is effective, isocyanates pose significant health hazards to the user, and the urea substrate scope is limited by the relatively small number of commercially available isocyanates. Our research group sought to address these two limitations by expanding upon recent advances in ruthenium-catalyzed dehydrogenation of amines and formamides to make ureas and polyureas. Ethyl formate proved to be very effective for the *in situ* formylation of amines and diamines to yield formamides and diformamides, respectively. Subsequent dehydrogenation of these compounds furnishes the desired ureas and polyureas. This approach provides access to a large structural variety of ureas and polyureas because a wide range of primary amines can be readily converted to the corresponding ureas in high yields. Furthermore, the ease with which hydrogen can be removed from the reaction medium enables the synthesis of relatively high molecular weight polyureas. These ureas and polyureas can also be hydrogenated back to their starting amines and diamines using the same ruthenium catalysts, thus demonstrating the chemical recyclability of polyureas prepared by this route.



POLY 321: Developing two-dimensional copolymerization

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Due to their intriguing properties and potential applications, two-dimensional polymers (2DPs) currently attract considerable attention as new solely organic chemistry-based 2D materials. In particular, 2D copolymers, in which two different repeat units co-exist, are of great importance due to their diverse structures and well-tuned properties. In the case of two-component 2D copolymers, according to the distributions of the repeat units, four types of 2D copolymers can be defined, *i.e.* block copolymer, gradient copolymer, random copolymer and alternating copolymers. Notably, the spatial distributions of repeat units within the 2D copolymers would have a great impact on their properties. In this study, two monomers 1 and 2, which are derived from structures reported by B.T. King, were designed and synthesized. By using these structurally similar amphiphilic monomers as key building blocks, interfacial approach was employed towards the preparation of a series of 2D copolymers. Starting from varying amounts of monomers, compressed monolayers of these monomers at the air/water interface can be converted into the corresponding 2D copolymers through photochemically achieved [4+4]-cycloaddition between pairs of anthracene blades that are co-facially (face-to-face) arranged. Further investigations will focus on the distribution mapping of repeat units within the 2D copolymers on the nanometer scale with the help of Electron Energy Loss Spectroscopy (EELS) and tip-enhanced Raman Spectroscopy (TERS).

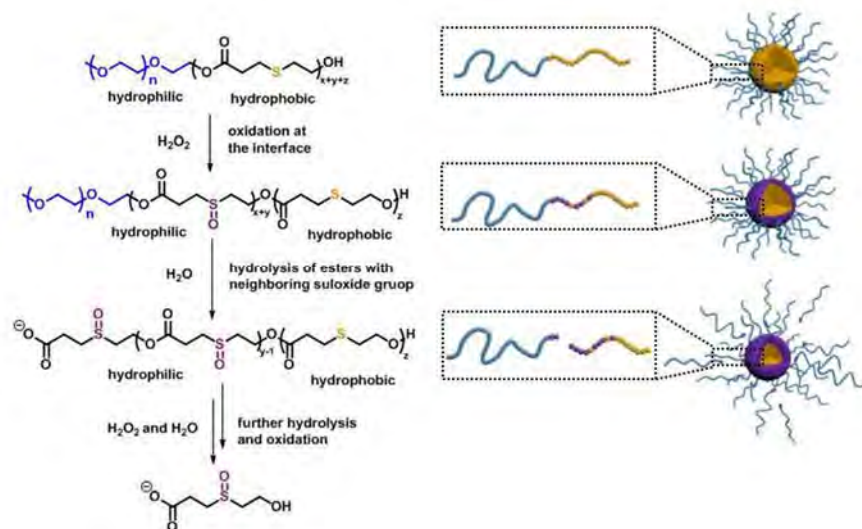


Monomer structures and four types of 2D copolymers

POLY 322: Synthesis and oxidation-promoted degradation of β -thioether containing polyester

Ling-Gao Li, Fusheng Du, **Zi-Chen Li**, zcli@pku.edu.cn. College of Chemistry, Peking University, Beijing, China

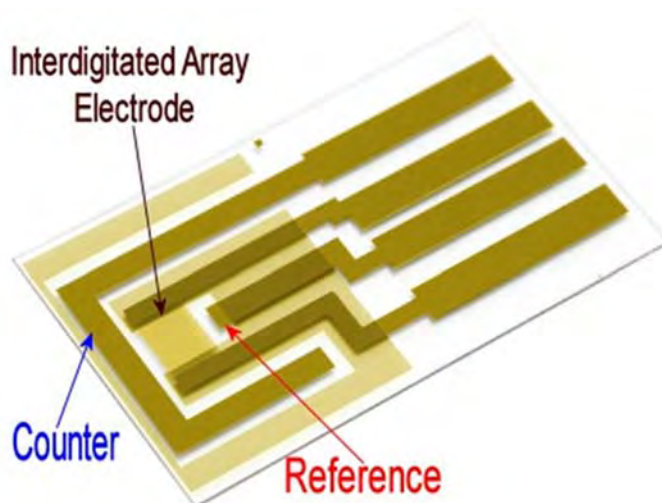
Polymers containing β -thioether ester moieties in the backbone are important biodegradable materials that have been found applications in bio-related fields. This kind of polymer exhibits unique property change (increased hydrophilicity and degradation) upon oxidation of the β -thioether groups. Though several methods have been developed to synthesize such polymers, the control over the molecular weight, distribution, as well as end groups could not be achieved, which greatly limited the preparation of well-defined block copolymers and the structure-property relationship studies. We developed a simple approach to synthesize a β -thioether containing lactone monomer, 1,5-oxathian-2-one (OTO). The process is a one-pot two step procedure, Michael addition reaction between 2-thioethanol and p-nitrophenyl acrylate followed by intramolecular cyclization. The ring-opening polymerization (ROP) of OTO catalyzed by an organocatalyst DPP was investigated, and the results confirmed that living polymerization could be achieved under optimized conditions. Moreover, block copolymers of POTO and PEG or PCL were prepared in a controlled way. The amphiphilic block copolymer PEG-*b*-POTO could self-assemble into micellar like assemblies in water. We systematically studied the oxidation of the molecular assemblies with hydrogen peroxide. Based on the results of the oxidation of model small molecules, we proposed the pathway of the oxidation of POTO: the thioether groups were first oxidized into sulfoxides; before the sulfoxides were further oxidized into sulfones, the ester linkages began to break, causing the detachment of the PEG chains from the assembly surfaces. Finally, with more thioether groups have been oxidized and more ester groups have been broken, the assemblies began to change its morphology and disassembled into small molecules. This work clearly revealed that the oxidation of thioether group can increase the degradation of POTO in the interface of the micellar assemblies, thereby providing a guideline for using oxidation-responsive polyesters in drug delivery application.



POLY 323: Radical electro-copolymerization: Improvement of conductivity in furan / thiophene copolymers

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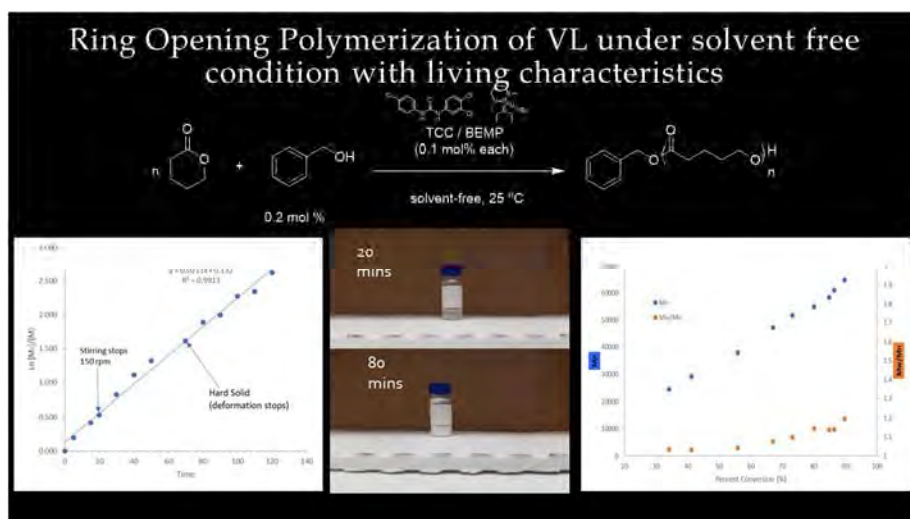
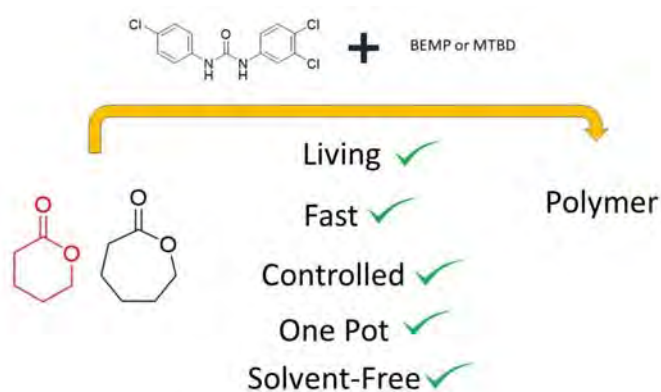
Conventional polymers such as plastics and rubbers offer significant resistance to electrical conduction and are either dielectrics or insulators. With the invention of conducting polyacetylene in the 1970s, conducting polymers have received significant attention from both science and engineering communities. Conductive polymers are plastics (which are organic polymers) and therefore can combine the mechanical properties (processibility, flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. In doped polymers, the doping of conjugated polymers generates high conductivities by increasing the carrier concentration. This is accomplished by oxidation or reduction with electron acceptors or donors respectively. The polymer is oxidized by the acceptors, thereby producing a radical cation (hole) on the chain. Conducting polymers with improved conductivity can be used in electronic devices as metal substitute. Polyfuran and polythiophene are conductive polymers that have less conductivity than many other conductive polymers such as polyaniline but have desirable mechanical properties that make them more valuable in the production of micro robotics and sensors. Specifically, their high boiling point and insolubility make them stand out from other conductive polymers. In this research several copolymers of furan and thiophene were synthesized by radical electro copolymerization method with different ratios of monomers. The conductivity of copolymers was determined using an IDA electrode and compared with control homopolymers. In conclusion some of the copolymers showed more conductivity possibly due to better expansion in the resonance system of the polymer.



POLY 324: Solvent-free approach to the ring-opening polymerization of lactones with commercially available organocatalysts

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A 'greener', solvent-free approach towards a fast and controlled synthesis of biocompatible and sustainable polyesters with use of organocatalyst systems at ambient and elevated temperatures has been evaluated. The activity of trichloroacetyl and base co-catalyst systems in solvents for the ring opening polymerization (ROP) of cyclic lactones has been previously characterized. In this study, we evaluate its activity under solvent-free conditions. These ROPs exhibit fast rates and good control and have the characteristics of living polymerizations, despite solidifying prior to full conversion. One-pot diblock and triblock copolymerizations, which were inaccessible in solution phase, have been achieved under these conditions. A mechanism of action is proposed, and potential applications discussed. The synthetic utility of the catalysts combined with their commercial availability, make these systems very attractive for the synthesis of specialized polymers.



POLY 325: Synthesis and characterization of novel fluorene-containing conjugated polymers

Daniel Jones, derg28@gmail.com. Chemistry, University of Rhode Island, Kingston, Rhode Island, United States

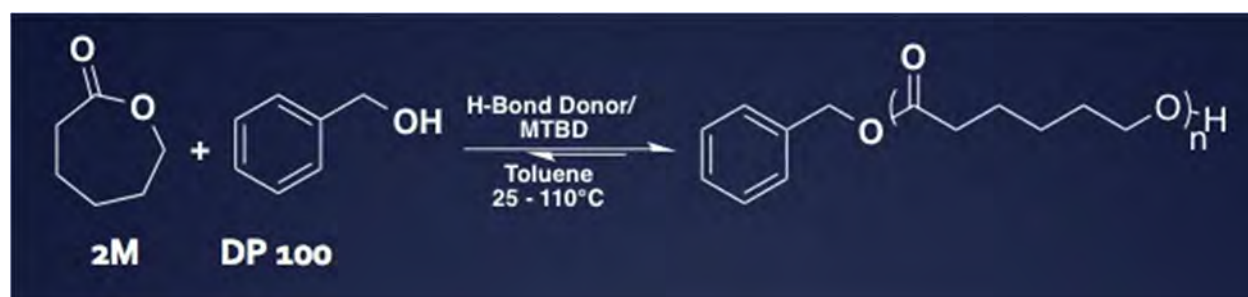
Several novel fluorescent conjugated polymers were synthesized by the Suzuki polycondensation of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and the corresponding conjugated dihalogenated monomer. The photophysical properties of these polymers were investigated, as well-dissolved solutions in chloroform, as spin-coated thin films on glass slides, and as nanoparticle suspensions in water. Two of the polymers had large Stokes shifts (greater than 100 nm), two polymers had distinctly different fluorescent responses in aggregated versus non-aggregated forms, and all of the polymers had high quantum yields. A number of potential applications for these polymers can be envisioned in areas such as fluorescence-based detection, solid state materials, and more.



POLY 326: Mechanistic study of the ring opening polymerization of cyclic esters with varying temperature and solvent

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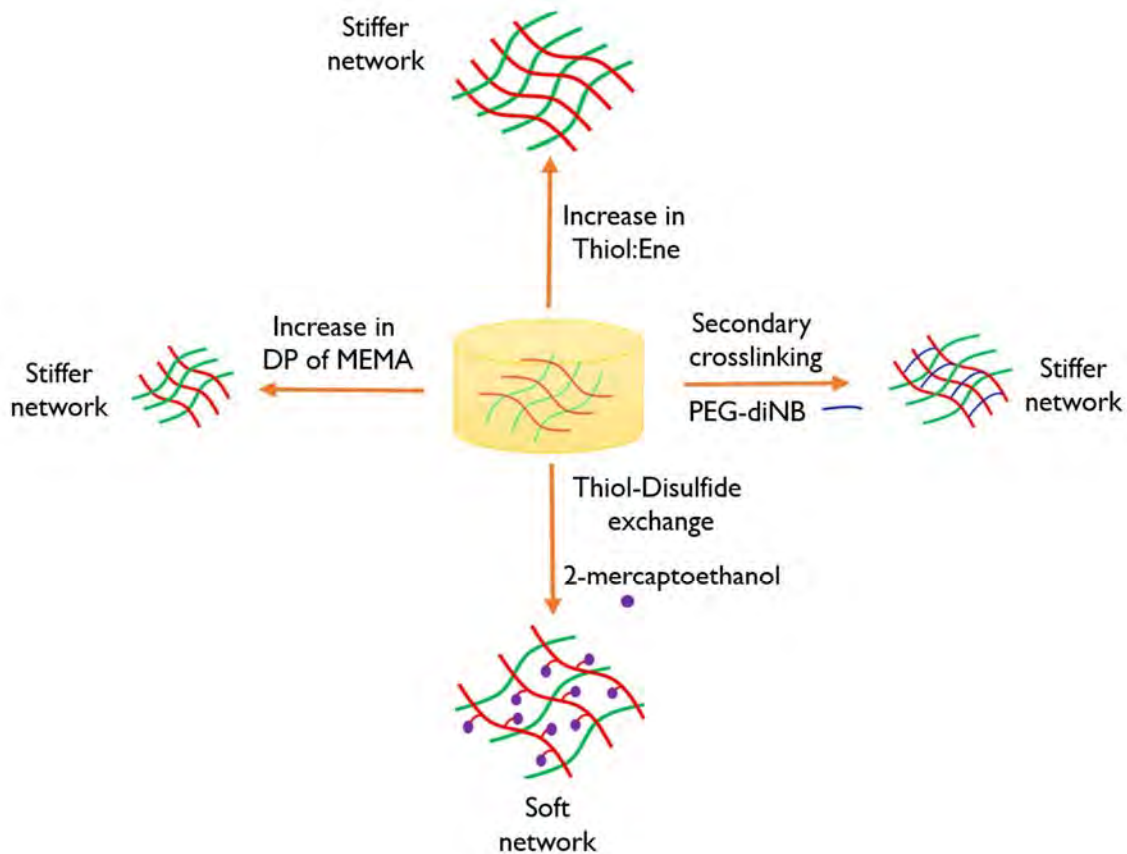
Temperature dependent studies were conducted on the ROP of cyclic esters using various H-bond donating (thio)ureas with base cocatalyst. Several previous studies suggest the inoperability of these catalysts at elevated temperatures due to decomposition of catalyst species. ROP experiments were conducted from 25 to 110°C. The resulting Arrhenius trends indicate both linear and non-linear trends for various H-bonding catalysts, with the non-linear trends breaking from linearity at ca. 80°C. Curved Arrhenius trends were observed to straightened out when polar solvent was used. A mechanistic explanation will be presented.



POLY 327: Gelatin based dynamic hydrogels via thiol-norbornene reactions

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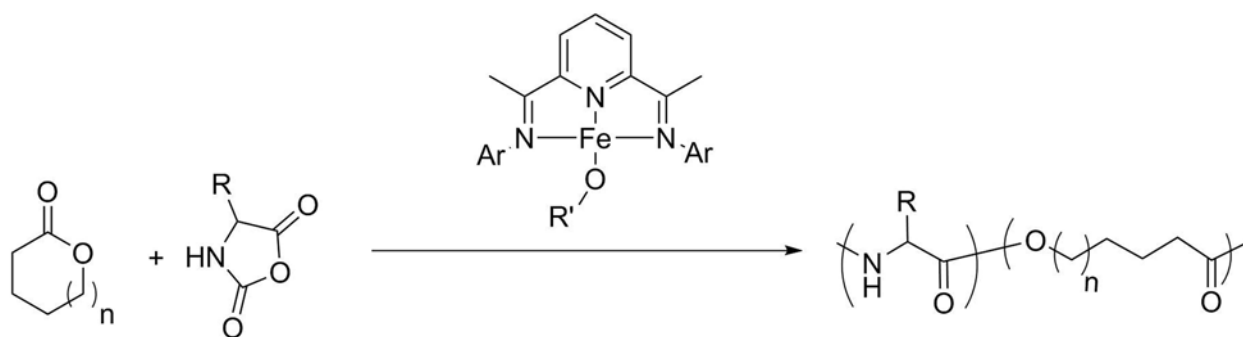
Gelatin-containing dynamic hydrogels were synthesized by crosslinking norbornene functionalized gelatin with poly(2-hydroxypropyl methacrylate-*s*-mercaptoethyl methacrylate) (poly(HPMA-*s*-MEMA)) using thiol-norbornene reactions. These hydrogels demonstrate controllable stiffness over a 9.5 kPa – 17.8 kPa range. Poly(HPMA-*s*-MEMA) was prepared using poly(2-hydroxypropyl methacrylate-*s*-pyridyldisulfide-ethyl methacrylate), which was synthesized using reversible addition-fragmentation chain-transfer polymerization. Subsequent reduction of disulfides in the polymer afforded a copolymer with pendent thiols. Increase in material properties including the swelling ratio and storage moduli (G') was observed with increasing thiol/ene molar ratio due to the formation of disulfide crosslinks. Thiol exchange reactions with 2-mercaptoethanol softened the hydrogel, whereas stiffening was achieved through secondary thiol-norbornene cross-linking between norbornene capped poly(ethylene glycol) (PEG-d_iNB) and unreacted thiols in the hydrogel. Fibroblast cell-culture studies demonstrate that these hydrogels are candidates for studying dynamic cell processes, for example fibrosis.



POLY 328: Synthesis of polyamides and poly(ester-amides) through ring-opening polymerization catalyzed by iron alkoxide complexes

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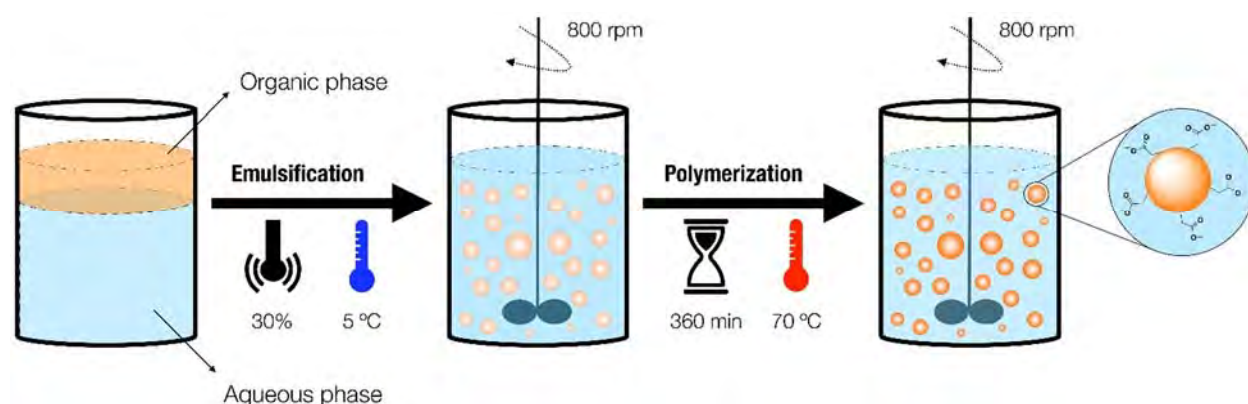
Bis(imino)pyridine alkoxide complexes previously used for the polymerization of lactones are reported for the polymerization of N-carboxyanhydrides (NCAs) and the copolymerization of NCAs. The polymerization of NCAs and lactones to polyamides and poly(ester-amides) respectively. Although many catalysts have only been developed for the polymerization of NCAs and lactones, few have been reported for both monomers. The unique capabilities of the iron complexes used for producing polyamides poly(ester-amides) stems from the unique electronics of the low-valent, iron catalysts. These features along with the generality of the current system will be discussed. Preliminary mechanistic insight into the unusual reactivity of these complexes will also be disclosed.



POLY 329: Synthesis and characterization of drug-loaded methacrylate nanoparticles via in-situ RAFT mini-emulsion polymerization

Ivan R. Rosa, Letícia M. Sampaio, Gisele C. Pinto, Janaína M. Perez, Cesar L. Petzhold, **Marco Oliveira**, macucorj@icloud.com. Organic Department - Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil

In a recent work, our research group developed an optimized miniemulsion polymerization protocol makes 4-cyano-4-[(dodecyl-sulfanyl-thiocarbonyl)-sulfanyl] pentanoic acid (CDPA) act as both a chain transfer agent (CTA) and a stabilizer. Therefore, methacrylate nanoparticles with precise size, morphology, and molecular properties can now be prepared without first preparing CTAs block copolymers and/or macro-monomers. In this work, we further investigate the CDPA multi-function properties to synthesize drug loaded methacrylate nanoparticles. Using the same polymerization protocol, distinct formulations were tested, using methyl (MMA) and butyl methacrylate (BMA) as co-monomers, rifampicin as drug, 2,2'-azobisisobutyronitrile as initiator, and hexadecane as co-stabilizer. The polymerization kinetics and final particle properties are directly correlated to the CDPA function in the system. In this case, pH of miniemulsion's aqueous phase was adjusted to allow CDPA molecules act as both CTA and stabilizer. Therefore, both PMMA and P(MMA-co-BMA) nanoparticles could be synthesized with defined spherical morphology and size ($d \sim 100$ -150 nm), in addition to kinetic and molar mass properties that agrees with the RAFT polymerization process. Since it was found that the rifampicin acts as an inhibitor of the radical polymerization, higher levels of initiator were used, without prejudice to the nanoparticles properties or the RAFT process. In vitro test showed the mid to high amounts of drug can be extracted from the nanoparticles in phosphate buffers. The release profiles are directly linked to (co)polymer molecular properties. The molar mass distributions, MMA/BMA ratio, and the glass transition temperature can be used to control or adjust the drug release rates.

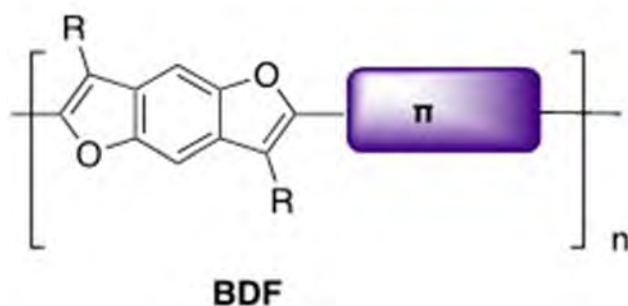


Surfactant-free RAFT miniemulsion process

POLY 330: Design and synthesis of novel heterocyclic building blocks based on benzo[1,2-*b*:4,5-*b'*]chalcogenophenes

Amy E. Brown, *chemterp2012@gmail.com*, Malika Jeffries-El. Chemistry, Boston University, Boston, Massachusetts, United States

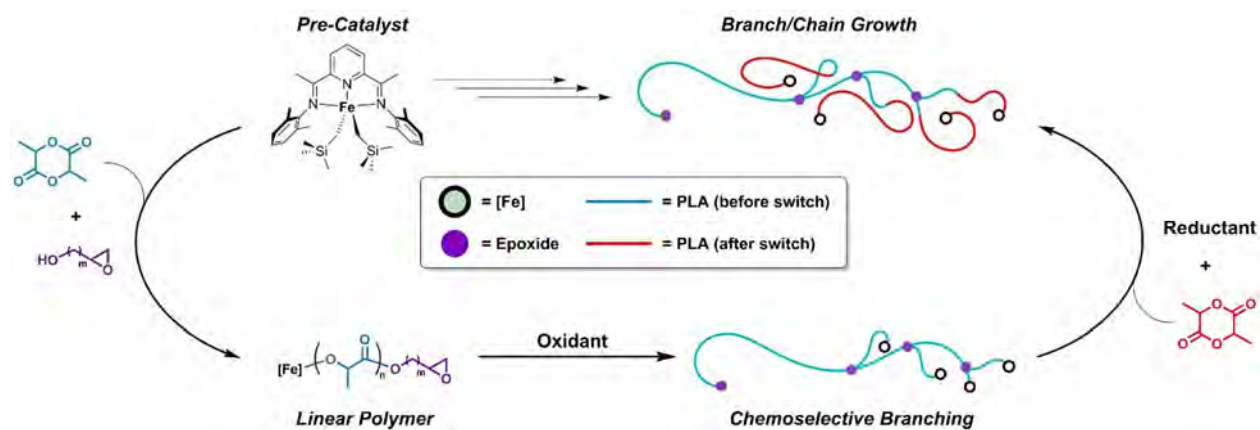
Conjugated polymers possess many exceptional electronic, optical and thermal properties and thus are well suited for organic semiconducting applications, such as photovoltaic cells, thin film transistors, and light emitting diodes. Since the properties of organic semiconductors can be readily modified through chemical synthesis, we have turned our attention towards the design and synthesis of novel building blocks. Of particular interest is the development of materials with narrow band gaps and broad absorption profiles for use in organic solar cells. We have also pioneered the synthesis of the electron-rich benzo[1,2-*b*:4,5-*b'*]difuran (BDF), the oxygen analog of the popular electron rich building block benzodithiophene and are developing narrow band gap conjugated polymers based on it. We have been comparing these building blocks to the sulfur and selenium analogs. Our work on the synthesis and properties and utility of these polymers will be presented.



POLY 331: Utilizing chemoselective, redox-switchable iron-based catalysts for the synthesis of branched PLA

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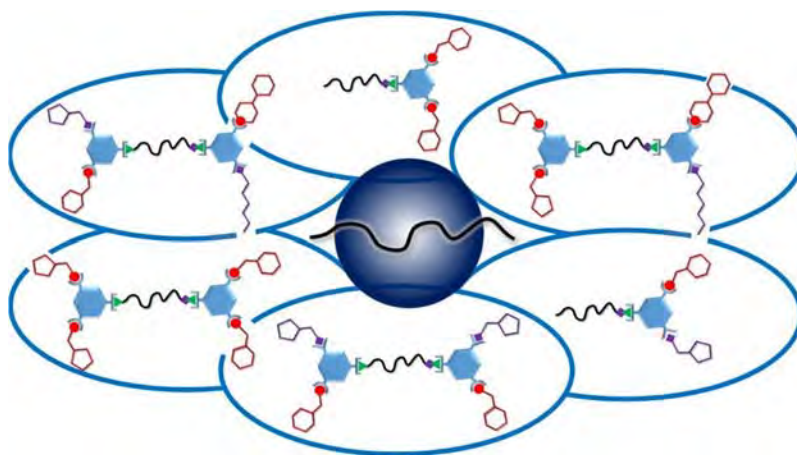
A method was developed using redox-control as a means to induce branching in poly(lactic acid) (PLA). Combining lactide with an iron-based pre-catalyst, and using an epoxy alcohol as the initiator leads to the production of linear PLA containing epoxide end groups. In situ catalyst oxidation changes the chemoselectivity of the iron-based catalyst, resulting in the ring opening of the epoxide end groups. Branches or loops are formed depending on whether this reaction occurs intramolecularly or intermolecularly. Investigations into the ability to control branching in this system using redox cycling at the metal center will be discussed for the synthesis of PLA with tunable, branched architectures.



POLY 332: Functionalization to the fourth power: Towards chemoselective heterotetrafunctionalization of polymer end-groups

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Using precise functionalization techniques, the synthesis of polymers with a variety of end groups will be covered. End-group functionalization, along with other post-polymerization modification techniques, is used for the removal of color and odor, the incorporation of additional molecules, and the addition of functionality which is incompatible with the polymerization method. However, end group functionalization reactions must be complete and efficient due to the fact that separation is not practical for most applications. This project focuses on the expansion of current end-group modification methods for both the α - and ω -ends of polymers synthesized using different polymerization methods.

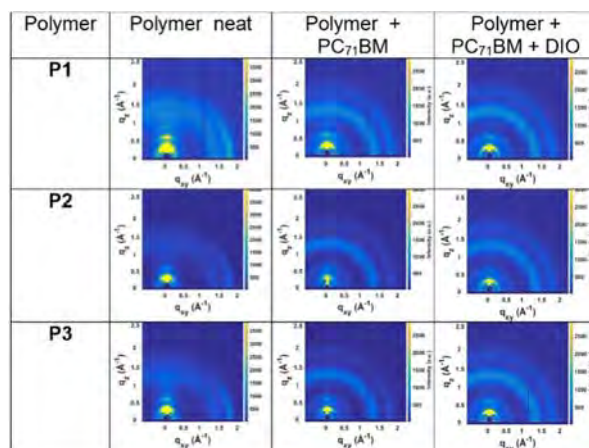
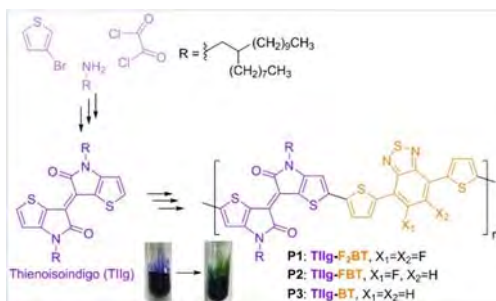


POLY 333: Thienoisindigo-based full-conjugated polymers for next generation of solar cells

Marc Comi Bonachi¹, marc.comi_bonachi@qatar.tamu.edu, Su Haw-Lih^{1,5}, Eric Manley², Tobin J. Marks³, Hassan S. BAZZI¹, Mohammed Al-Hashimi⁴. (1) Chemistry Department, Texas A&M University at Qatar, Doha, Qatar (2) Chemistry, Northwestern University, Chicago, Illinois, United States (3) Northwestern Univ, Evanston, Illinois, United States (4) 3511 Texas AM Eng Bldg, Texas AM University at Qatar, Doha, Qatar (5) Qatar University, Doha, Qatar

Polymeric conjugated materials, or conductive polymers, are organic polymers having conductivities similar to metals or semiconductors due to their continuous π -conjugated double bonds. However, unlike metals or inorganic semiconductors, this type of materials are essentially like plastics, having the advantage of processability. Moreover, their properties could be finely tuned with related structure designs. In most cases, they are also low-cost, earth-abundant, lightweight, flexible, and non-toxic, providing excellent alternative materials to metals and inorganic semiconductors. Today, polymeric conjugated materials has been extensively applied on organic electronics, optoelectronics, and photovoltaics, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs, or organic solar cells). The importance of this area has been recognized by 2000 Nobel Prize in Chemistry.

In many cases, the properties of polymeric conjugated materials are depended on their morphology, *i.e.* how the polymers pack each other. Crystallinity thus became a very important property in the area. Here we are reporting a series of conjugated polymers with highly crystallinity.

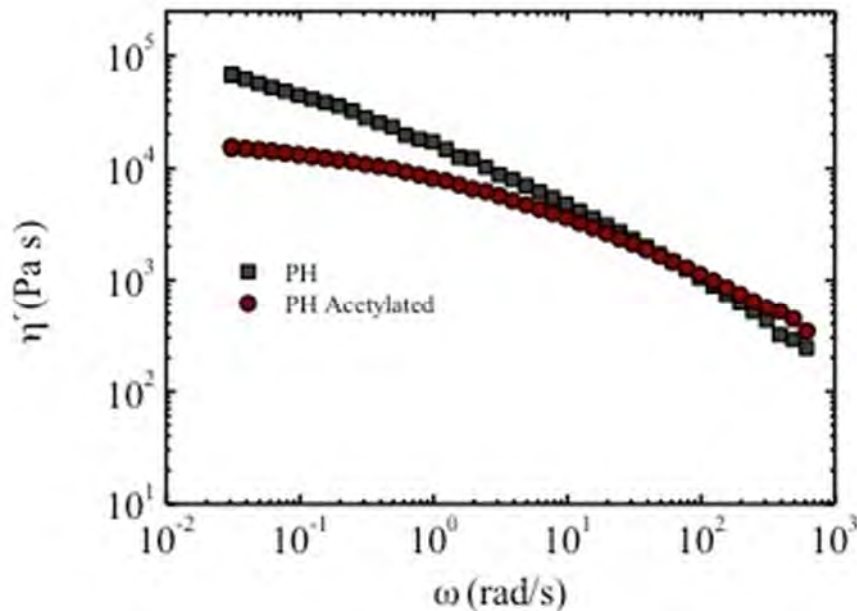


POLY 334: Studying the effect of hydrogen bonds on an amorphous thermoplastic

Ainara Sangroniz¹, ainara.sangroniz@ehu.es, Leire Sangroniz¹, Alejandro Muller^{1,2}, Marian Iriarte¹, Antxon Santamaria¹, Agustin Etxeberria¹. (1) POLYMAT, Department of Polymer Science and Technology, University of the Basque Country, Donostia-San Sebastian, Gipuzkoa, Spain (2) IKERBASQUE, Basque Foundation for Science, Bilbo, Bizkaia, Spain

In this work the effect of the hydrogen bonds in the different properties has been studied. For that phenoxy resin and the corresponding modified samples have been analyzed. The resin contains hydroxyl groups that can easily form hydrogen bonds with acceptor groups, i.e. carboxyl groups, ether, ... This hydroxyl content has been modified by acetylation obtaining samples with different hydrogen bond content.

The level of modification and the presence of hydrogen bonds have been studied by NMR and FTIR. In order to analyze the effect of the different functional groups and the hydrogen bonds thermal analysis by means of DSC and DMA has been performed. The results show that for the samples without hydrogen bonds (modified samples) a decrease on the glass transition temperature is observed, as could be expected. In addition the rheological properties of these samples has been studied, which has not been reported before. The rheological parameters are very sensible to this kind of interactions. The results obtained in the linear viscoelastic regime show that the phenoxy resin has higher viscosity in comparison with modified sample, due to the presence of hydrogen bonds. On the other hand the measurements performed under extensional flow reveal that the resin shows strain hardening and higher extensional viscosity in comparison with the modified sample. Finally, a relationship between the measurements in the linear regime and those obtained in extensional flow is shown.

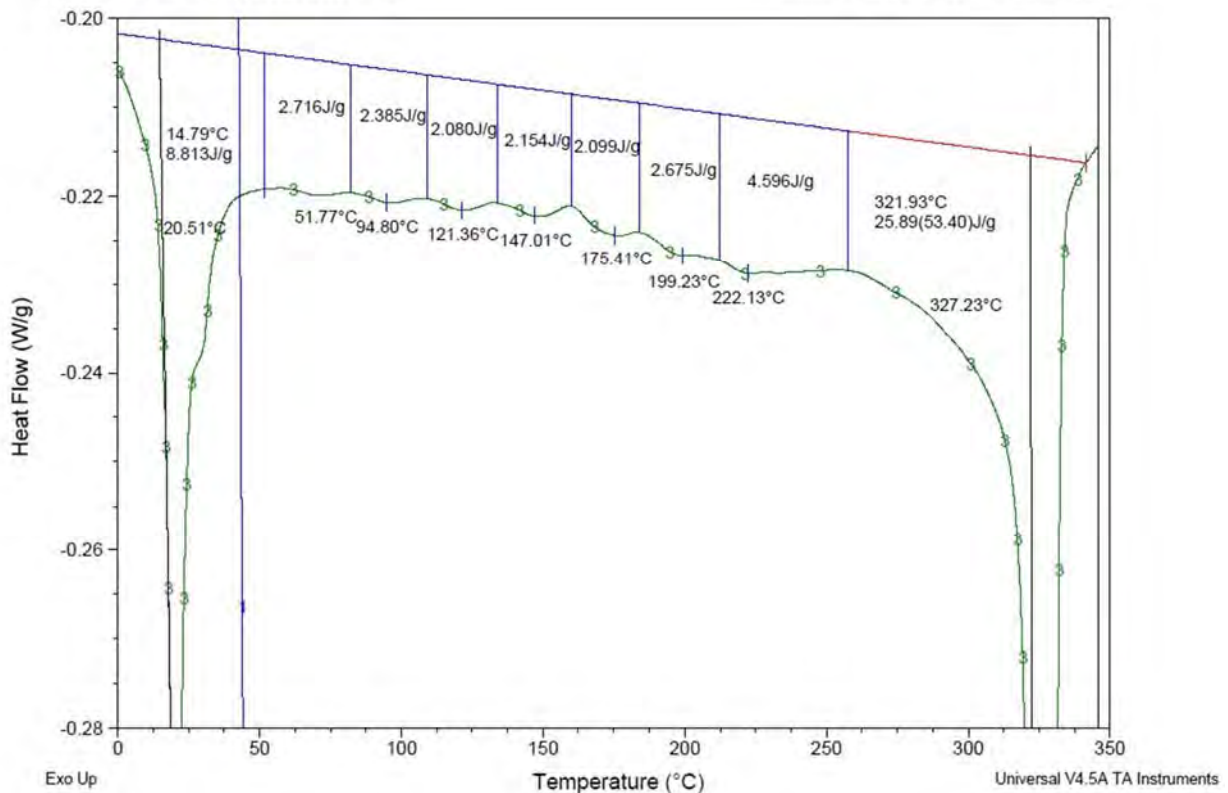


Real part of the viscosity against frequency for phenoxy and modified phenoxy

POLY 335: Simultaneous quantification of homopolymer and sequence analysis of copolymer in semi-crystalline fluoropolymer blends by differential scanning calorimetry

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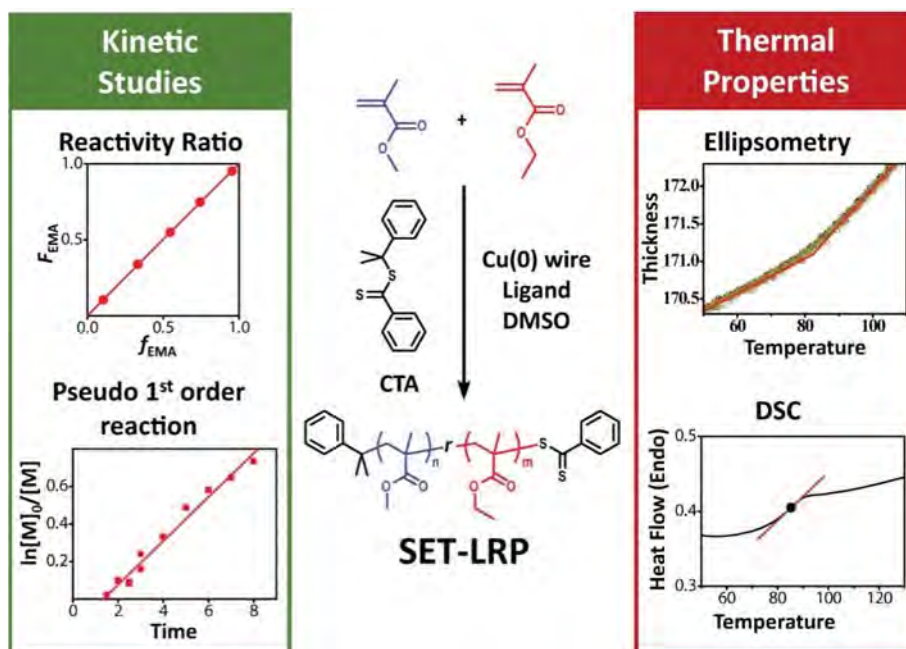
Differential scanning calorimetry (DSC) is a powerful technique applied to the quantification of components in polymer blends, and likewise to analysis of the degree of crystallinity in polymers. In blends of poly(tetrafluoroethylene) [PTFE] homopolymer and poly(tetrafluoroethylene-co-perfluoro vinyl ether) copolymer, a single DSC experiment can quantify the fraction of PTFE in the blend and the fractions of TFE runs of different lengths in the copolymer by isothermal annealing steps. This fractional recrystallization experiment assigns crystalline PTFE domains to TFE runs of different length, from > 35 units (recrystallizing at 300 °C) to < 3 units (recrystallizing at 25 °C). The magnitude of each of the subsequent melt endotherms indicates the amount of material containing that particular TFE segment length. This data contributes to understanding process conditions that may affect polymerization.



POLY 336: Random copolymers of simple methacrylates synthesized by Cu(0)-mediated single-electron transfer living radical polymerization: Copolymerization kinetics and thermal properties

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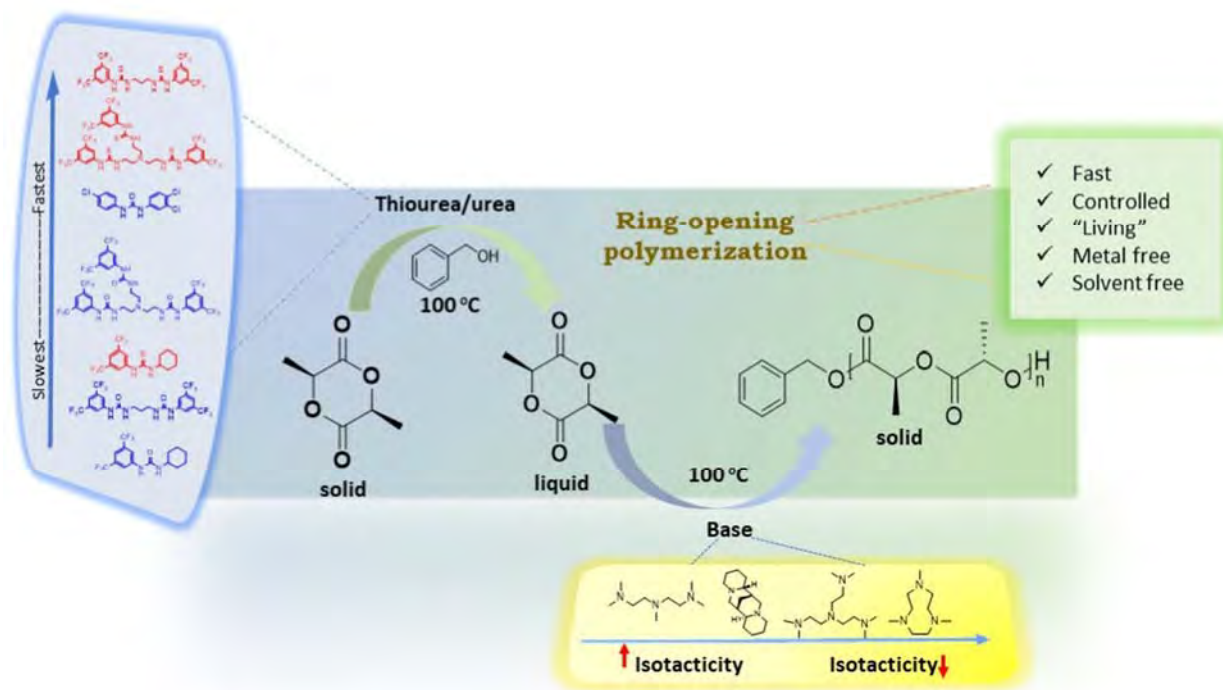
Although controlled radical polymerizations (CRPs) has been extensively utilized to synthesize random copolymers to achieve desired properties for a number of applications, the fundamental studies such as kinetics and reactivity ratio in the copolymerizations, required for the expansion of the CRPs towards many different applications, have not been thoroughly investigated. In this work, we demonstrate detailed kinetic studies for the copolymerizations of two different simple model monomers, methyl methacrylate (MMA) and ethyl methacrylate (EMA) via single-electron transfer living radical polymerization (SET-LRP) which is well-established and versatile technique for controlled radical polymerization of a broad range of monomers including acrylates and methacrylates. Particularly, SET-LRP is beneficial in achieving a broad range of molecular weight (up to hundreds kg/mol), low dispersity (down to ~1.1), and tailored functionalities simultaneously under relatively mild conditions. In kinetic studies, apparent propagation rate constants were estimated with the variation of the feed ratio and polymerization temperature. Furthermore, reactivity ratio values were determined by the approach using Mayo-Lewis equation and other modified approaches, *i.e.* Finemann-Rose and Kelen-Tudos methods. We also explored the glass transition behaviors of resulting random copolymer samples in bulk and thin films as a function of composition. Our findings provide deeper understanding of the fundamental aspects in the copolymerization via the SET-LRP.



POLY 337: “Greener” approach to the ring-opening polymerization of L-lactide

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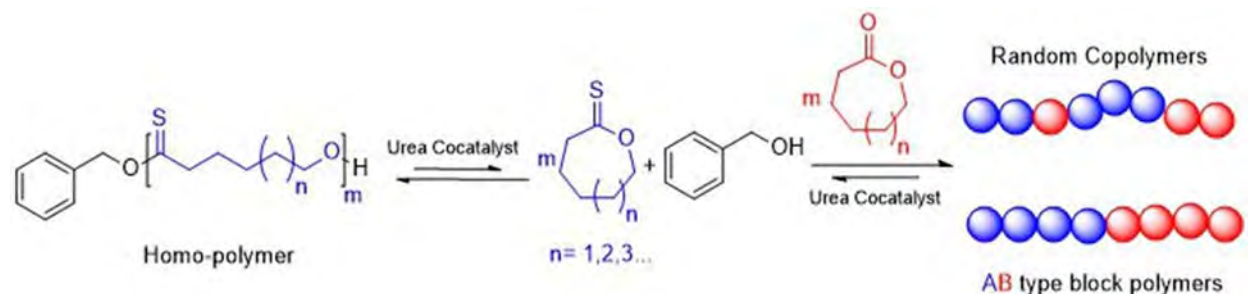
Poly lactides (PLA) are a class of bio-derived polymers that are known to be biodegradable, biocompatible, and mechanically similar to polystyrene, that makes them ideal candidates as plastics. PLAs are synthesized via a condensation reaction of lactic acid or a ring-opening polymerization (ROP) of lactide. The latter approach produces polymers in a more controlled fashion. A greener approach towards ROP would mean conducting reactions under solvent-free, metal free conditions. In this regard, ROP of L-lactide was studied under bulk conditions using H-bonding thiourea and urea/ base co-catalyst systems. The polymerizations were conducted at 100 °C under melt conditions of the monomer. Thiourea catalysts were shown to be more effective and controlled in carrying out the polymerization under bulk condition when compared to their urea analogs. The ROPs show “living” characteristics even though the polymer solidifies prior to full conversion and produces PLA that contain 75%-95% L-lactide units. The one-pot copolymerization of L-lactide and valerolactone was previously known to be unsuccessful using organocatalysts in solvent, but the copolymerizations were shown to successfully produce block copolymers under bulk conditions. The activity of our thiourea and urea organocatalysts in the ROP of L-lactide at elevated temperatures under solvent-free conditions open new avenues for the ROP of monomers.



POLY 338: Organocatalytic Ring opening polymerization of macrolactones and thionolactones

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The organocatalytic ring-opening polymerization (ROP) of cyclic esters has been explored in depth over the past decade. Though the ROP of small and medium ring sized cyclic esters have been illustrated in a vast number of publications, fewer studies have been done concerning the organocatalytic ROP of macrolactones. Our recently developed H-bond mediated organocatalysts demonstrate highly controlled and a living polymerization behavior for macrolactones. The organocatalytic ROP of a thionolactone, ϵ -thionocaprolactone was reported recently. Indeed, the ROP of large thionolactones was previously unexplored, but we conducted their ROP with H-bond mediated cocatalysts. This reaction also shows excellent control and 'living' character. Copolymers of lactones and thionolactones were synthesized, the low melting points and the amorphous nature of the copolymers promise new applications.



POLY 339: Synthesis and characterization of novel anti-coagulants, sulfated poly-amido-saccharides (sulPAS)

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Poly-amido-saccharides (PAS) are well-defined, enantiopure carbohydrate polymers that share many important features with natural polysaccharides, including stereochemical definition, hydrophilicity, and pyranose rings in the backbone. By introducing sulfate groups to the PAS, a heparin mimetic is prepared as the activity of heparin and synthetic FXa targeting molecules is attributed to the presence of sulfate functionalities within the structure. Specifically, we report the synthesis and characterization of a novel anti-coagulant, sulfated poly-amido-saccharide (sulPAS), having the advantages of a synthetic anti-coagulant along with reversibility and a relative ease of synthesis. sulPASs were prepared by first synthesizing the PAS by the anionic ring opening polymerization of a protected lactam monomer and then deprotection, followed by sulfation using SO_3 , NMe_3 (Fig. 1). The sulfated PAS exhibit anti-coagulant activity as determined by FXa binding assay and clotting assay.

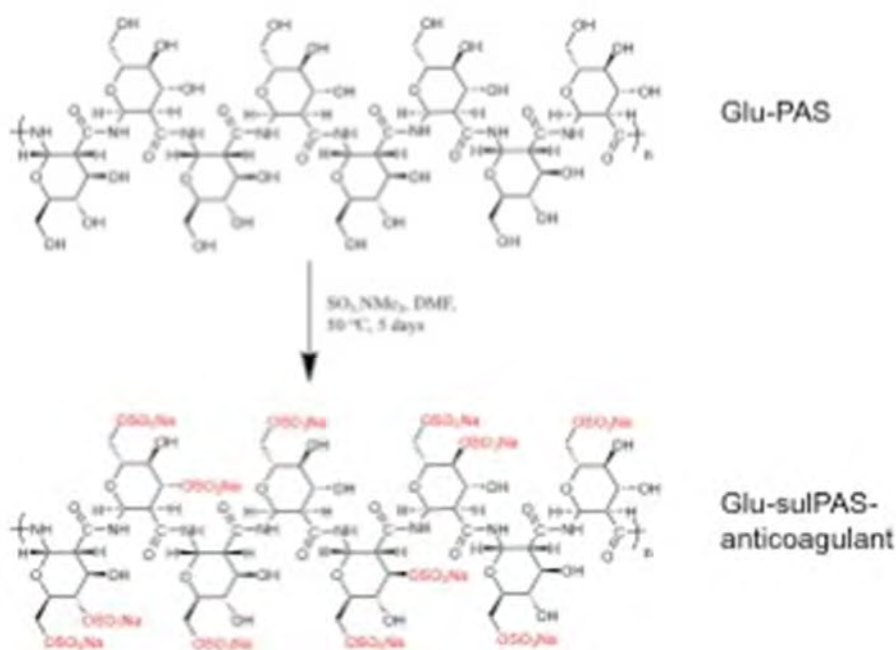
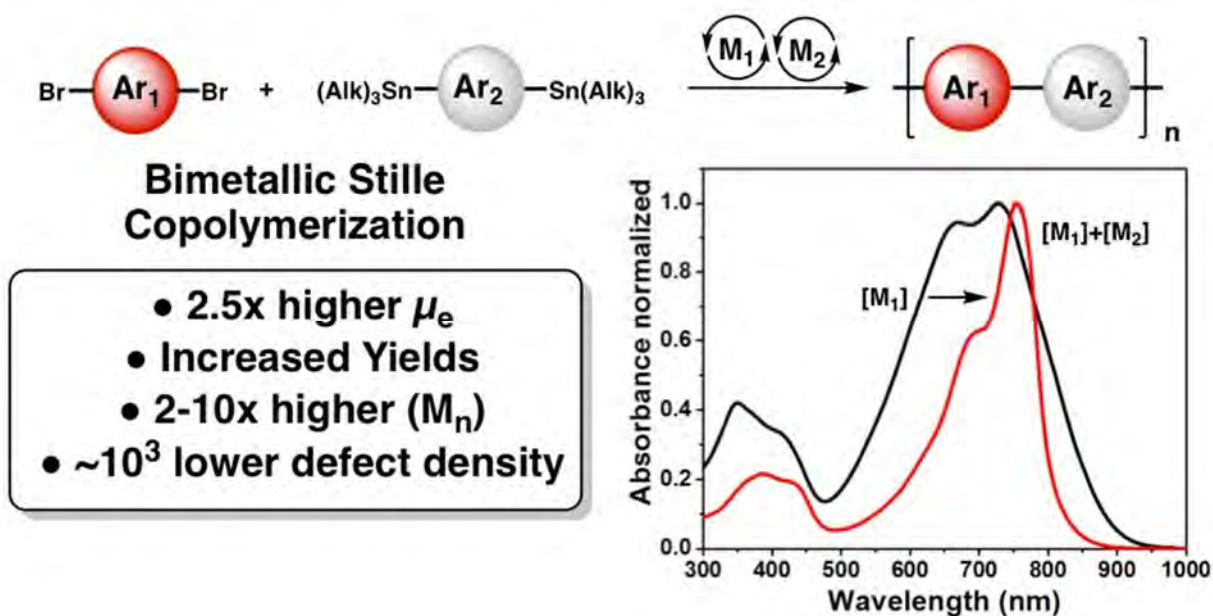


Fig. 1: Synthesis of sulPAS from PAS

POLY 340: High performance electron-transporting acceptor-acceptor conjugated polymers made via bimetallic Stille polymerization

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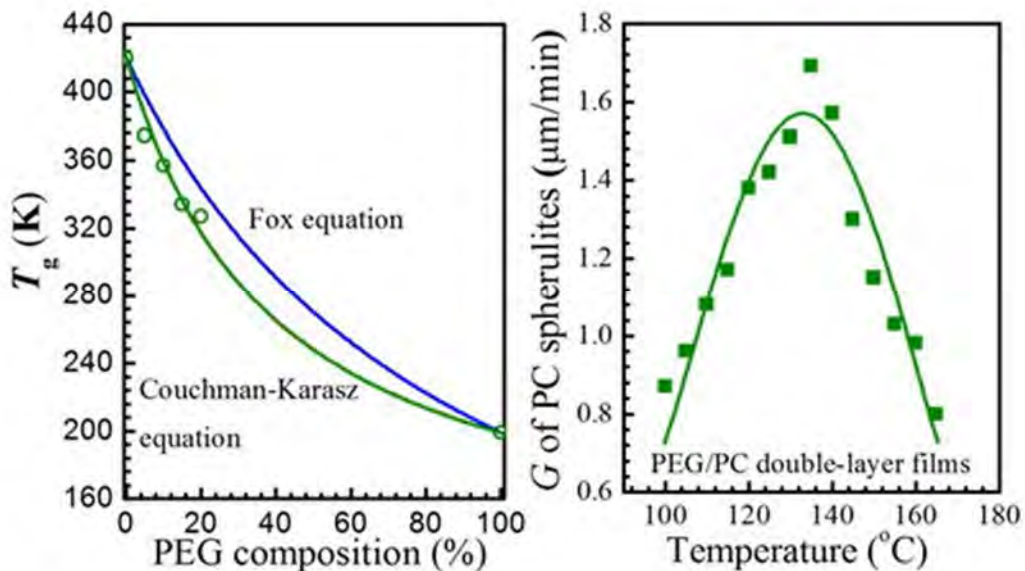
π -Conjugated alternating copolymers represent promising low-cost semiconducting technologies. While many examples of high performance in-chain donor-acceptor (D-A) hole-transporting copolymers have been developed, the prevalence of their electron transporting analogs remains scarce. One effective strategy to improve electron transporting properties of conjugated copolymers is by combining two electron deficient monomers in an acceptor (1)-acceptor (2) (A1-A2) architecture. However, practical synthesis of such copolymers via traditional Stille polymerization is highly challenging due to electron deficient/non-nucleophilic nature of the employed (hetero)aryl stannane comonomers. As a result, copolymers are typically obtained in reduced yields, with low molecular weights and/or low regioregularity due to high incorporation of homocoupling defects, which subsequently lead to reduced copolymer optoelectronic performances. Herein, we report a bimetallic catalytic system that addresses the above copolymerization challenges for the A1-A2 copolymers. Our method provides copolymers in excellent yields with 2-10x increase in number-average molecular weight (M_n), reduced dispersity, and up to $\sim 10^3$ x lower homocoupling defect density compared to that of the classical monometallic Stille catalysts. Preliminary studies indicate that these properties enable increased electron mobilities (>2 x) in OFET devices over literature precedents for the same copolymer structures. The scope of the bimetallic Stille polymerization, the role of ligands/metals on the copolymer characteristics, mechanistic, and copolymer characterization details will be presented.



POLY 341: Making completion of spherulitic growth within eight minutes for Bisphenol A polycarbonate by a double-layer film method

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In this study, it was found that bisphenol A polycarbonate (PC) could accomplish crystallization only within eight minutes by covering a molten PEG layer on it. The spherulitic growth rates of the underneath PC layer in poly(ethylene glycol)/PC (PEG/PC) double-layer film, which isothermally crystallized at various temperatures above the melting point of PEG layer, were studied by polarized optical microscope (POM). The results showed that the change of spherulitic growth rate with isothermal crystallization temperature (T_c) presented a “bell-shape curve”, just like some other semicrystalline polymers did. The PEG/PC double-layer films were *in-situ* prepared by laying a PEG film on a PC film at 250 °C and holding for 5 min before quenched to different T_c 's for POM observation. It was interesting to find that the covering molten PEG layer could greatly accelerate the spherulitic growth rate of the underneath PC layer and shorten the crystallization time within eight minutes. The miscibility for PEG/PC blends was investigated by using differential scanning calorimetry (DSC), which played a key role on observing the crystallization accelerating effect.

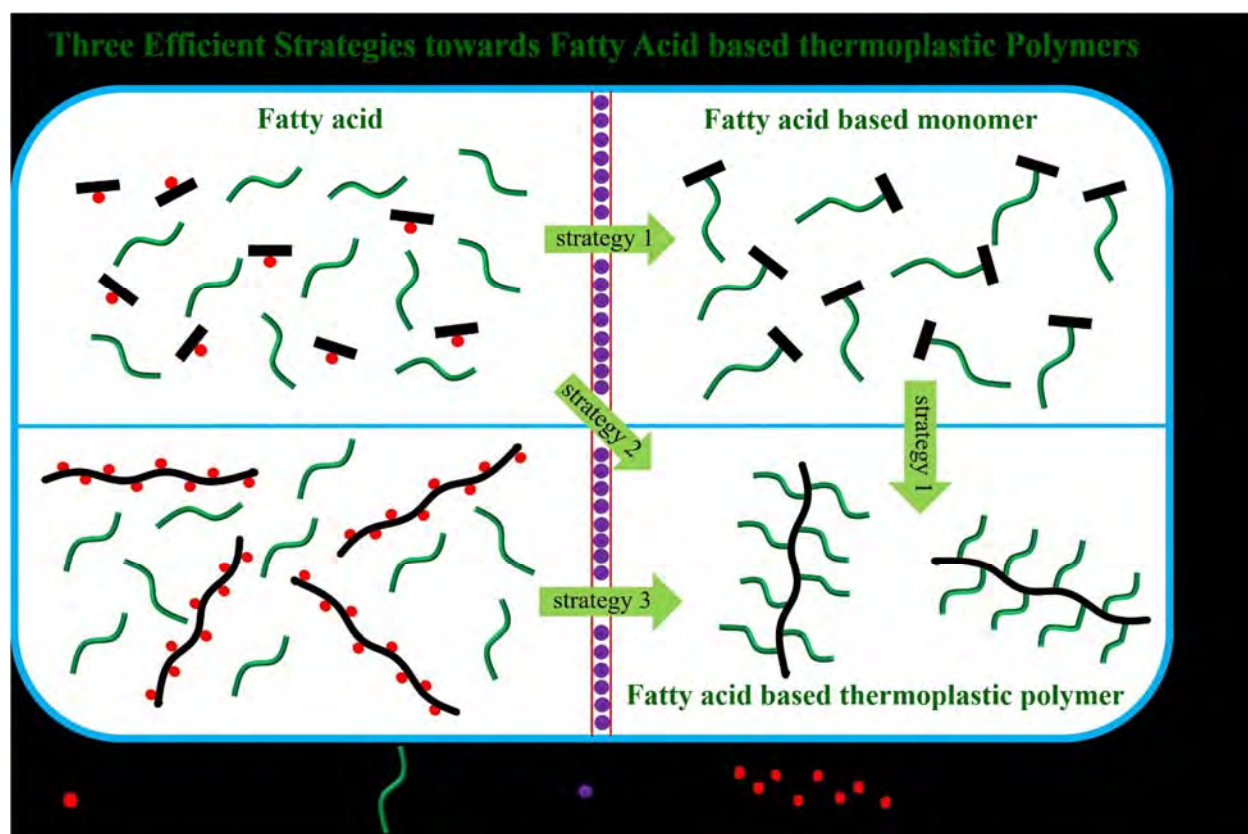


The change of T_g with PEG composition (left) and change of G with temperature for PEG/PC double-layer films (right).

POLY 342: Highly efficient strategies towards sustainable monomers and polymers derived from fatty acids via tetramethylguanidine promoted esterification

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Three facile and efficient strategies for preparing sustainable monomers and polymers derived from renewable fatty acids have been investigated. All these strategies rely on high efficient esterification between halogenated compounds and fatty acids, promoted by 1,1,3,3-tetramethylguanidine (TMG). In strategy 1, fatty acid-derived sustainable polymers were synthesized by TMG promoted esterification of fatty acid with halogenated monomers followed by polymerization. In strategy 2, esterification and polymerization reactions were performed in a one pot process. While in strategy 3, TMG catalyzed esterification between halogenated polymers and fatty acids was performed to obtain fatty acid based thermoplastic polymers. ¹H NMR and SEC were performed to trace the transformation of fatty acids to thermoplastic polymers. To demonstrate the versatility of these strategies, a series of fatty acid based monomers were developed by using varied halogenated monomers. Moreover, reversible addition-fragmentation chain transfer (RAFT) polymerization on the prepared monomers was performed successfully.

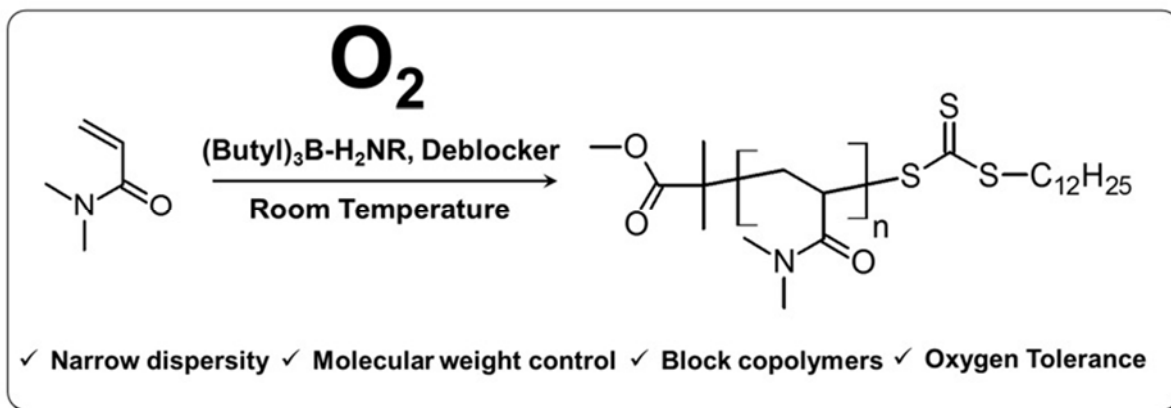


Three efficient strategies towards fatty acid based thermoplastic polymers.

POLY 343: Initiation through alkylborane complexes for oxygen tolerant and ambient temperature RAFT

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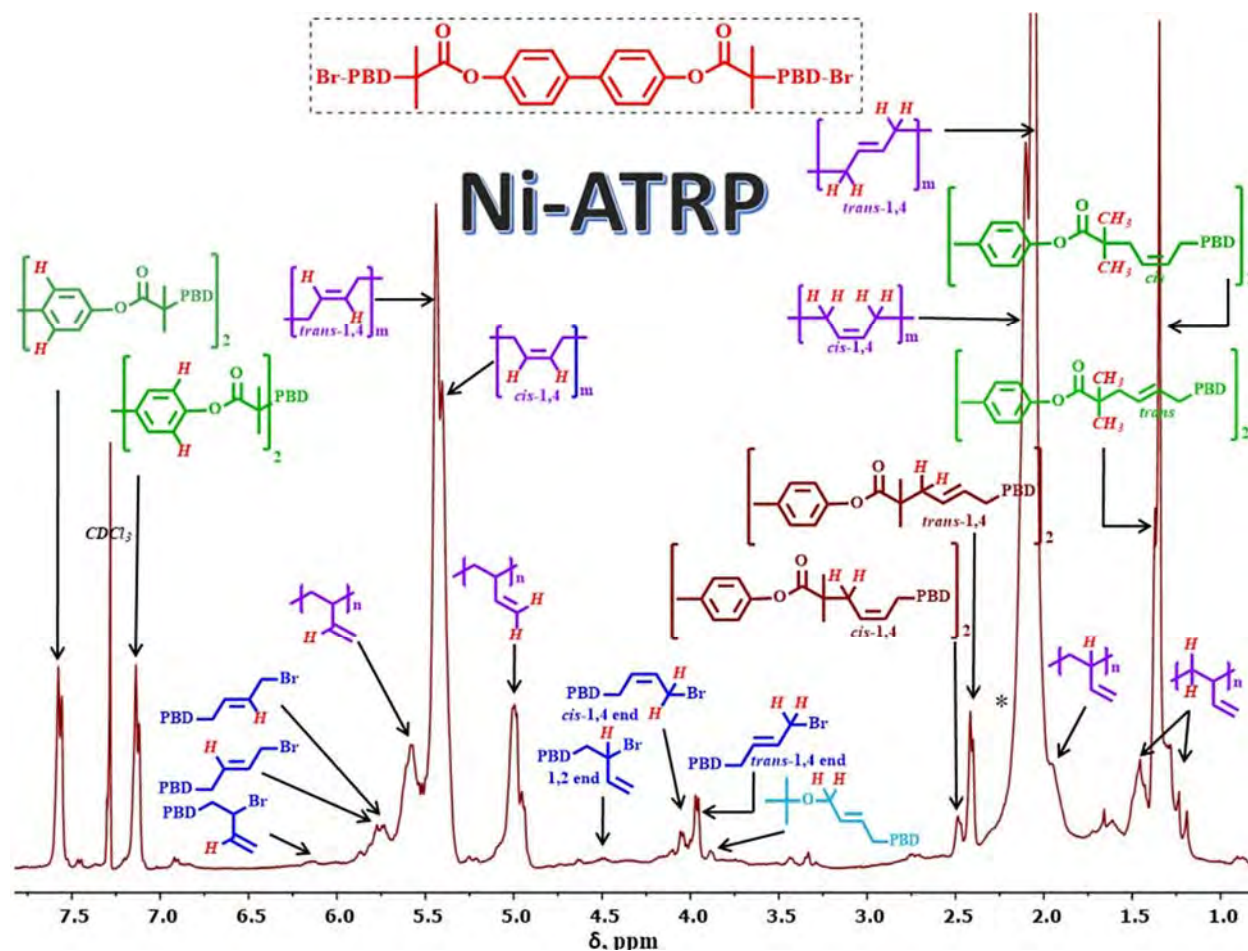
An air-stable alkylborane-amine complex was utilized to initiate reversible addition-fragmentation chain transfer (RAFT) at room temperature and in the presence of oxygen. To chemically deblock the air-stable complex, carboxylic acid or isocyanate functionalities were employed, liberating a reactive trialkylborane that spontaneously consumes oxygen and generates radicals to drive RAFT. Due to these attributes, alkylborane initiated RAFT (AI-RAFT) was capable of synthesizing well-defined polymers over a wide range of molecular weights, having narrow molecular weight distributions, and of various compositions within oxygen. Deblockers employed in the AI-RAFT process were found to impact polymerization kinetics, molecular weights, and dispersities. Using specific formulations, rapid polymerization was also possible within minutes under ambient conditions without any prior deoxygenation. The scope of chemically induced AI-RAFT was shown by polymerizing acrylamide, acrylate, and methacrylate monomers and by synthesizing block copolymers without any thermal, photochemical, electrical, or mechanical stimulus. Complex polymer architectures were also explored by incorporating multifunctional crosslinking agents into polymerizations using convenient conditions within oxygen and at room temperature.



POLY 344: Butadiene-ATRP with Ni, Pd and Pt complexes

William Bannerman, william.bannerman@uconn.edu, Mark Johnson, Vignesh Vasu, Joon-Sung Kim, Hyun-Seok Yu, Alexandru D. Asandei. Institute of Materials Science, Polymer Program and Department of Chemistry, University of Connecticut, Storrs Mansfield, Connecticut, United States

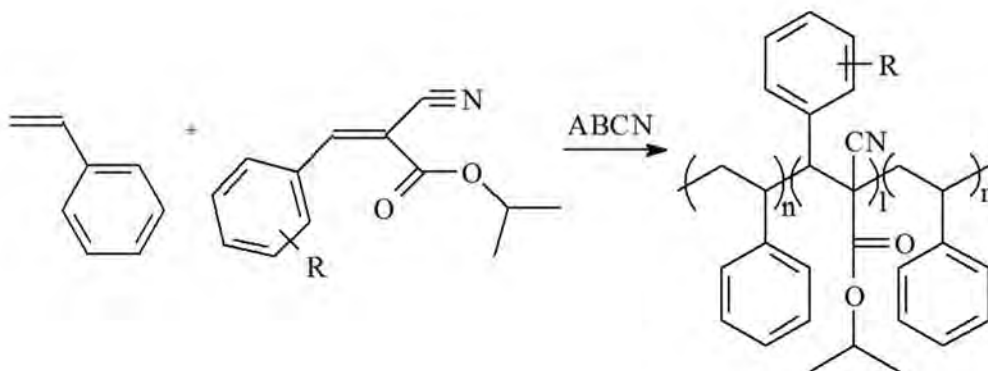
A series of Group 10 (Ni, Pd, Pt) complexes with C-, N-, and P-based ligands were investigated in the ICAR ATRP of butadiene initiated from bromoesters in toluene at 110 °C. A set of trends such as $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2 \gg \text{Ni}(\text{COD})_2$, NiBr_2/L : $\text{L} = \text{bpy} \geq \text{PMDETA} > \text{MeO-bpy} > \text{TPMA}$, $\text{Cp}_2\text{Ni} \geq \text{NiTPP}$, $(\text{PPh}_3)_2\text{NiCl}_2 \gg (\text{PBu}_3)_2\text{NiCl}_2 > (\text{PCy}_3)_2\text{Ni}(\text{Napht})\text{Cl} \gtrsim (\text{PCy}_3)_2\text{NiCl}_2$, $\text{Pd}(\text{PPh}_3)_4 > (\text{PPh}_3)_2\text{PdCl}_2$ are apparent in each group and for $(\text{PPh}_3)_2\text{MtCl}_2$ where $\text{Ni} \gg \text{Pd} \sim \text{Pt}$. However, only $(\text{PPh}_3)_2\text{NiCl}_2 > (\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ are capable of initiator activations as well as of good polymerization control which affords polybutadiene with high (> 65%) Br chain end functionality.



POLY 345: Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 5. Oxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates

William S. Schjerven, WSCHJERV@depaul.edu, Kumail M. Hussain, Saira Ahmed, Andrea Baldi, Nina M. Benton, Aerin L. Nilsen, Taylor J. Rager, Jacob N. Sanderson, Dej Scott, Jeannette G. Zapien, Omar Zavala, Gregory B. Kharas. Chemistry, DePaul University, Chicago, Illinois, United States

Novel trisubstituted ethylenes, oxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ (where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido) were prepared and copolymerized with styrene. The ethylenes were synthesized by the piperidine catalyzed Knoevenagel condensation of oxy ring-substituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, 1H - and ^{13}C -NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by FTIR, 1H and ^{13}C NMR. Thermal properties of the copolymers are characterized by DSC and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500C range with a residue, which then decomposed in the 500-800C range.

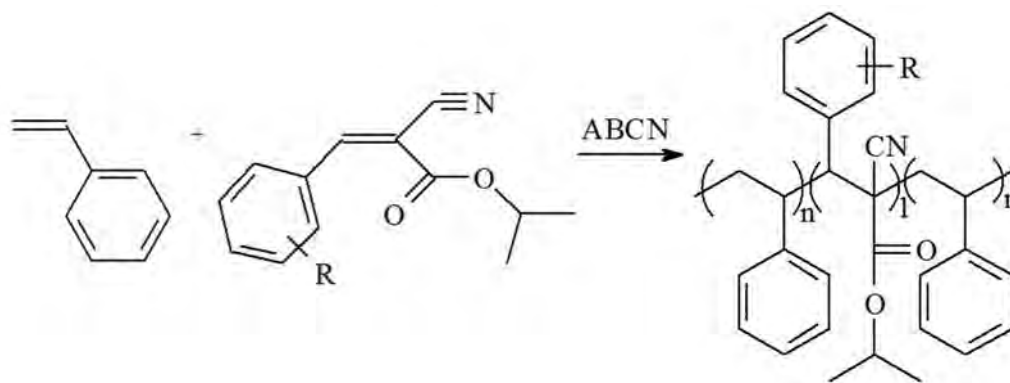


Copolymerization of ST and the ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido.

POLY 346: Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 6. Halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates

Sara M. Rocus, SROCUS@depaul.edu, Benjamin Y. Killam, Timothy S. Bullock II, Juliana Carmichael, Shelby J. Carvalho, Anais A. Dominguez, Tyler Faith, Jesse Garcia, Andrew D. Gould, Emily E. Jacobs, Kristen Kochan, Gregory B. Kharas. Chemistry, DePaul University, Chicago, Illinois, United States

Novel trisubstituted ethylenes, halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ (where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F) were prepared and copolymerized with styrene. The ethylenes were synthesized by the piperidine catalyzed Knoevenagel condensation of oxy ring-substituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, 1H - and ^{13}C -NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by FTIR, 1H and ^{13}C NMR. Thermal properties of the copolymers are characterized by DSC and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500C range with a residue, which then decomposed in the 500-800C range.

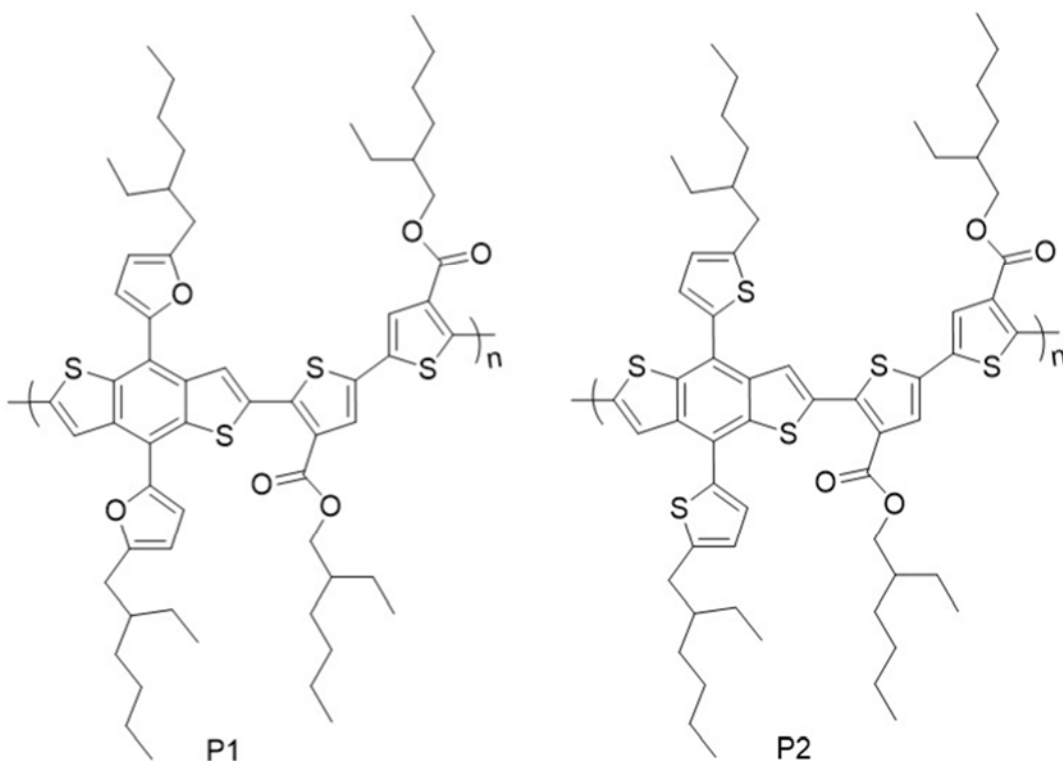


Copolymerization of ST and the ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2CH(CH_3)_2$. R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F.

POLY 347: Benzodithiophene (BDT) based polymers for organic photovoltaics

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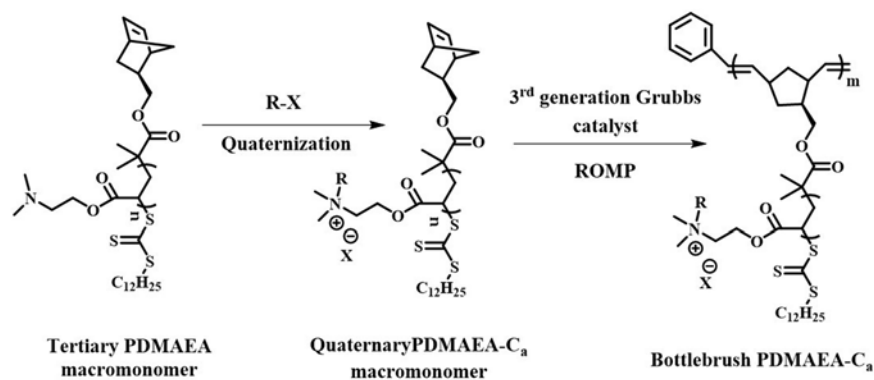
Conjugated organic polymers for organic photovoltaics have gained attention owing to their attractive properties such as low cost solution processability, mechanical flexibility and better charge carrier mobility. Herein, two conjugated polymers (P1, P2) with benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) as the donor and bis(2-ethylhexyl)[2,2'-bithiophene]-4,4'-dicarboxylate as the acceptor are reported. The synthesized polymers are characterized and their photophysical properties and electrochemical properties are studied. The bulk-heterojunction photovoltaic devices are fabricated from blends of these polymers with fullerene derivatives as the acceptors and the space charge limited current (SCLC) model is used to determine charge carrier mobilities. The morphology of the thin films are investigated by the tapping mode atomic force microscopy (TMAFM) and transmission electron microscopy (TEM).



POLY 348: Synthesizing amphiphilic cationic bottlebrush polymers for anti-marine fouling

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Adhesion of marine fouling on surfaces such as ship hulls, pipelines, and fishing nets causes higher fuel consumption and maintenance costs. Microorganism settlement on medical equipment also causes infection to patients. To overcome these problems, amphiphilic cationic polymers containing a quaternary ammonium moiety can be used to prevent settlement. The positive charges of ammonium groups along the polymer chains destructively interact with the negative charge on the cell wall of bacteria, inhibiting bacteria adhesion. Longer alkyl chains off the ammonium improve antimicrobial activity due to better hydrophobic interaction with the cell wall. A challenge with linear polymers is that their flexible structures lead to different morphologies when wet versus dry, likely changing their anti-fouling ability. Bottlebrush polymers with dense branches off the polymer backbone are less flexible and help stabilize the structure when they are used under water, potentially improving their anti-biofouling nature. To create bottlebrush polymers with dense branches of quaternary ammonium macromonomers quaternary ammonium salt polymers from poly(dimethylamino ethyl acrylate) (quaternary PDMAEA-C_a, where a is the number of carbons in alkyl group) were synthesized through ring opening metathesis polymerization (ROMP). Prior to ROMP, the tertiary amine macromonomers of PDMAEA were made via reversible addition-fragmentation chain transfer (RAFT) polymerization to generate polymers with a polymerizable norbornene end group with the desired molecular weight. The PDMAEA macromonomers were reacted with butyl bromide, hexyl bromide, and dodecyl bromide to obtain quaternary ammonium polymers with different length alkyl chains. Quaternary PDMAEA-C₄, PDMAEA-C₆ and PDMAEA-C₁₂ macromonomers were synthesized via RAFT polymerization and subsequent quaternization. Bottlebrush polymers were synthesized by ROMP with different molecular weights by varying the macromonomer to catalyst ratio. Changes to the length of the alkyl chain and polymer molecular weight affected polymer solubility and morphology in water.



R-X = butyl bromide, hexyl bromide, and dodecyl bromide

Figure 1. synthesis of cationic bottlebrush polymers via ROMP

POLY 349: Polymerization of “controlled release” monomers containing a hydrolytically sensitive ester linkage via RAFT polymerization

Maan A. Al-Ali¹, Malali@email.sc.edu, Savannah L. Witcher², Brian C. Benicewicz³, Alan Decho⁴. (1) Department of chemistry and biochemistry, University of south carolina, Columbia, South Carolina, United States (2) Department of Environmental Health Sciences , University of South Carolina, Columbia, South Carolina, United States (3) Dept of Chem Biochem, Univ of South Carolina, Columbia, South Carolina, United States

Grafted “controlled release” polymers containing a hydrolytically sensitive ester linkage on silica nanoparticles were successfully prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization. Two potential “controlled release” monomers (HEMA-LA) and (HEMA-SA) were synthesized by the ring opening reaction of L-lactide or succinic anhydride with 2-hydroxyethyl methacrylate (HEMA), respectively. The polymerization of the methacrylate monomers was carried out using 4-cyanopentanoic acid dithiobenzoate (CPDB) as RAFT agent. Both polymers poly(HEMA-LA) and poly(HEMA-SA) were characterized by NMR spectroscopy and gel permeation chromatography (GPC). The degradation rates of these two polymers were investigated using phosphate buffer solution (PBS, pH = 7.4) at 37 °C as a function time using conjugated dyes. Such polymer grafted nanoparticles are being developed for use as delivery vehicles for anti-bacterial applications.



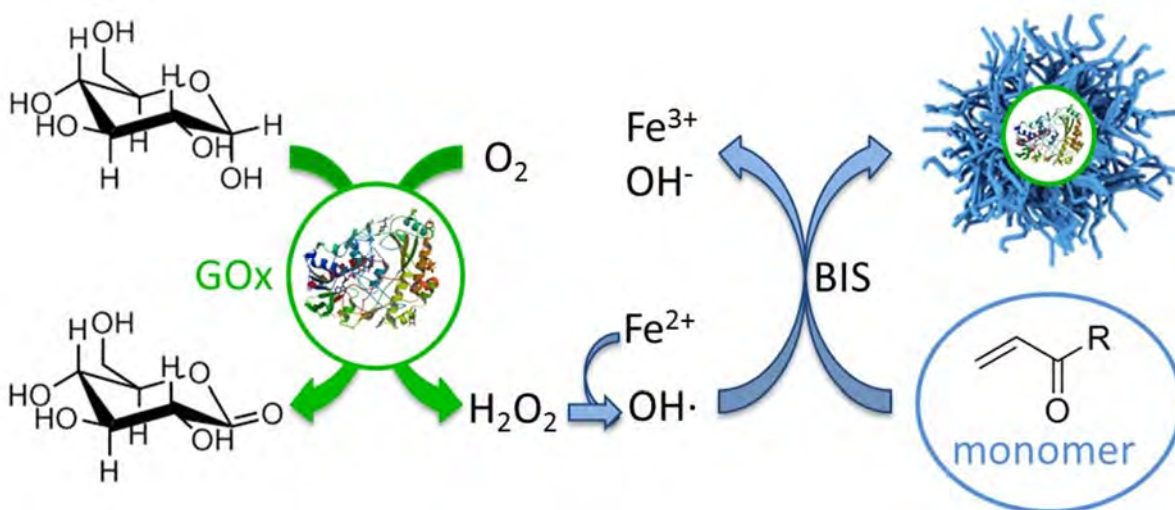
POLY 350: Enzymatic synthesis of stimuli-responsive microgels

Elisabeth Gau^{1,2}, gau@dwi.rwth-aachen.de, Franziska Flecken^{1,2}, Agnieszka N. Ksiazkiewicz^{1,2}, Andrij Pich^{1,2}. (1) DWI - Leibniz-Institute for Interactive Materials, Aachen, Germany (2) Institute for Technical and Macromolecular Chemistry, Functional and Interactive Polymers, RWTH Aachen University, Aachen, Germany

Recently, aqueous microgels turned out to be suitable candidates for numerous biomedical applications due to their unique properties. Microgels are highly crosslinked, soft polymer colloids which exhibit stimuli-responsive behavior depending on the incorporated monomers. The conventionally used method for microgel synthesis is precipitation polymerization, mainly initiated by thermic initiation with azo- or peroxide-based compounds. The heat needed for radical formation limits the possible reactants to thermo stable substances and thus hinders the direct incorporation of biomolecules into the polymer structure during synthesis.

The use of enzymes for radical formation and polymerization initiation poses a promising alternative to thermic initiators. Enzymes are active at moderate temperatures and therefore enable a decrease of the polymerization temperature.

In this work, we present the use of the fungal enzyme Glucose oxidase (GOx) for the synthesis of aqueous microgels. GOx catalyzes the oxidation of β -D-glucose with molecular oxygen to D-glucono-lactone and hydrogen peroxide. Through the addition of ferrous ions (Fe^{2+}), the hydrogen peroxide gets cleaved into hydroxyl radicals. These radicals act as initiators for the polymerization reaction. With this method, we successfully synthesized temperature-responsive microgels based on *N*-vinylcaprolactam (VCL), showing that the active GOx gets encapsulated into the polymer network during synthesis. This enables the facile synthesis of core-shell microgels by the addition of a second monomer and new enzyme substrate.

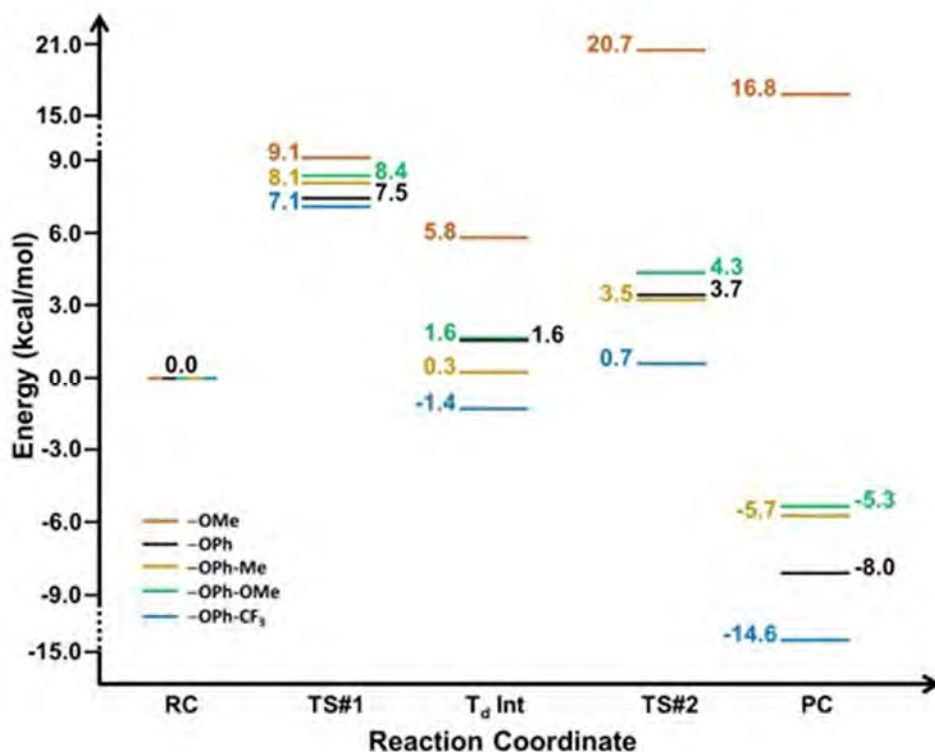


Reaction scheme for the enzymatic synthesis of microgels with Glucose Oxidase (GOx)

POLY 351: Computational investigation of the effects of leaving groups and protecting groups on the kinetics of chain-growth polycondensation polymerization

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Polycondensation techniques are effective methods to produce a wide variety of polymers for various applications. The chain-growth condensation (CGC) process allows for controlled synthesis of block copolymers, and most interestingly, the synthesis of surface-initiated polymer brushes of polymers such as aromatic polyamides that contain many industrially relevant properties. However, the factors dictating the kinetics and termination of aromatic polyamide polymer brush growth are relatively unknown. In this investigation, the effect of different leaving groups on a variety of ester-based monomers was performed to computationally probe the chemical properties that govern the CGC polymerization. Linear and branched alkane ester leaving groups were compared to phenyl-based leaving groups with varying functionality to observe the effect on the polymerization rate and by-product formation. It was found that for the alkyl-based leaving groups, steric hindrance and pKa are the dictating factors limiting polymer growth, while for the phenyl-based leaving groups, electron withdrawing character improves the CGC kinetics by stabilizing the phenoxide leaving group. Additionally, the effect of varying the protecting group on the nucleophilicity of the attacking amine will be presented.

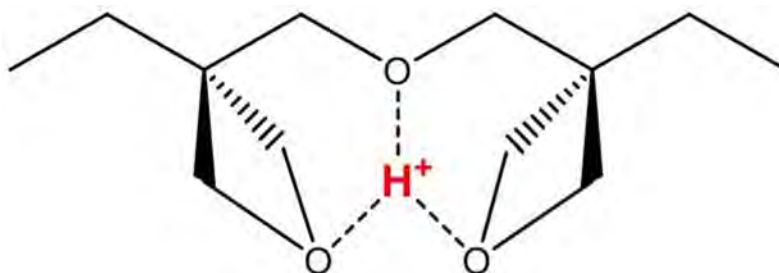


POLY 352: Induction time and hydrogen bonding complexes of epoxide and oxetane monomers in photo-initiated cationic polymerization

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Photopolymerization is an important technique; its applications lie in coatings and adhesives as well as additive manufacturing and 3D printing for stereolithography. In most applications, radical photopolymerization is utilized rather than cationic or anionic photopolymerization because it is more well-known. The goal of this study is to advance the fundamental understanding of cationic photopolymerization to aid in the design of more advanced stereolithography technology.

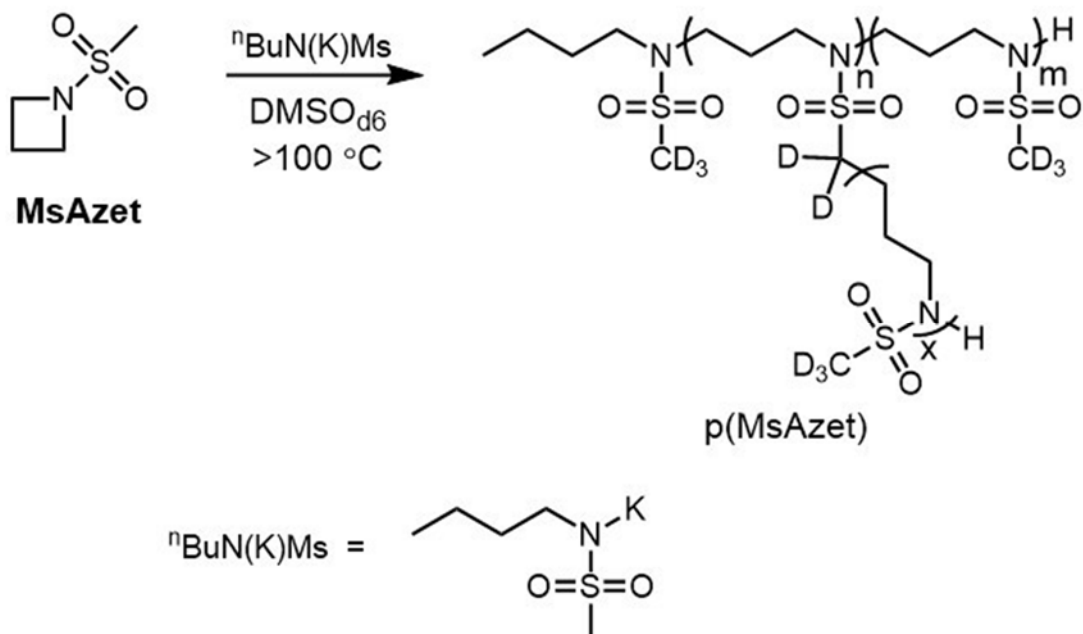
Some epoxide and oxetane monomers are resistant to cationic photopolymerization; they exhibit a lengthy period of inactivity (induction time) before they rapidly polymerize. We have developed a hypothesis to describe this behavior that involves the formation and breakdown of a hydrogen bonding complex involving the monomer and the photo-initiator. We believe that the glycidyl ether structural motif (and its oxetane-based analog) is key to this hydrogen bonding behavior. Preliminary FT-IR and DSC experiments have been conducted which support this hypothesis, and it will be investigated further in this study through the use of NMR, DSC, FT-IR, and Optical Pyrometry.



POLY 353: Anionic polymerization of azetidine

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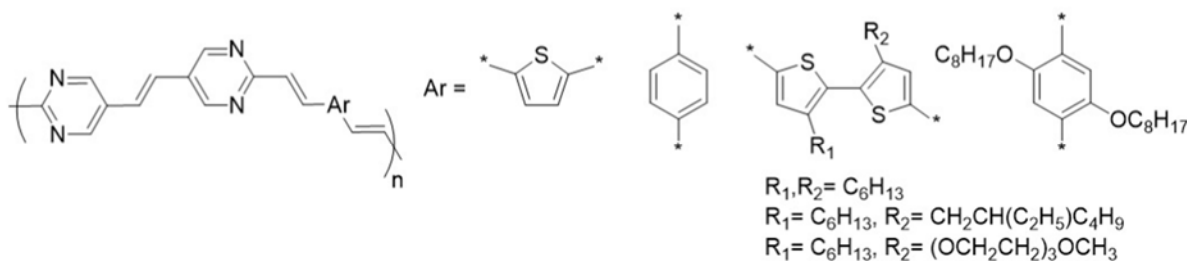
Although similar to many anionic ring-opening polymerization (AROP) capable monomers, cyclic imines do not undergo anionic polymerizations. For example, aziridine and azetidine only polymerize through cationic ring-opening polymerization (CROP) and produce hyperbranched polymers with broad molecular weight distributions. Building upon the progress made with *N*-(sulfonyl)aziridine polymerizations, we now report the first example of the AROP of an activated azetidine *N*-(methanesulfonyl)azetidine (**MsAzet**). **MsAzet** undergoes anionic polymerization at high temperature (>100 °C) in DMSO to form p(MsAzet). However, unlike the sulfonylaziridine systems, light branching of p(MsAzet) does occur, although the mechanism for branching is very different from what occurs in CROPs of aziridine and azetidine. This branching occurs due to activation of the sulfonyl group. The kinetics of the polymerization of **MsAzet** are also studied.



POLY 354: Bipyrimidine based donor-acceptor conjugated polymers for organic electronics

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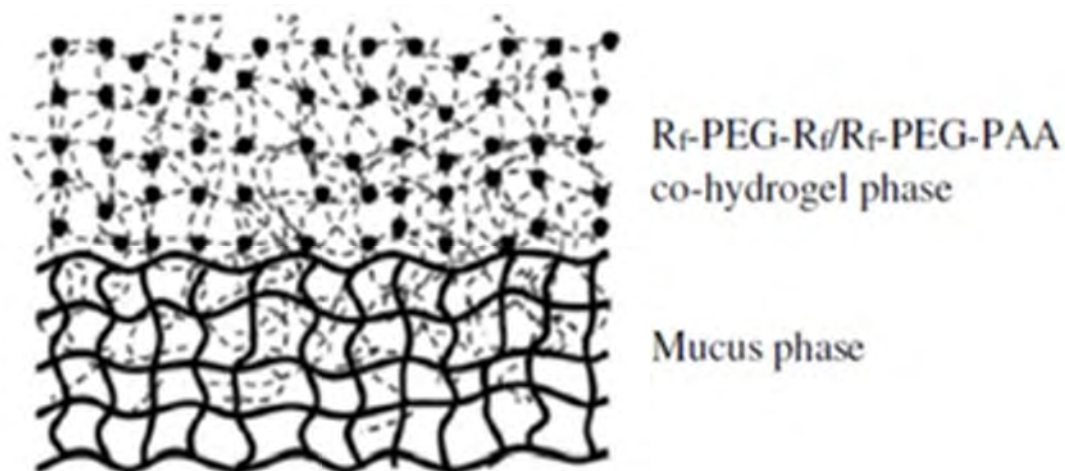
The synthesis of various vinyl pyrimidine polymers via aldol polycondensation reactions is reported. Methyl-substituted pyrimidines are used as building blocks to generate polymers for organic electronic applications. Their inherent electron withdrawing nature can result in the formation of n-type polymers. In order to increase the conjugation in donor-acceptor type polymers containing pyrimidines as the electron acceptor, the reactive site was changed from -meta to -para position. A more electron deficient, pyrimidine dimer was designed instead of one pyrimidine unit. Herein, a pyrimidine dimer which is 1,2-bis(2-methyl-5'-pyrimidyl)ethene, conjugated with a double bond that has a methyl group on each pyrimidine ring is used to generate para pyrimidine based polymers conjugated with various aromatic dialdehydes to yield six different polymers. The photo-physical and electrochemical characteristics of these polymers are determined and used in organic electronics.



POLY 355: Interaction of R_f -PEG- R_f / R_f -PEG-g-PAA co-hydrogel system with mucus

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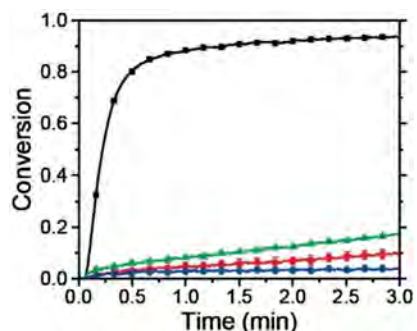
The single fluoroalkyl terminated polyethylene glycol grafted polyacrylic acid (R_f -PEG-g-PAA) tri-block copolymer was synthesized as a mucosal binder for a double fluoroalkyl terminated polyethylene glycol (R_f -PEG- R_f) hydrogel. The R_f -PEG- R_f hydrogels have a sol-gel two-phase coexistence character. However, they lack mucoadhesive properties. Because PAA-based polymers are known having mucoadhesive applications, integration of the R_f -PEG-PAA into the R_f -PEG- R_f hydrogel resulted in the mucoadhesive cohydrogel system. Different mass percentages of R_f -PEG-g-PAA in the cohydrogel (0%, 5%, 7.5%, 10%, 12.5%, 15%, and 20%) in different pH conditions were prepared, and the detachment forces with mucus surface were observed. In addition, the rheological measurements for the cohydrogel mixed mucin were also done. The experimental results demonstrated that the R_f -PEG-g-PAA/ R_f -PEG- R_f cohydrogel system possesses the mucoadhesive property. The maximum detachment force increased with the increased amount of R_f -PEG-g-PAA in the cohydrogel system. Furthermore, it was found that the mucoadhesion is pH dependent. We believe that the R_f -PEG-PAA/ R_f -PEG- R_f cohydrogel system can be further developed as a mucoadhesive drug delivery depot for controlled drug release applications.



POLY 356: Hexaarylbiimidazoles as efficient photoinhibitors of radical-mediated chain growth photopolymerizations

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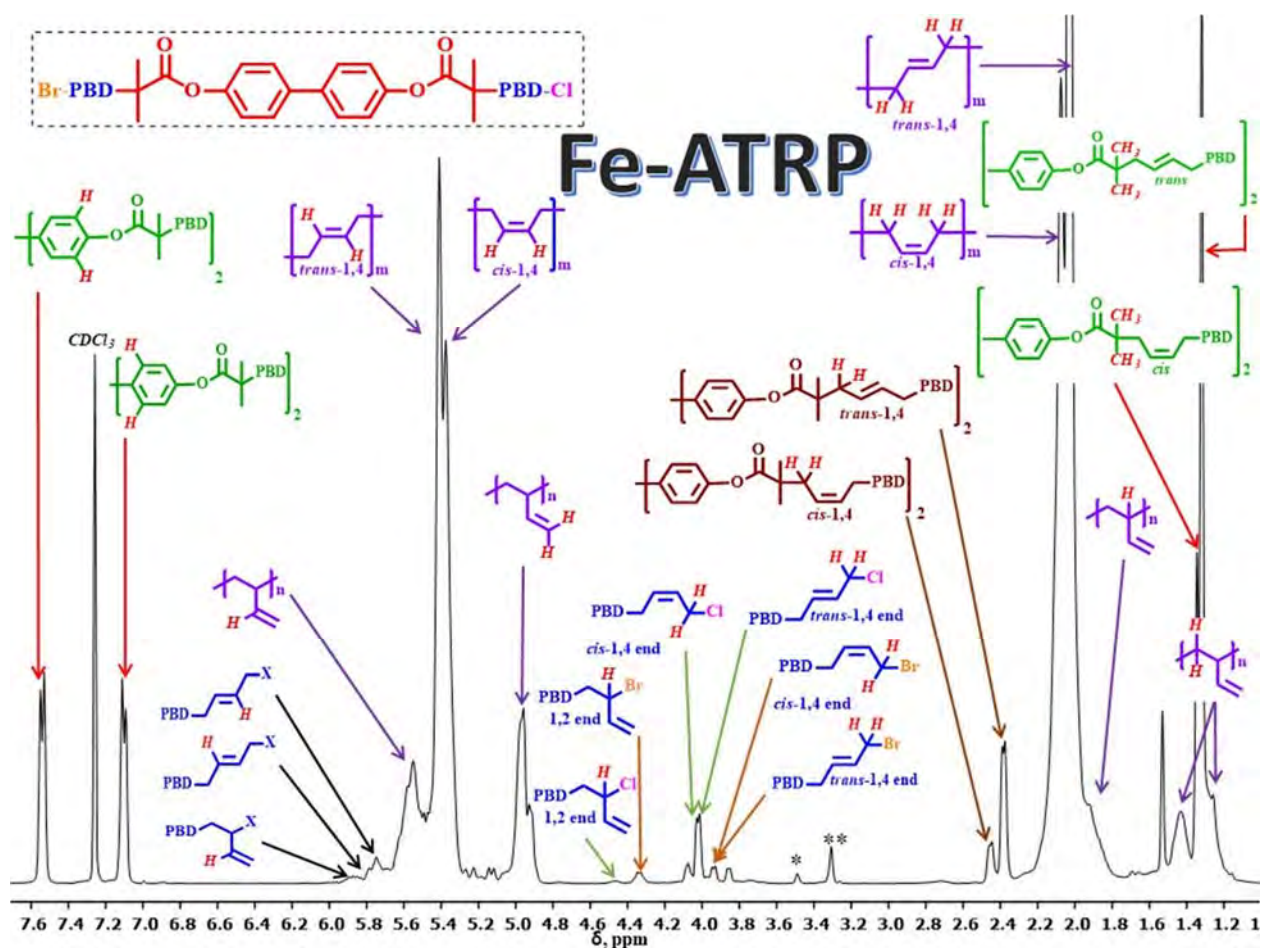
Owing to the inherent reactivity of organic radicals, the identification of photo-cleavable radical polymerization terminators that do not initiate polymerization has proven challenging. Moreover, to obtain wavelength-selective photoinitiation and photoinhibition in a formulated resin, initiating species need to be generated by irradiation at one wavelength while inhibiting species are generated at a second, independent wavelength, necessitating complementary photoinitiator and photoinhibitor absorbance spectra. Hexaarylbiimidazoles (HABIs) to generate poorly reactive lophyl radicals upon UV light irradiation which recombine slowly and do not directly initiate the radical-mediated chain growth polymerization of (meth)acrylates; nevertheless, in the presence of hydrogen-donating species such as thiols, HABIs are well-known as photoinitiators of radical polymerizations. Here, we discuss the potential of HABIs as efficient radical polymerization photoinhibitors when used in conjunction with complementary photoinitiators, such as the camphorquinine/tertiary amine system. By monitoring the polymerization of formulated acrylate, methacrylate, and maleimide/vinyl ether resin formulations with Fourier transform infrared (FT-IR), UV-vis, and electron paramagnetic resonance (EPR) spectroscopic techniques, we establish the temporal and spatial control over the cure of these resins through wavelength-selective photoinitiation and photoinhibition via the photo-generation of polymerization-inhibiting lophyl radicals.



POLY 357: Iron mediated butadiene-ATRP

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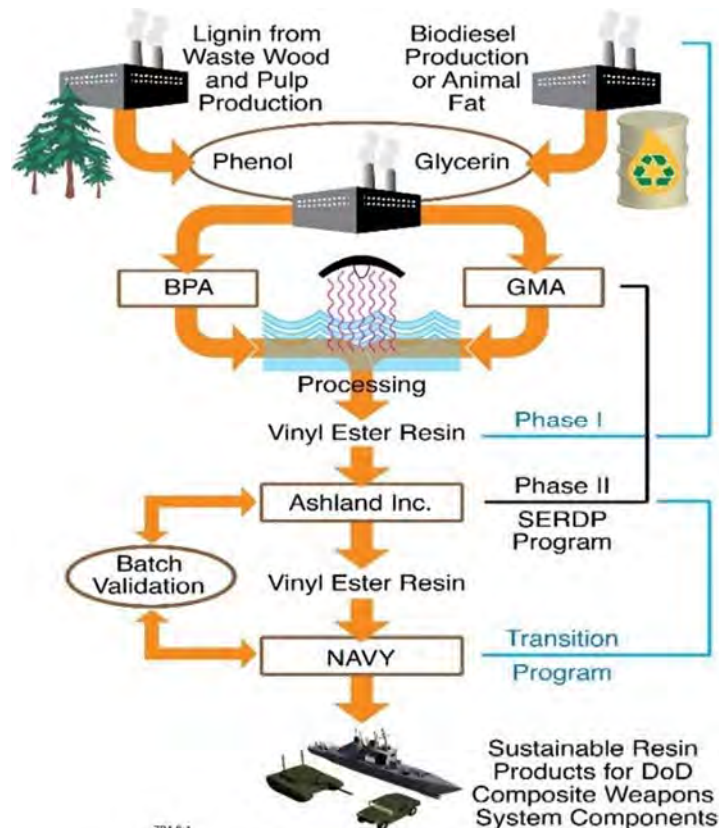
A series of iron complexes ($\text{FeX}_{2,3}$, $\text{X} = \text{Cl}, \text{Br}$)/L with C ($\text{Cp}_2\text{Fe}_2(\text{I})(\text{CO})_4 > \text{Cp}_2\text{Fe} > \text{Fe}(\text{CO})_5 > (\text{Ph}_2\text{PCp})_2\text{Fe}$), N (phthalocyanine \gg bpy \geq MeO-bpy \gg PMDETA $>$ phen), halide ($\text{FeX}_m\text{Y}_{4-m}/\text{Bu}_4\text{N}$, $\text{X}, \text{Y} = \text{Cl} \gg \text{Br} > \text{I}$), O (12-crown-4 \gg 15-crown-5 \geq dibenzo-18-crown-6) and P ($\text{P}[\text{Ph}(\text{OMe})_3]_3 \gg \text{PPh}_3$) ligands were evaluated in the normal, ICAR, and photo-ATRP of butadiene (BD) initiated from bromoesters in toluene at 110 °C. Good polymerization control was observed in many cases and two clear trends *i.e.* $\text{P}[\text{Ph}(\text{OMe})_3]_3 \gg \text{Bu}_4\text{NX} > \text{crown ethers} > \text{amines} > \text{C-ligands}$ and $\text{FeCl}_{2,3} \gg \text{FeBr}_{2,3}$ occur consistently across all polymerizations. Photoirradiation significantly improves the rate, conversion and chain end functionality albeit with a slight PDI increase.



POLY 358: Environmentally benign vinyl ester resin (VER) and its fabrication for anti-flammable VER composites

Yongwoo Lee, *yongwoo_lee@uml.edu*, Namjoon Kim, Priyank Shah. Chemistry, University of Massachusetts at Lowell, Lowell, Massachusetts, United States

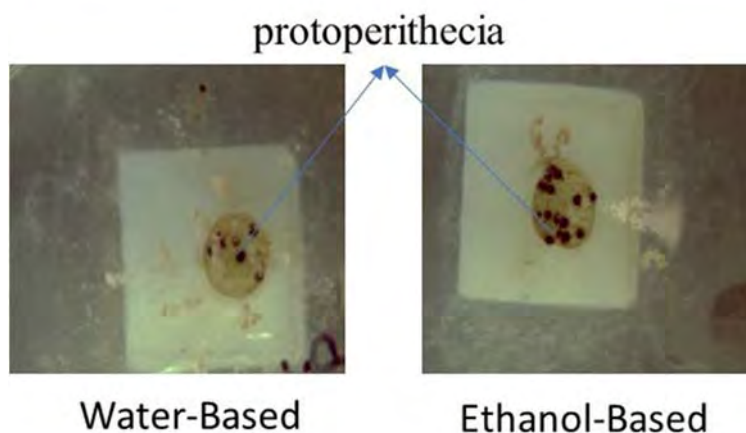
Vinyl Ester Resin (VER) is a low cost material that was introduced in the 1960's and can be processed to form a matrix of fiber reinforced composites that are used in ship hulls and transportation vehicles. There is an increased need of VER in marine industry, construction, transportation and in wind energy industries. VER is normally synthesized from petroleum feedstock which is not sustainable, however, our process uses glycerin generated as a waste product from biodiesel manufacturing plant at Maine Standard Biofuel (Portland, ME). The waste Glycerin was found useful in the making of Glycidyl methacrylate (GMA), a precursor of Vinyl Ester Resin (VER). GMA thus made can then be used to react with Bisphenol A (BPA) to make Vinyl Ester resin (VER). The main component (glycerin) of this method of VER production is readily available as a biodiesel waste product, making this process more environmentally friendly, and conveniently employed for VARTM based greener VER composites. The formulated GVER (FVER) as blended reaches a similar viscosity as the commercial resin with only half the styrene monomer content thereby reducing the volatile organic compounds associated with manufacturing. The mechanical performance of carbon reinforced GVER compared favorably with commercial resin and provide a route for composites manufacturing from sustainably sourced vinyl ester matrix.



POLY 359: Enzymatic degradation by *Neurospora Crassa* of polysaccharides/protein based biocomposite regenerated from ionic liquids and various coagulation agents

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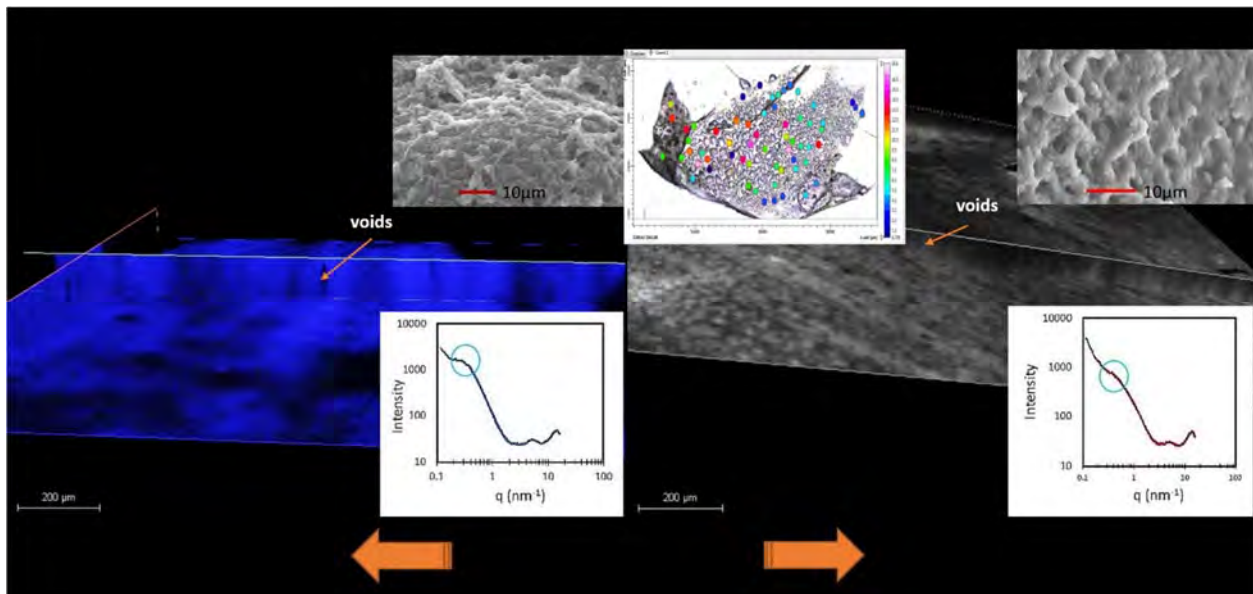
As interest in understanding the structural and physicochemical properties of natural-based biopolymers is increasing in the scientific community, new characterization methods command development. In this investigation a series of cellulose/silk biocomposites regenerated from 1-ethyl-3-methylimidazolium acetate ionic liquid in various coagulation agents (water and ethanol) were investigated to understand their potential antifungal growth capacity. The hypothesis stated that the fungal growth is affected by two factors (i) the percent crystallinity and (ii) topology of the material. The characterization of the membranes was characterized by FTIR and TgA. Percent beta-sheet was calculated by performing Fourier Self-Deconvoluted Spectra. The enzymatic degradation was analyzed by qualitative and quantitative observation and DNS assay. Results provided evidence of protoperithecia and profound degradation changes as a function of percent crystallinity. In other words, the fungus stopped growing and consume itself showing potential antifungal capacity. The various results provided evidence to suggest that by increasing the beta-sheet crystallinity, the cellulose crystallinity is reduced causing an increase in amorphous regions. This enable us to suggest that antifungal properties depend on the percent crystallization of the biocomposite.



POLY 360: Protein/polysaccharides biocomposite characterization via confocal microscopy

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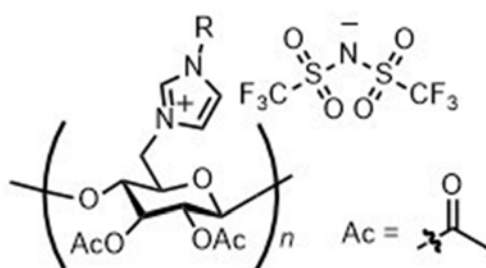
As interest in understanding the structural and physicochemical properties of natural-based biocomposites is increasing in the scientific community, new characterization methods command development. Biomaterials are presently characterized by many instruments such as FT-IR, TgA, AFM, SEM, DSC, and X-ray Scattering. While these instruments have led to our understanding of compositional, thermal, structural, and mechanical properties of biomaterials, the answer to the main question regarding understanding the relationship between structure and morphology is still unclear. Herein, a new characterization method using Confocal Microscopy is presented to study the morphology of a biomaterial composed of silk and cellulose regenerated from ionic liquids. Taking advantage of the silk amino acid sequence, this method utilizes an ELISA maker to study and map the location of the protein within the matrix. This renders a 3D representation of how the silk is interacting with the cellulose, revealing the influence of beta-sheets composition, and cellulose crystallinity, into the physicochemical properties. This characterization tool, in combination with X-ray Scattering and AFM, could enhance understanding into how the protein chains are intercalated with the polysaccharide chains, and will allow us to map the location of how the proteins interact with the polysaccharides at the molecular level.



POLY 361: Synthesis and evaluation of cationic cellulose (IV): Effect of side chain length of cation on properties

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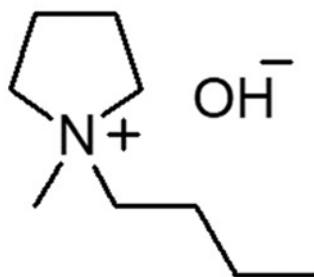
Cellulose is carbon-neutral polymer material and abundant in nature. Cellulose and its derivatives have been expected as functional materials to replace petroleum derived materials. By the chemical modification of the hydroxyl groups of cellulose, functional cellulose derivatives will be developed. One of the promising cellulose derivatives is a polycation in which a cation is introduced as a pendant group. Cationic celluloses with various anion species will be easily obtained by anion exchange reactions. We prepared cationic celluloses with Br anion and bis(trifluoromethylsulfonyl)amide (TFSA) anion. It was revealed that the hydrophilicity of cationic celluloses was controllable by changing the anion structure. In this study, cationic celluloses introduced imidazolium cations with various side chain lengths, 1-methyl-3-imidazolium-deoxy-acetyl-cellulose (MIMCA-Br), 1-butyl-3-imidazolium-deoxy-acetyl-cellulose (BIMCA-Br), and 1-octyl-3-imidazolium-deoxy-acetyl-cellulose (OIMCA-Br), were synthesized, and their properties were evaluated. For obtaining these cationic celluloses, an anion exchange reaction was carried out to exchange Br anions for TFSA anions. For TFSA-based cationic celluloses, TG and contact angle measurements were conducted. The thermal stability of cationic celluloses with TFSA anion was higher than that of cationic celluloses with Br anion. The 5% weight loss temperatures of MIMCA-TFSA, BIMCA-TFSA, and OIMCA-TFSA were 252, 256, and 242°C, respectively. The side chain length of imidazolium cation did not affect the thermal stability of cationic celluloses. The water contact angles of MIMCA-TFSA, BIMCA-TFSA, and OIMCA-TFSA were 66, 80, and 86°, respectively. The hydrophobicity of cationic celluloses increased with increasing the alkyl side chain length.



POLY 362: Synthesis and evaluation of cellulose/lignin hydrogels (IV): Effect of lignin on network structure

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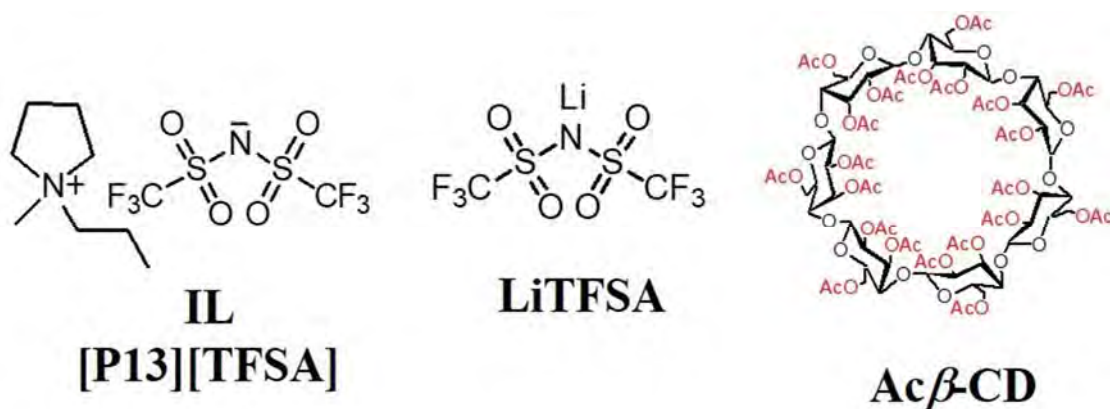
Cellulose hydrogels have biodegradability, biocompatibility, and excellent mechanical properties. They have been expected to apply to foods and medical products. We have recently reported one-pot synthesis of cellulose hydrogels by using an ionic liquid (1-butyl-1-methylpyrrolidinium hydroxide ([P14][OH])), which can dissolve cellulose even in the presence of water at room temperature. In order to provide new functions to cellulose hydrogels, we focused on lignin which has hydrophobicity and antioxidant property. In this study, hydrogels with various mass ratios of cellulose and lignin were synthesized, and their properties were evaluated to investigate the effect of lignin. Cellulose and lignin are soluble in [P14][OH] aqueous solutions. Given amounts of cellulose (Avicel[®]) (5 ~ 20 wt%) and lignin (0 ~ 15 wt%) were dissolved in [P14][OH] (water content: 60 wt%), and then epichlorohydrin was added to the solutions as a crosslinker to give cellulose/lignin iongels. To extract [P14][OH], the iongels were immersed in ultrapure water for a week. Cryogels were prepared by lyophilizing the hydrogels. In SEM observations, the pore size of cryogels with lignin was larger than that of cryogels composed of cellulose only. This difference should be based on the bulky and branched structure of lignin. The swelling degree of cryogels was determined by using aqueous solutions with various pH values (pH = 6.5, 7.4, and 8.0). The hydrogel composed of cellulose only showed the highest swelling degree in 0.1 M phosphate buffer (pH = 6.5). On the other hand, the hydrogel with the highest lignin content (15 wt%) showed the highest swelling degree in 0.1 M phosphate buffer (pH = 7.4 and 8.0). The hydrogel (swollen in ultrapure water for a week) with the highest lignin content (15 wt%) showed the highest compressive strength of 1.51 MPa. Antioxidant property of the hydrogels with lignin (5 ~ 15 wt%) was superior to that of the hydrogels with cellulose only.



POLY 363: Addition effects of cyclodextrin in ionic liquid electrolytes (VI): Analysis of lithium-ion transport property

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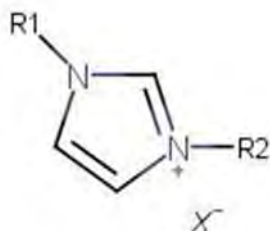
Ionic liquids (ILs) with bis(trifluoromethylsulfonyl)amide (TFSA) anion show high ionic conductivity over 10^{-2} S cm^{-1} at room temperature and thermal stability over 400 °C. We have been investigating additives to improve the Li-ion conductivity in ILs. One of candidates is β -cyclodextrin (β -CD), which is known to form a host-guest complex by the inclusion of TFSA anion. In this study, we investigated the effect of β -CD on Li-ion transport properties of IL electrolytes. A hydrophobic IL, *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([P13][TFSA]), was synthesized and was mixed with a given amount of LiTFSA (IL : LiTFSA = 18 : 1 (mole ratio)). Acetylated β -cyclodextrin (Ac β -CD) in which the hydroxyl groups are substituted with acetyl group was used since β -CD was insoluble in the IL. After the addition of Ac β -CD to the IL/LiTFSA composites in the range of mole ratio from LiTFSA : Ac β -CD = 1 : 0.5 to 1 : 1.5. ¹⁹F NMR measurements were carried out to investigate the interaction between Ac β -CD and TFSA anion. The chemical shifts of the CF₃ group of IL/LiTFSA/Ac β -CD (18 : 1 : x) (x = 0, 0.5, 1.0, and 1.5) composites were -80.00, -79.88, -79.80, and -79.73 ppm, respectively. In all IL/LiTFSA/Ac β -CD composites, the chemical shift of the CF₃ group shifted to a higher magnetic field as compared with that of IL/LiTFSA, suggesting that Ac β -CD formed a complex with TFSA anion. The Li transference number (t_{Li^+}) values of IL/LiTFSA/Ac β -CD (18 : 1 : x) (x = 0, 0.5, 1.0, and 1.5) composites were 0.27, 0.17, 0.09 and 0.08 at 60 °C, respectively. The t_{Li^+} values decreased with increasing the mole ratio of Ac β -CD. The oxidation potential of the IL/LiTFSA composite was 3.5 V vs Li/Li⁺, whereas the oxidation stability of the IL/LiTFSA/Ac β -CD was improved when the mole ratio of Ac β -CD was above 1.0.



POLY 364: Enumeration and literature analysis of n-alkyl imidazolium-based ionic liquids and monomers

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Ionic liquid (IL) researchers have at their disposal a multitude of available substituent and counter ion combinations, allowing for direct design and tuning of material properties. For example, in common imidazolium-based ILs, the available combinations of substituents and counter ions that are synthetically accessible can quickly reach tens or hundreds of thousands. As such, it is not clear what percentage of the available imidazolium-based ILs are actively being explored. This poster presents our efforts to analyze n-alkyl (1-12) imidazolium-based IL use and availability in the chemical literature. We enumerated all unique combinations of n-alkyl imidazolium-based ILs with 16 different anions and associated each substance with the number of references and commercial availability in the literature. Our work will help researchers understand popular vs. unexplored n-alkyl imidazolium-based ILs. Further, we are extending this research by enumerating and exploring the literature of imidazolium-based IL functional monomers (e.g. vinyl, acrylate, styrene).



[X-].R1N1C=C[N+](R2)=C1

POLY 365: Enhanced sampling of polymer solutions by molecular-dynamics simulation: implementation and use cases

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Characterizing solutions of long polymer chains by molecular dynamics (MD) simulations with quantitative force fields is a significant computational challenge. Modern MD software can treat systems large enough to accommodate realistic chain lengths (up to 100 nanometers), but the time scales needed to cover the equilibrium ensemble remain largely inaccessible. Building on previous work, we introduce protocols for parallel-tempering simulations driven by geometric selection criteria. Configurations are sampled by iterative changes in the molecular connectivity, using protocols implemented in the LAMMPS software. Benchmark simulations of liquid-crystalline polymers show that the computational overhead is minimal, and the increase in relaxation rates greatly outweighs the cost of using multiple replicas.



POLY 366: Phase behavior of diblock copolymer free-standing films: Insights from simulations

Kyle Hall, *kyle.hall@temple.edu*. CST, Temple University, Philadelphia, Pennsylvania, United States

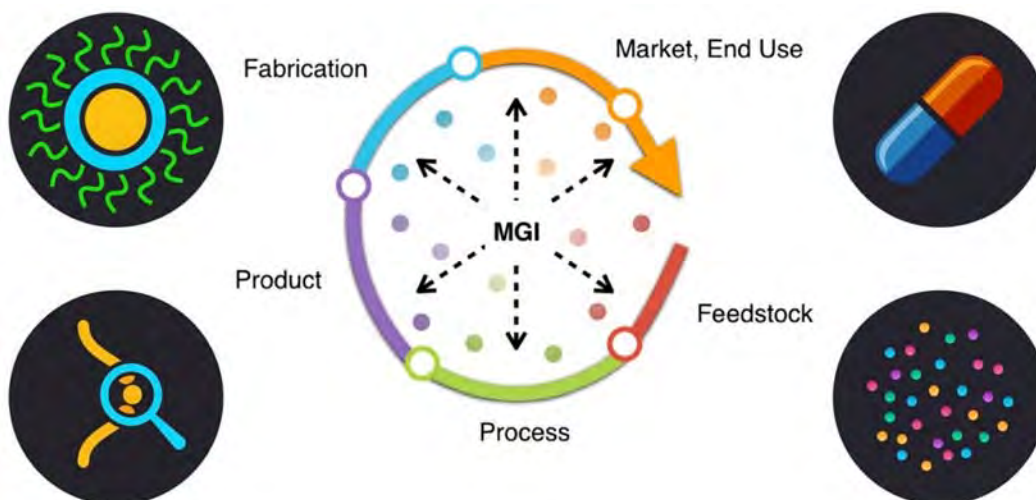
Homopolymer nanomaterials (e.g., nano-fibers) are becoming increasingly achievable in experiments, and can exhibit a variety of desirable properties. Moreover, block copolymers can exhibit rich bulk phase behaviors (e.g., spherical and cylindrical phases as well as more exotic ones such as gyroid phases). Herein, preliminary work exploring the potential phase behaviors of diblock copolymers under nano-confinement via free-standing films will be presented. Using Molecular Dynamics (MD) simulations, film thickness and block cross-interactions are systematically varied to provide molecular-level insights into phase behaviours, thus enabling a bottom-up perspective on free-standing diblock copolymer films and their morphologies. Results from diblock copolymer films are compared to those from MD simulations of polyethylene films (i.e., homopolymer films) to understand differences in polymer responses to nano-confinement. We envision that leveraging chemical simulations to systematically vary molecular architecture and interactions in the context of nano-confinement will afford opportunities for identifying interesting nano-morphologies to guide experimental endeavors.



POLY 367: Rapid discovery and development of designer RAFT polyelectrolytes

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Polyelectrolyte complexes (PECs) materialize through associative phase separation of oppositely-charged polymers in aqueous settings. Depending on the chemical attributes, electrostatic interactions, and arrangement of the constituent monomers, these ion-containing macromolecules can be tailored toward completely hydrophilic, compartmentalized assemblies in aqueous solution, positioning them to more easily encapsulate and deliver challenging biomolecules such as nucleic acids, peptides, or proteins. However, fundamental molecular design principles on how chemical and ionic character relate to physical laws in hierarchical PEC assemblies have been elusive, and often times non-equilibrium states emerge as a consequence of this interplay. A materials-genome approach, motivated by expanding experimental and simulation datasets of well-defined PEC systems, can build a materials information infrastructure for elucidating how specific non-covalent intermolecular interactions prevail in polyelectrolyte behavior. Herein, we describe a series of block polyelectrolytes from a modular synthetic platform using aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization in a 12-reactor parallel synthesizer. This rapid synthesis approach enabled us to prepare RAFT polyelectrolyte systems at various neutral and charged block lengths from different ionic monomer families (e.g., styrenics, (meth)acrylates, and (meth)acrylamides), balancing electrostatic and hydrophobic effects. The formation kinetics and structures of PEC assemblies were evaluated using a suite of time-resolved scattering, rheology, and spectroscopy tools. We also investigated the temporal stability and disassembly of these PEC micelles and gels as a function of polymer combination, concentration, and salt. These findings reveal how the rational pairing of model polyelectrolytes can be used to navigate and process path-dependent assemblies over relevant length- and time-scales, thereby enhancing future prediction capabilities of materials-by-design for end-use biotechnologies.



POLY 368: Energy dissipation in polymers for ballistic applications from molecular simulations

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Polymeric materials for ballistic applications are able to withstand large impacts due to their high strength and ability to efficiently dissipate energy. In order to guide the development of new polymeric systems for these applications, the molecular-scale details governing energy dissipation in polymer systems must be understood. To address this issue, we investigate energy dissipation pathways in polymer systems using molecular simulations. We discuss the importance of various pathways, and our results suggest strategies for guiding energy dissipation in polymer-based materials.



POLY 369: Glycoconjugates as cell membrane mimics and galectin functions

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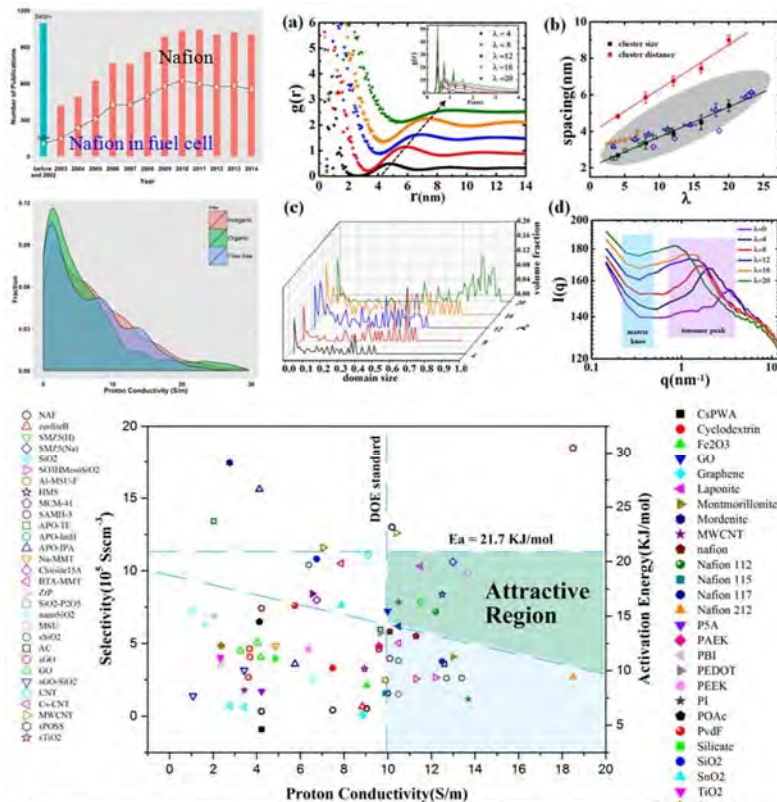
Biological cell membranes are decorated with glycans, which are known to interact with proteins such as lectins and galectins. The functional pairing between glycans on membranes and lectins are relevant to many biological events, including signaling and immune response. Recently we developed synthetic nanoscale vesicles known as glycodendrimersomes (GDSs), self-assembled by Janus glycodendrimers. These biomimetic vesicles can be programmed with glycan density, charge, structural and topological complexity, and are employed to dissect design aspects of glycan presentation, with specificity for lectin-mediated cross-linking. Agglutination of GDSs reveal the extent of cross-linking of these biomimetic vesicles with disease-related galectins, and offer the possibility of unraveling the nature of these fundamental sugar-receptor interactions.



POLY 370: Insight into the structure and proton conductivity of Nafion® membranes using simulation and statistical approaches

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Nafion® membranes have outstanding proton conductivities attributed to its unique assembled structures[1-2]. Unfortunately, structure models for Nafion membranes are still in hot debates[3-4]. We carried out statistical analysis and molecular dynamics simulation to address the unique structure and its correlation with proton conductivity. The statistical analysis revealed that water in the membrane is crucial as distributed like typical fluid in porous material. It can be fitted using the Brunauer–Emmett–Teller equation, and the saturation of water molecules around a sulfonate group is about 20. Further integration of Nernst-Einstein equation provides a quantitative understanding for proton conductivity in Nafion membranes as a function of water content and temperature. Fillers to construct Nafion composite membranes were also investigated and most potent types are circled out accounting for Robeson upper bound[5], DOE standard and active energy. To clarify the microstructure in Nafion membranes, the anisotropy in the backbone of polymers in molecular dynamics simulations was introduced. It has well matched morphologies and intensity profiles comparing with those characterized by electron microscopy and small angle X-ray scattering experiments.

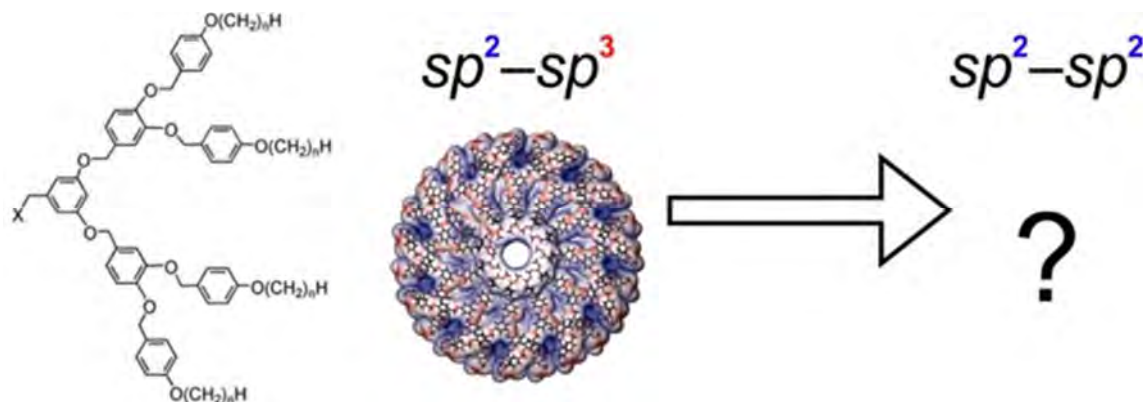


L-up: number of publications about Nafion and distribution of proton conductivity of pristine and composited Nafion membranes; R-up: unique structure of Nafion from anisotropic MD simulation; Below: performance of composited Nafion membranes.

POLY 371: Replacing sp^2-sp^3 bonds with sp^2-sp^2 bonds in self-assembling dendrons

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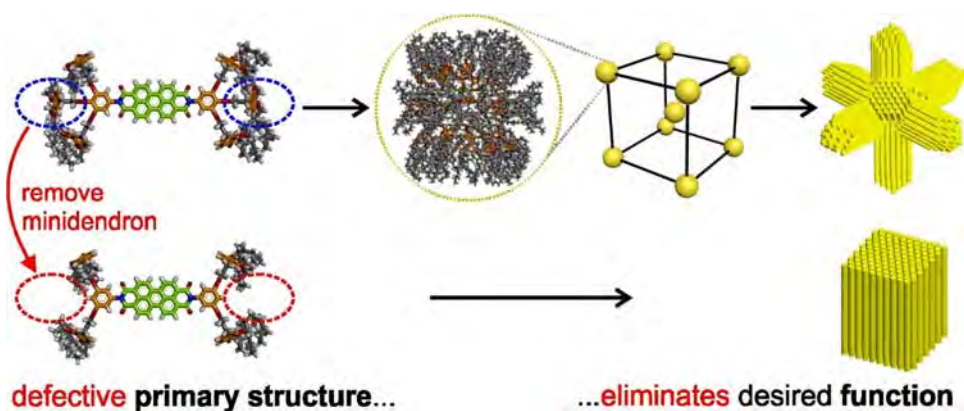
Benzyl ether, biphenylmethyl ether, propyl ether, and biphenylpropyl ether self-assembling dendrons rely on sp^2-sp^3 bonds to build dendrimers with multiple generations. In this work, these sp^2-sp^3 bonds are replaced with sp^2-sp^2 bonds, and their significance on the self-assembly of the resultant molecules is elucidated.



POLY 372: Elucidating the hierarchical basis for supramolecular orientational memory

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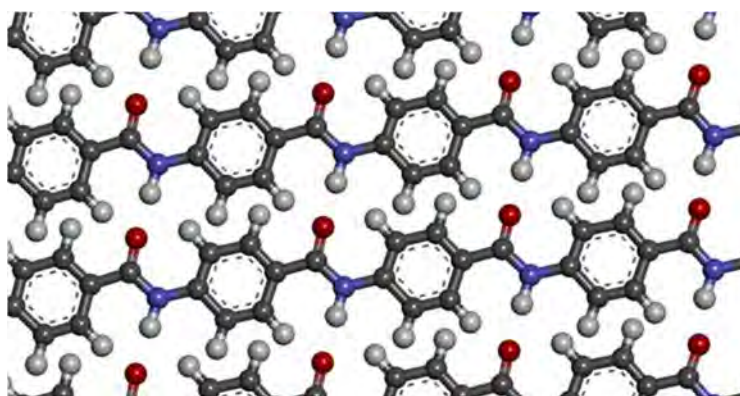
Certain molecules which self-organize into both columnar and 3D phases generated from supramolecular spheres exhibit a *supramolecular orientational memory* (SOM) effect: a reorientation of their building blocks to generate otherwise inaccessible nanoscale architectures. Specifically, columnar domains reorient upon heating to, and cooling from, a phase generated from supramolecular spheres, including a body-centered cubic (BCC) and $Pm\bar{3}n$ cubic phase (known also as Frank-Kasper A15). The reoriented supramolecular columns preserve the directions of that preceding cubic phase. However, the exact requirements for a given molecular building block to exhibit SOM remain poorly understood. Herein recent progress on the elucidation of the basis for SOM will be shared. The synthesis, structural analysis and retrostructural analysis of two related perylene bisimide (PBI) derivatives, dendronized with self-assembly benzyl ether dendrons, will be detailed. One PBI, with three minidendritic building blocks (**3,4,5-G2-PBI**), assembles into three columnar hexagonal phases and one BCC phase, and exhibits SOM. In contrast, removal of one minidendritic building block to give a second PBI, **3,5-G2-PBI**, eliminates the formation of the cubic phase and the associated memory effect. This hierarchical transfer of structural information, from a defective primary structure to elimination of a function, mirrors the misfolding of proteins, such as those implicated in Alzheimer's and Prion diseases.



POLY 373: Investigating the effect of *ortho*-, *meta*-, and *para*-conformers on the structure of aromatic polyamides

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Aromatic polyamides are widely used in material applications due to their heat-resistance and mechanical strength. Herein, molecular modeling and simulation is used to elucidate the significance of *ortho*-, *meta*-, and *para*-conformers on the generation of both planar and helical polyamide structures.



POLY 374: Synthesis of poly(dichlorophosphazene) by melt phase polymerization of P-trichloro-N-(dichlorophosphoryl)monophosphazene

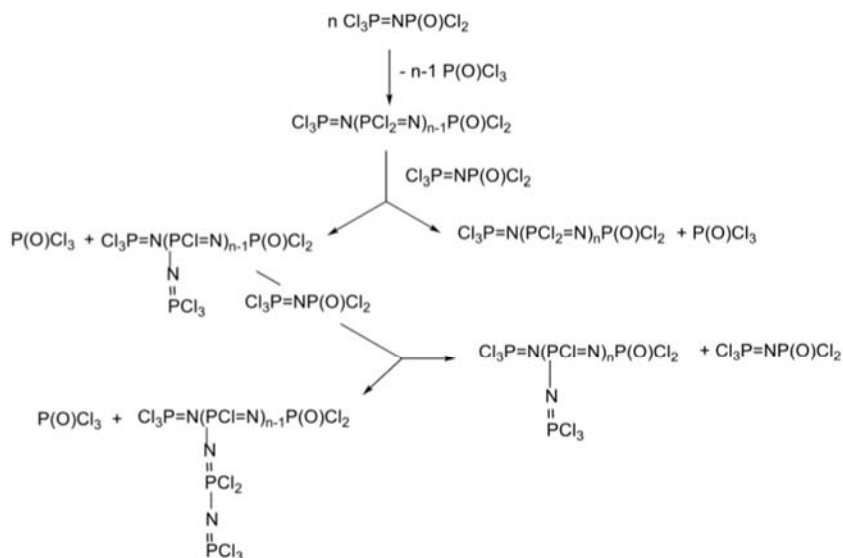
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A major barrier to commercialization of any of the many exciting applications of the poly(phosphazenes) has been the cost and ease of preparation of the most widely utilized starting polymer, poly(dichlorophosphazene), $[\text{Cl}_2\text{P}=\text{N}]_n$ (**1**). One attractive route is the thermal polycondensation reaction of P-trichloro-N-(dichlorophosphoryl)monophosphazene,

$\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ (**2**). We are reporting a modified bulk polymerization of **2** which represents

a convenient route to laboratory scale amounts of $[\text{Cl}_2\text{P}=\text{N}]_n$ with moderate molecular weights and polydispersity. GPC characterization data were obtained on the corresponding phenoxy derivatives, $[(\text{PhO})_2\text{P}=\text{N}]_n$. We also have developed a one pot synthesis of **1** from ammonium sulfate and phosphorus pentachloride which are the starting materials for the synthesis of **2** and examined the major variables, time and temperature, for this process. The resulting poly(phosphazene) exhibits more branching than the product of bulk polymerization of **1**.

Scheme 1 Polymerization pathways

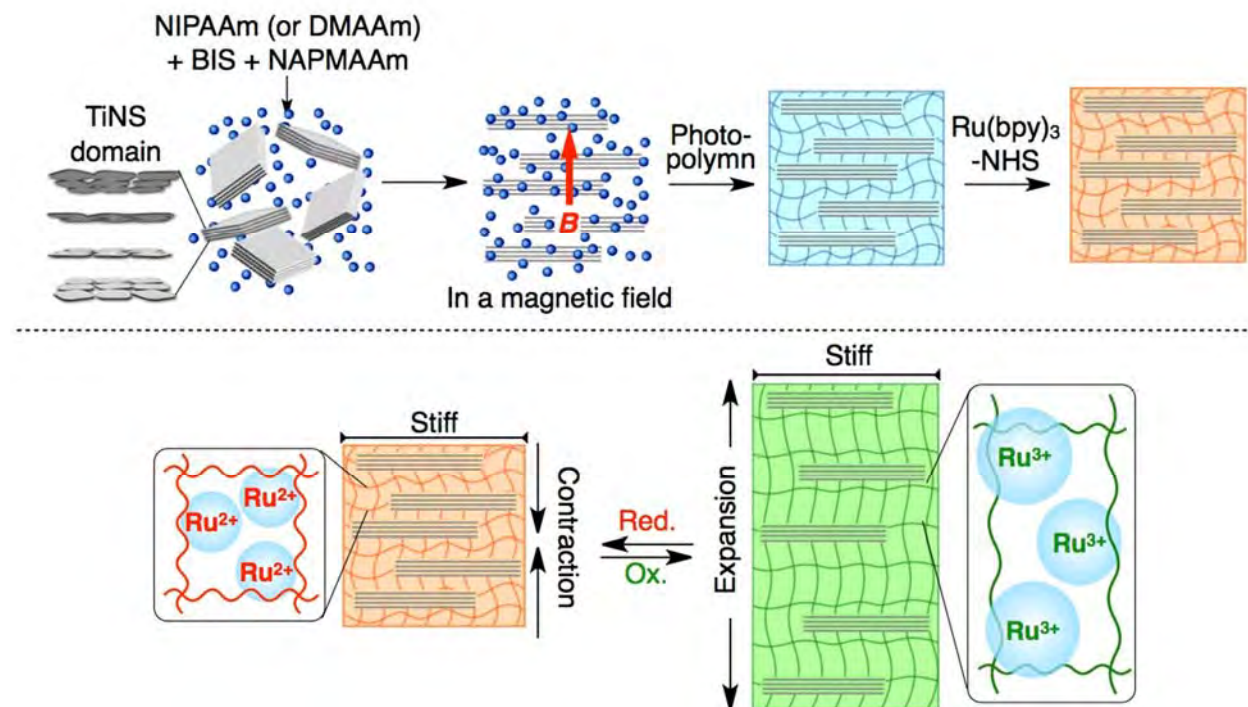


Scheme 1. Polymerization Pathways

POLY 375: Spatiotemporal control of self-oscillating gel by uniformly aligned inorganic nano sheets

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A novel “self-oscillating” gel that exhibits an autonomous mechanical swelling–deswelling oscillation without any on–off switching of external stimuli has been developed since 1996. The basic chemical structure of the self-oscillating polymer is a copolymer of N-isopropylacrylamide (NIPAAm) and Ru(bpy)₃ as a catalyst for the Belousov–Zhabotinsky (BZ) reaction. In response to the redox change of Ru(bpy)₃ units, hydrophilicity and LCST of gel matrices change, which causes the swelling and deswelling of the gel networks. Unilamellar titania nanosheet (TiNS) is quite attractive, owing to its highly anisotropic shape and unique magnetic properties, where TiNSs in an aqueous dispersion magnetically align cofacially. Through in-situ polymerization, the aligned structure of TiNSs can be chemically locked in the hydrogel network. Based on this strategy, we fabricated an anisotropic self-oscillating hydrogel by hybridization of poly(NIPAAm) and Ru(bpy)₃ units with uniformly aligned TiNSs. The as-prepared hydrogel showed autonomous swelling/deswelling behavior driven by BZ reaction, in a highly anisotropic manner.



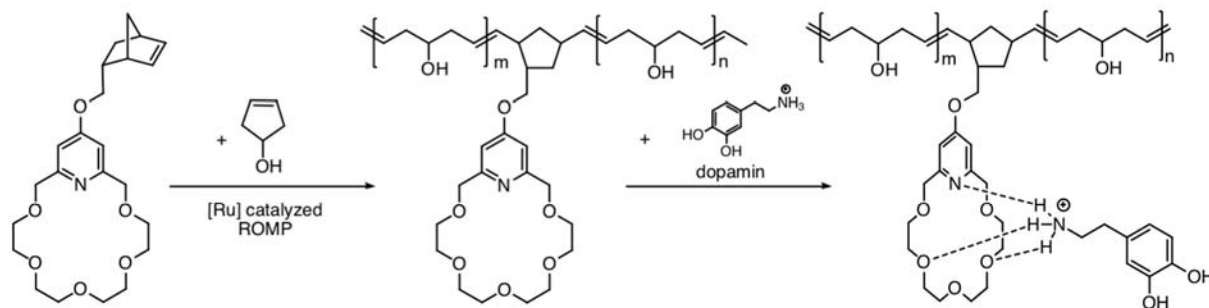
POLY 376: Synthesis of supramolecular vinyl alcohol (VA) copolymers via ring-opening metathesis polymerization (ROMP) for biogenic amine delivery

János Deme¹, Ervin Kovács¹, Gabriella Merza¹, Gábor Szolnoki¹, Virág Kiss¹, Györgyi Szarka¹, Béla Iván¹, Péter Huszthy³, John A. Gladysz², **Robert Tuba¹**, tuba.robert@ttk.mta.hu. (1) Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary (2) Chemistry, Texas A&M University, College Station, Texas, United States (3) Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary

Copolymers of vinyl alcohol (VA) are hydrophilic synthetic macromolecules having prominent biomedical applications. The concentration of hydroxyl groups along the polymer chain determines its polarity. Catalyst systems, which are able to produce well-defined VA copolymers with adjustable polarities, are of great pharmaceutical interest. For example, fine tuning the polarity of VA copolymers used in drug delivery applications can control targeted drug release. Ring opening metathesis polymerization (ROMP) or acyclic diene metathesis polymerization (ADMET) using well-defined ruthenium catalyzed systems are one of the most promising synthetic tools to fabricate such polymers.

Copolymerization of pyridine containing ROMP-ready, norbornene functionalized crown-ethers with hydroxyl-functionalized cycloolefins results in biodegradable polymers bearing supramolecular moieties. Encapsulation of hydrophilic amines into semipolar biodegradable supramolecular polymers should facilitate for example the transport of highly polar dopamine through the blood brain barrier making possible an alternative treatment of Parkinson diseases.

The synthesis of the supramolecular moieties containing VA copolymers and their complexation to biogenic amines will be presented.

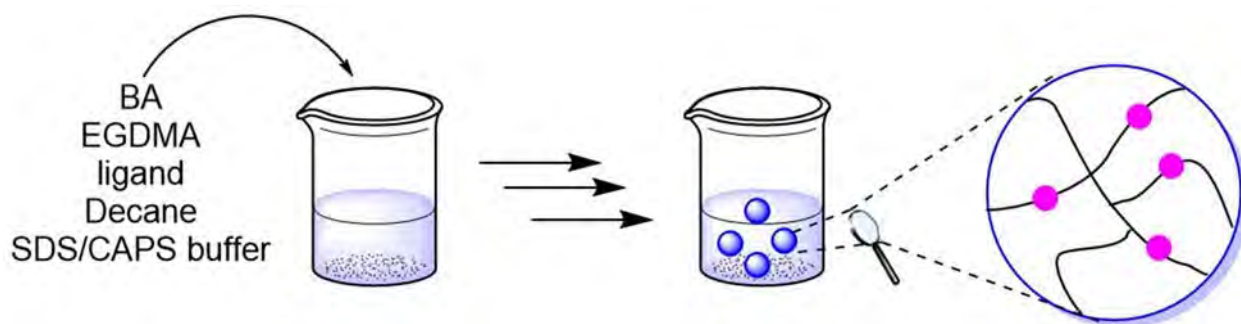


Scheme 1. Biogenic Amine Carrier Supramolecular Vinyl alcohol (VA) Copolymer

POLY 377: Microgel matrix effect (MME): Influence of crosslinking on catalytic behavior

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Microgels support and enhance the performance of immobilized catalysts through their allosteric and induced fit effects, and thus provide a new valuable platform for advanced materials. To obtain efficient biomimetic glycosyl transfer catalysts, a polymerization protocol was developed that is applicable to the synthesis of crosslinked microgels via UV-initiated free radical polymerization of miniemulsions at ambient temperature and below. The synthesized microgels were characterized in the solid state and in solution before establishing their catalytic activity toward the hydrolysis of glycosidic bonds. Matrix effects were elaborated as a driving force of the observed catalytic proficiency of the microgels and will be discussed in detail.



Schematic synthesis of crosslinked microgels

POLY 378: Supramolecular micelles based on multi-arm star-shaped phosphoester copolymers for controlled drug delivery

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Poly(phosphoester)s (PPEs) have the properties of functional adjustability, stealth effect, excellent biodegradability and biocompatibility to have the potential application in biomedical field. To meet more versatile and diverse biomedical applications, multi-arm star-shaped phosphoester copolymer was designed and prepared. Firstly, amphiphilic block copolymer poly(amido amine)-*block*-poly(2-butenyl phospholane)-*block*-poly(2-methoxy phospholane) conjugated with folic acid (abbreviated as PAMAM-PBEP-PMP-FA) was synthesized by organo-catalyzed living ring-opening polymerization (ROP) and post-modification. Supramolecular micelles formed by this copolymer via self-assembly exhibited good architectural stability, uniform spherical structures, efficient loading capacity and low protein adsorption in aqueous solution. Afterwards, *in vitro* drug release experiment showed that anticancer drugs doxorubicin (DOX) could be released from the micelles in a slow and sustained way in the environment of simulated intracellular lysosome (pH 5.0 with phosphodiesterase I). Subsequent research on cytotoxicity and cellular uptake showed that DOX also could enter tumor cells quickly by the enhanced permeability and retention (EPR) effect and FA receptor-mediated active targeting ability, and inhibit tumor cell growth effectively. Therefore, these supramolecular micelles based on multi-arm star-shaped phosphoester copolymers have great potential in controlled drug delivery for tumor treatment.

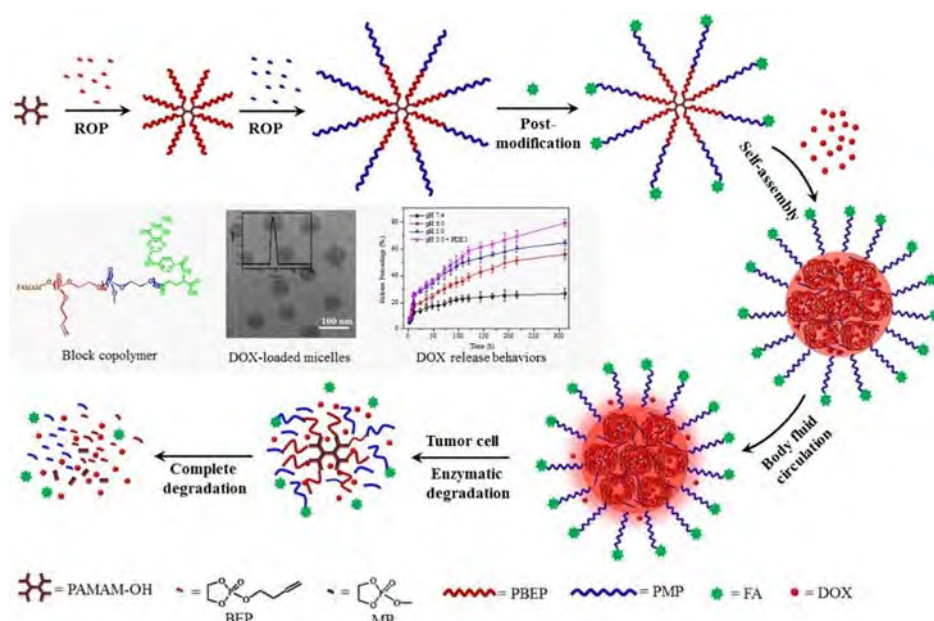
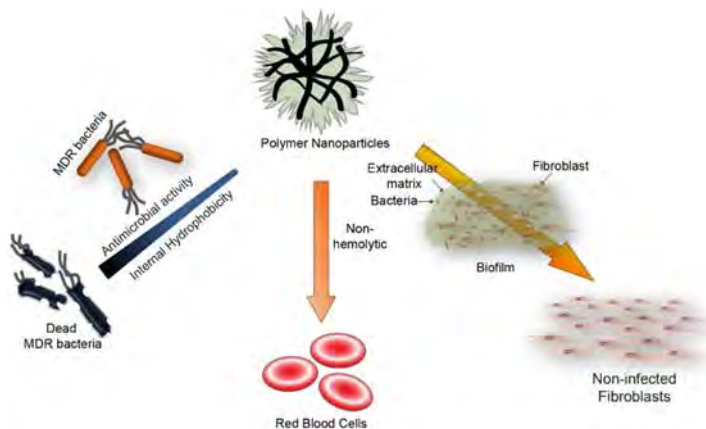


Illustration of synthetic route of folate-conjugated multi-arm star-shaped phosphoester copolymer PAMAM-PBEP-PMP-FA and supramolecular micelles formed by this copolymer for sustained release of hydrophobic anticancer drugs triggered by enzymatic and acidic microenvironment in tumor cells.

POLY 379: Functionalized polymeric nanoparticles for the treatment of MDR bacteria and biofilm infections

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Overuse of antibiotics has created “superbugs” such as methicillin-resistant *Staphylococcus aureus* (MRSA) that pose serious threat to global health due to treatment failure and high mortality rates. The threat is further aggravated by chronic infections from biofilms, which exhibit high resistance towards both the host immune response and traditional antimicrobial therapy. Synthetic macromolecules have emerged as an alternative to conventional antibiotic therapy exhibiting broad spectrum activity against antibiotic-resistant bacteria. However, high toxicity towards mammalian cells and concomitant low therapeutic indices have limited their practical applications in clinical settings. Here, we report engineered polymers that can effectively eradicate pre-formed biofilms while maintaining a high therapeutic index against human red blood cells (RBCs). We synthesized a library of quaternary ammonium poly(oxanorborneneimides) possessing different degrees of hydrophobicity and screened their antimicrobial and hemolytic activities. These polymers form 10-15 nm nanoparticles in aqueous solution, increasing their overall cationic charge and molecular mass. We determined that increasing hydrophobicity of the alkyl chains bridging the cationic head group and polymer backbone greatly enhances toxicity against planktonic bacteria while maintaining excellent hemolytic activities towards RBCs (Therapeutic Index >5000). Additionally, polymeric nanoparticles readily penetrate and eradicate pre-formed biofilms while still maintaining high therapeutic indices (~120) relative to RBCs. Polymeric NPs demonstrated a 6-log reduction in bacterial count in a biofilm-mammalian cell coculture model. Significantly, we observed that bacteria did not develop any resistance against polymeric NPs even after 20 serial passages. Overall, our engineered polymeric nanoparticle platform shows strong potential as an infectious disease therapeutic and simultaneously provides a rational approach to design novel antimicrobials for long-term combating of bacterial infections.



Antimicrobial polymers eradicate MDR bacterial infections, with minimal hemolysis.

POLY 380: Tetraphenylmethane shape-persistent dendritic polymers as versatile multifunctional materials

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In spite of the regular highly branched structure that defines dendrimers, it is well documented that they can adopt a myriad of conformations with a tendency to concentrate a bigger mass density at the interior of the molecule, as a result of the pronounced back-folding of terminal segments. This general model –the so called dense core model– is not strictly followed by pi-conjugated dendrimers, which show restricted conformational freedom. As a result, they are shape-persistent and, in some particular cases, they are better described by the dense shell model.

In our research group, we have used tetraphenylmethane as a building block to synthesize shape-persistent dendrimers, because of its rigidity, tetrahedral 3D geometry, 4-fold connectivity and synthetic accessibility. Computer-generated models show that at the second and third generation the dendrimers adopt a persistent globular shape having well-defined internal voids or cavities and the terminal groups located at the periphery with negligible back-folding. It must be noted that the second generation dendrimers (Fig. 1) have a high number of terminal groups and a size of a few nanometers, similar to the fourth generation in Fréchet-type dendrimers. The privileged architecture of shape-persistent porous tetraphenylmethane dendrimers, their structural versatility and fluorescent properties are interesting features for potential applications of those nanomaterials.

In this communication, we will discuss the synthesis and properties of this new class of dendrimers as a function of the core, the rigid rod spacer (X) between tetraphenylmethane units and the periphery functional groups (R). In addition, we will describe our progress in the development of related hybrid lineal-dendritic copolymers.

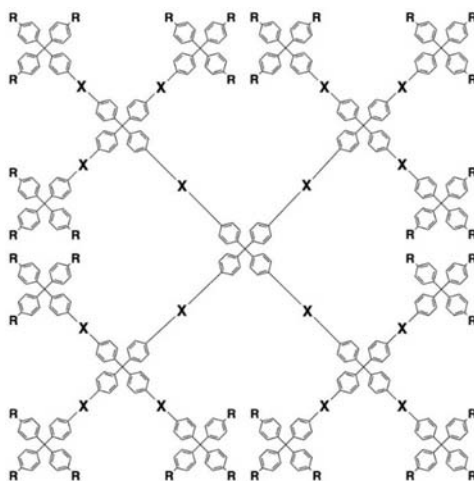
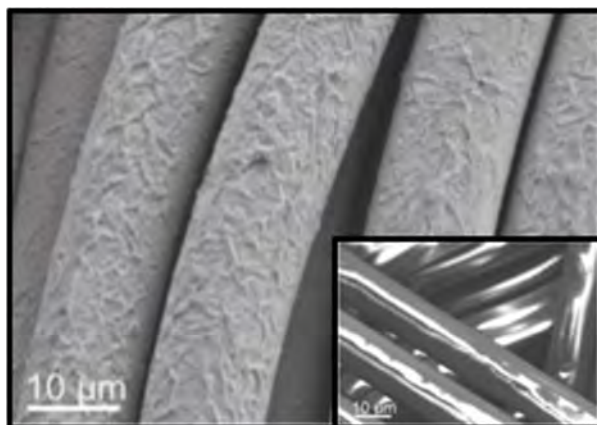


Figure 1. General structure of second generation tetraphenylmethane shape-persistent dendrimers with tetraphenylmethane core.

POLY 381: Vapor phase organic chemistry to deposit conjugated polymer films on arbitrary substrates

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Coating textured, high surface area substrates, such as paper and textiles, with conjugated polymer films is challenging. Selected vapor deposition techniques allow for the film forming process to be largely divorced of substrate properties, such as surface energy and surface roughness, and have the potential to yield conformal coatings. However, reliable vapor deposition techniques with which to fabricate structurally-diverse conjugated polymer films do not exist. Here, we report two vapor deposition chambers that, combined, allow for in situ vapor phase polymerization of a representative selection of common conjugated monomers. We believe the ability to deposit such a diverse array of monomeric species provides a potential path to the design of new electronic materials, such as n-type polymers, for applications concerning wearable electronic and energy harvesting textiles.



POLY 382: Improving performance of thin-film composite nanofiltration membranes by changing the properties of support membranes

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In this study, the polysulfone (PSf) support layers were prepared by incorporating the K^+ -responsive poly(N-isopropylacrylamide-co-acryloylamidobenzo-15-crown-5) (P(NIPAM-co-AAB₁₅C₅)). The thin-film composite (TFC) membranes were fabricated via the interfacial polymerization reaction between piperazine (PIP) and 1,3,5-benzenetricarbonyl trichloride (TMC) on the prepared PSf supports. The membrane surface morphology and chemical features were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and contact angle tests. The nanofiltration performance of the resultant TFC membranes was assessed in the mode of cross-flow filtration. The results showed that blending the PSf casting solution with P(NIPAM-co-AAB₁₅C₅) generated a PSf membrane with higher hydrophilicity and porosity. As a result, the formed NF membrane displayed a smooth surface and lower salt rejection. When the K^+ ions in the PIP solution made the P(NIPAM-co-AAB₁₅C₅) become hydrophobic, the resulting NF membrane had increased roughness and water permeability but a still low salt rejection caused by the high porosity. In these fabrication conditions, applying curing treatment achieved the optimal performance with the highest water flux of $10.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and the fair salt rejection of 75.0% under the pressure of 200 psi. Generally, this study provided more understanding about the effect of support membranes on the TFC NF membranes and proposed a useful additive to supports for improving the performance of TFC NF membranes.

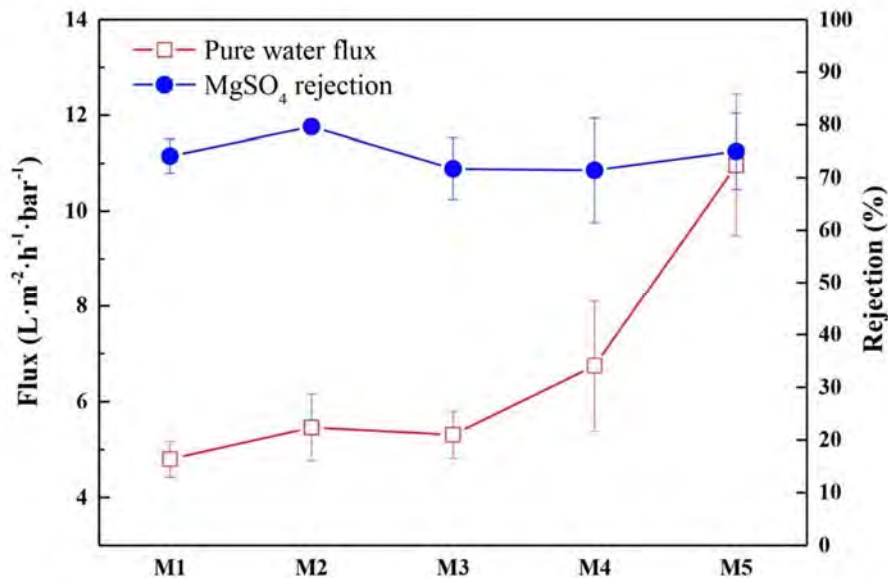


Figure 1. Water permeability and salt rejection of TFC NF membranes.

POLY 383: Stimuli-responsive Pt(0)-containing metallocupramolecular polymers

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The self-assembly of low-molecular weight telechelics equipped with terminal ligands in the presence of stoichiometric amounts of a metal salt furnishes metallocupramolecular polymers (MSPs). The properties of MSPs can be altered by stimuli such as heat, light, or mechanical force, which affect the dynamic non-covalent interactions and shift the equilibrium between the assembled and disassembled states. MSPs are therefore intrinsically stimuli-responsive and have been exploited to create functional materials for applications that range from healable surface coatings to mechanically responsive materials to shape-memory polymers. While the majority of MSPs make use of charged metal-ligand complexes, zero-valent metal complexes have remained largely unexplored. Building on previous work with bis(η^2 -alkyne)platinum(0) complexes as conjugated cross-links in poly(*p*-phenylene ethynylene)s, we prepared MSPs by linear chain extension of a ditopic diphenylacetylene carrying telechelic core with platinum(0) complexes. This approach afforded soluble and stable MSPs. We demonstrate that such polymers permit the spatially resolved generation of metal nanoparticles (NPs) via decomplexation, nucleation, and growth without requiring a reduction step. A study of the temperature-dependence of the complex dissociation showed that the MSPs are stable under ambient conditions, but undergo an irreversible decomplexation above a threshold temperature. A characterization of heated films by means of differential scanning calorimetry, small angle X-ray scattering, and high-resolution transmission electron microscopy showed that the Pt-complexes dissociate, covalent cross-links of the polymer form, and 1 nm-sized clusters of Pt-atoms are obtained. Upon annealing at 200°C, Pt-NPs with diameters between 1 and 3 nm form. The NPs are homogeneously distributed throughout the cross-linked polymer matrix, rendering such materials potentially interesting for applications that range from catalysis, to sensing and optoelectronic applications.

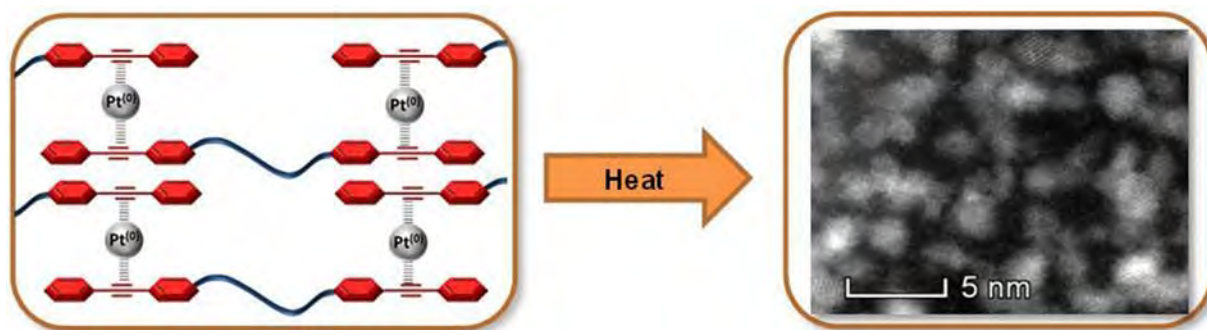


Figure 1: Schematic representation of the MSPs with Pt(0) complexes (left) and transmission electron microscopy of the polymer film with Pt-NPs (right).

POLY 384: Synthesis of pseudo-dendrimer functional

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Dendrimers are special macromolecules obtained by the implementation of a step by step process leading to a final macromolecule displaying a regular and perfectly monodisperse structure with numerous end groups.[1] Thus, several generations are connected onto the other ones, starting from a multifunctional core-molecule (typically 3 initial functional groups). Every generation can provide complementary properties and also to obtain one macromolecule with very specific properties.

The purpose of this study is to synthesize a dendrimer-like polyester with two generations. The first generation is prepared by grafting a cyclic anhydride such as succinic or maleic anhydride to trimethylolpropane, leading to a branched molecules displaying 3 carboxylic groups, and subsequently reacting these terminal carboxylic groups with glycidol leading after ring opening to 3 diol terminal unit, i.e. 6 hydroxy end groups. This sequence of 2 addition reactions leads to the formation of one generation and can be repeated several times to lead to higher generation dendrimer-like molecules.

The construction of a dendrimer requires perfectly selective and quantitative reactions, which is not strictly the case in our procedure. However, the implementation of such “easy” highly selective and highly quantitative reactions under relatively mild conditions in order to control the extent of transesterification reactions allows the preparation of relatively narrow polydisperse dendrimer-like polyesters. This can be exemplified by the comparative study with the synthesis of hyperbranched polyesters prepared according to a conventional polyesterification of succinic acid and glycerol.

Interestingly, this strategy allows the selective functionalization of the terminal end groups as already demonstrated earlier.[2]

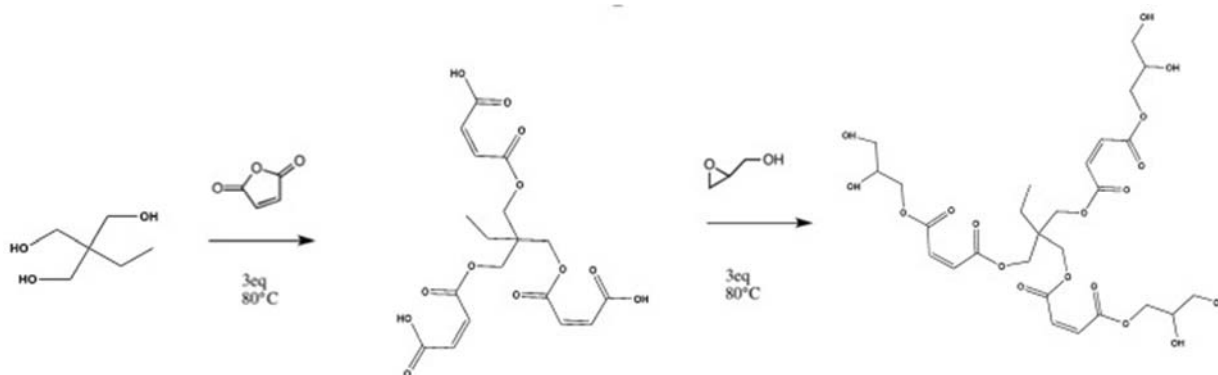


Figure 1: Reaction pathway for the synthesis of a first generation dendrimer-like polyester

POLY 385: Iterative synthesis of sequence-defined, multifunctional, biocompatible PEGs for biomedical applications

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Poly(ethylene glycols) (PEGs) have attracted enormous interest from synthetic chemists, materials scientists and biologists due to their excellent water-solubility, biocompatibility and stealth properties, particularly discrete PEGs with exactly defined chains and excellent biocompatibility. Because of the harsh Williamson etherification conditions required to extend these discrete PEGs, it is difficult to explore insoluble supports suitable for solid-phase synthesis of PEGs.

Instead, uniform PEGs have been fabricated by liquid-phase iterative strategies, although these approaches have usually depended on chromatographic separation to isolate the growing PEGs at each cycle. To our knowledge, the physical and biological advantages of PEGs have never been combined with the structural and information-bearing complexity of sequence-defined heteropolymers. Therefore, the creation of a general technology for the production of sequence-defined multifunctional PEGs with tunable side-arm functionalities directed to real-life applications is highly challenging and timely.

Herein, we describe a universal platform for the assembly of sequence-defined multifunctional PEGs via liquid-phase synthesis with molecular sieving (**Figure 1**). Synthetic PEGs were constructed by repeated etherification of four chiral α,ω -end-functionalised pentagols with side-arms growing from a central three-armed star, to give a sequence-defined PEG-star. The optimum liquid-phase kinetics and size-exclusion molecular separation technology make this platform a facile approach to the production of high-purity sequence-defined polymers. The introduction of reactive side arms along PEG backbone enables precise control over structure and properties, and allows for fast and precise site-selective multifunctionalisation at a later stage. This strategy offers opportunities to introduce structural versatility and further diversity into sequence-defined PEGs, thereby unlocking their potential for widespread bioapplications.

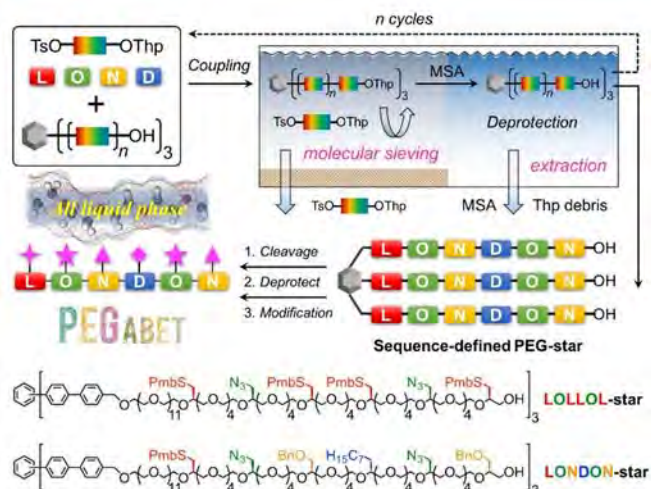


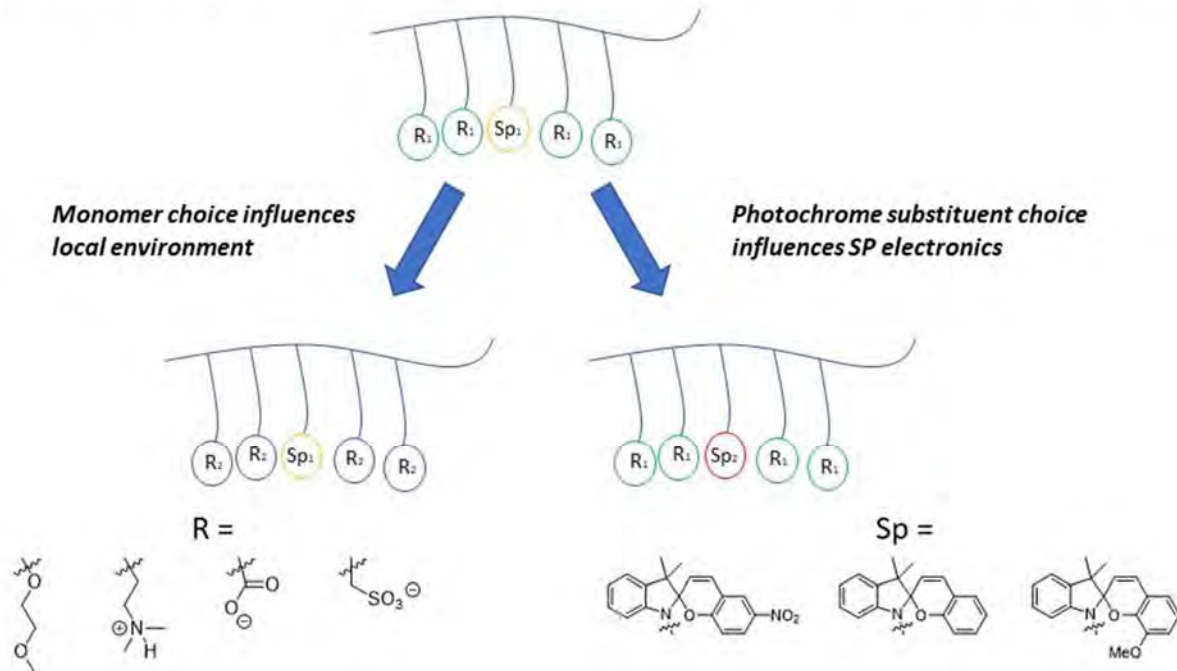
Figure 1. Iterative synthesis of sequence-defined, multifunctional, biocompatible PEGs using liquid phase strategy with size-exclusion molecular sieving.

POLY 386: Water soluble spiropyran polymers with tunable pKa and photoisomerization rates

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Spiropyrans, a class of photochromic molecules, have been utilized in numerous light responsive materials. However, they have been studied primarily in organic media, limiting their use in biological systems. Herein, we describe the systematic study of spiropyran-containing vinyl polyelectrolytes in aqueous media. We probed the photoisomerization kinetics and pKa of the protonated merocyanine (MCH) species in each of the polymers as a function of two variables: substituent effects on the spiropyran monomers and co-monomer effects. That is, it was observed that substitution on the chromene ring of the spiropyran monomers with electron donating and withdrawing substituents, as well as the choice of co-monomer, had observable effects on the behavior of the photochromic materials. By combining these two variables, an array of photochromic polyelectrolytes was prepared with a wide range of properties. This work shows the potential of using spiropyran as a means for controlling phase behavior of polyelectrolytes in a reversible fashion.

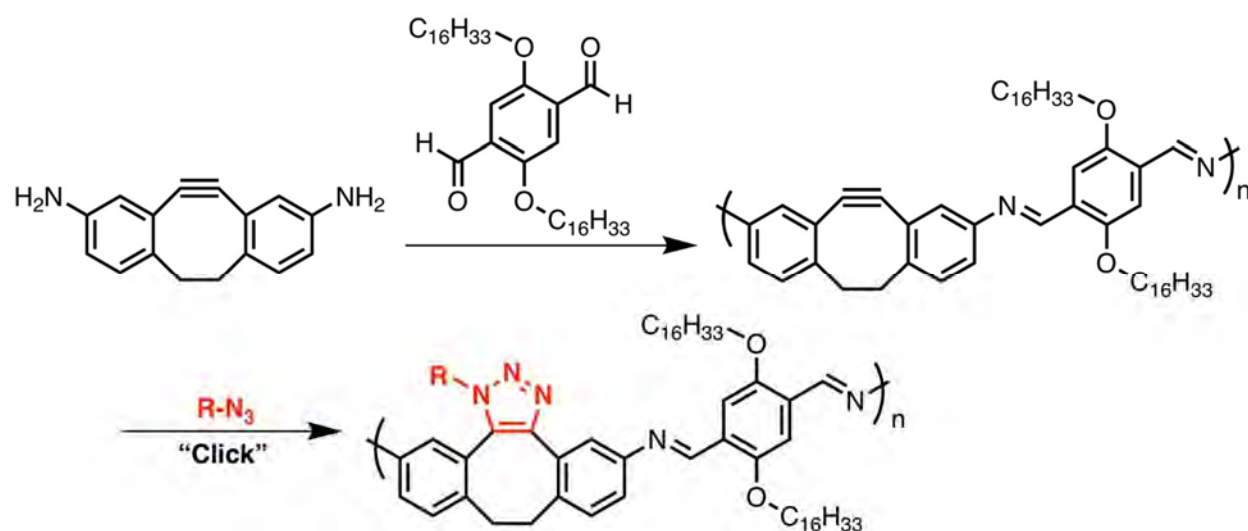
Control over photochromic properties through polymer synthesis



POLY 387: Strain-promoted cycloadditions for the synthesis and functionalization of polymers and nanocomposites

Vladimir Kardelis, Darryl Fong, Kelvin Li, Stuart A. Mcnelles, Christina Shamshoom, **Alex Adronov**, adronov@mcmaster.ca. Chemistry & Chemical Biology, McMaster University, Hamilton, Ontario, Canada

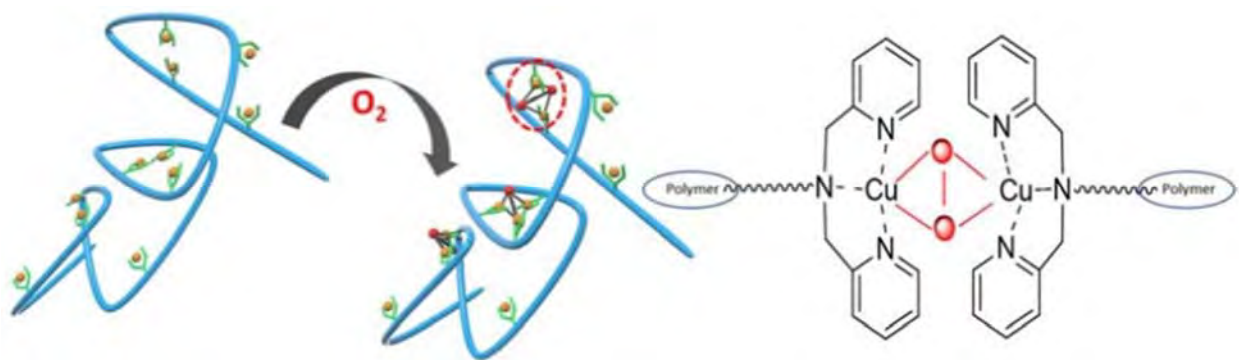
The use of strain-promoted azide-alkyne cycloaddition (SPAAC) chemistry has attracted significant attention due to its mild reaction conditions, orthogonality, and rapid reactivity. This synthetic strategy has been extensively used in bioconjugation chemistry, and in the development of some biomaterials. Despite their utility, the use of strained cyclooctynes has found few applications in polymer and materials chemistry. Recently, we reported the synthesis of a diamine derivative of dibenzocyclooctyne (DIBO-NH₂) and its Schiff-base polymerization with a dialdehyde co-monomer, which resulted in a DIBO-containing conjugated polyimine. This novel structure was found to exhibit a high degree of reactivity toward various azide derivatives, and can serve as a precursor for the preparation of numerous triazole derivatives. We have elaborated this material to the preparation of polymers bearing pillar[5]arenes and a variety of other side-chains, and have investigated these polymers as building blocks for supramolecular gels and as carbon nanotube dispersing agents that enable formation of novel reactive nanocomposites. In addition, we have used dibenzocyclooctynes as components of non-conjugated polymers, and have developed entirely new polymer structures using SPAAC chemistry. The synthesis of these structures is extremely simple, only requiring evaporation of solvent at ambient temperature over the course of several minutes in order to produce high molecular weight polymeric species.



POLY 388: Synergetic catalysis using type-2 Cu-containing polymers for oxygen activation

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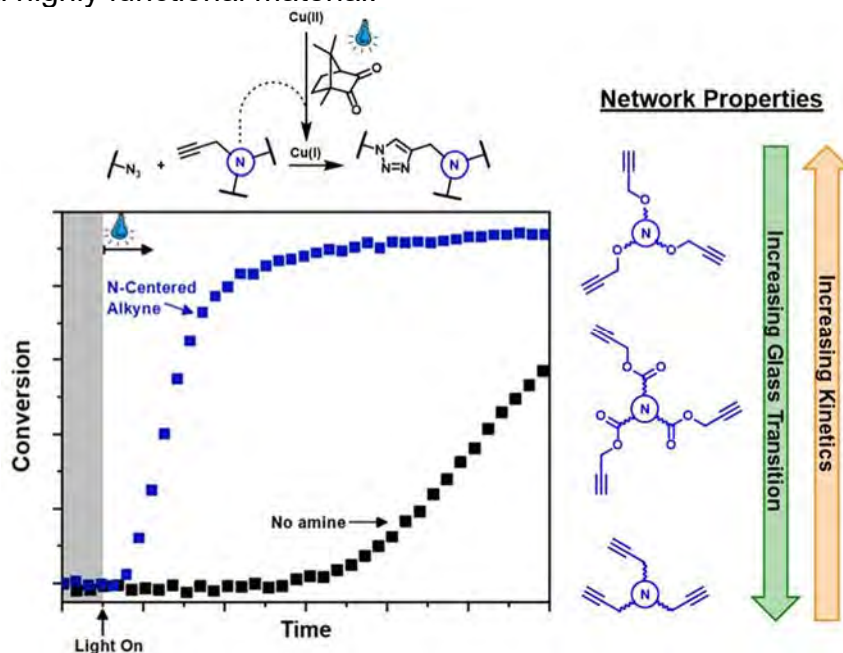
The design of dicopper complexes to mimic type-2 copper-containing metalloenzymes, e.g., tyrosinases, is of particular interest to develop green oxidation chemistry. We present a class of copper(II) containing copolymers of poly(N,N'-dimethylacrylamide-co-2-hydroxy-3-(dipicolylamino)propyl methacrylate) (P(DMA-co-GMADPA)) and our observation on synergetic catalysis of those Cu-containing metallopolymer for oxygen activation. The random copolymers of P(DMA-co-GMADPA) were synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization using 2-cyano-2-propyl benzodithioate (CPDB) as a RAFT agent. The copolymers contain dipicolylamine ligands as binding sites for copper(II) ions. Two model reactions, e.g., the aerobic oxidation of ascorbic acid and 3,5-di-*tert*-butylcatechol, were used to study the catalytic activity of Cu-containing metallopolymer. All Cu-containing metallopolymer show a significant enhancement on the oxidation reaction kinetics, compared to the uncatalyzed reaction and the reaction catalytic by small Cu complexes. For the oxidation of ascorbic acid, Cu-containing metallopolymer is found to boost the rate by 8.5 times compared with the reaction catalyzed by Cu-complexes. For the oxidation of 3,5-di-*tert*-butylcatechol, a 7-fold enhancement for Cu-containing metallopolymer is seen compared Cu-containing metallopolymer with small Cu-complexes. When coupling type-2 copper sites with hydrophilic polymers, this synergy to enhance oxygen activation is attributed to the flexibility of polymer backbones that allows dynamically vary the distance of Cu-Cu sites for oxygen activation. Our results will likely open the doors to design those bio-inspired polymer catalysts containing multi-metal sites.



POLY 389: One-component norrish type II initiation of CuAAC polymer networks under blue light

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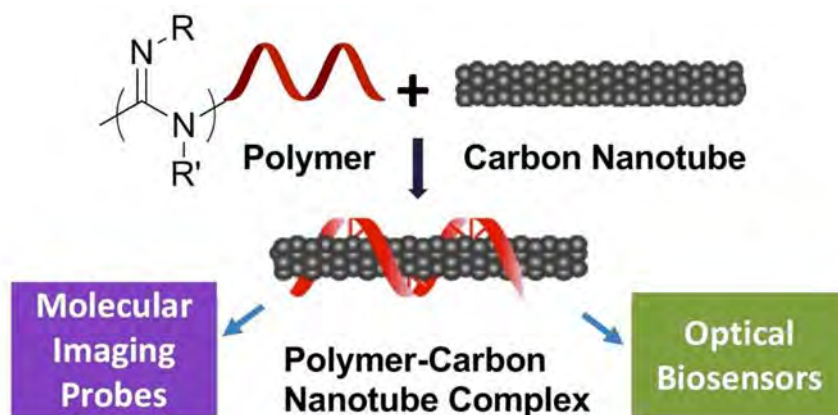
Photopolymerized copper catalyzed azide-alkyne cycloaddition (i.e. photo-CuAAC) networks are versatile materials due to their impressive toughness and homogenous architecture. The solvent-free (bulk) photo-CuAAC networks are glassy, proceed to high conversions, and produce stable triazole ring products making them an increasingly desirable system for applications such as dental composites and ionic membranes. Typically, the polymerization of the CuAAC network is performed under blue light utilizing a Type II photoinitiating system. Two-components are required to initiate the photo-CuAAC network: the photosensitizer and a tertiary amine. Although tertiary amines are required for rapid polymerization, introducing them in a material can often be detrimental. These amines can leach out of the network as well as act as a plasticizing agent in the glassy network. To enhance the applicability of photo-CuAAC networks, minimizing leachable components is of great importance. To maintain the fast kinetics of these polymerizations, we incorporated the tertiary amine moiety into the polymer backbone of the CuAAC network. We study three promising nitrogen-centered alkyne monomers that demonstrate rapid polymerization kinetics (>90% conversion within 20 min at 30 mW/cm²). The designed monomer structures provide a wide tunability in the glass transition temperature (46 °C to 82 °C) while maintaining the glassy nature of the network at room temperature. This approach of utilizing novel monomers that participate in the Type II photoinitiation mechanism and exhibit a rapid rate of network polymerization is ideal to further push forward the photo-CuAAC networks as a highly functional material.



POLY 390: Polymer-functionalized carbon nanotubes as optical probes

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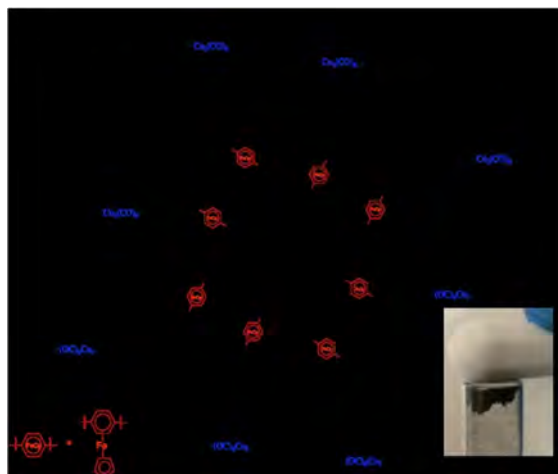
Polymers are versatile tools to functionalize nanomaterials for modulation of their electronic and optical properties. Single-walled carbon nanotubes (SWCNTs) are emerging molecular imaging probes and biosensors owing to their unique photophysical, thermal, and electrical properties. Surface chemistry plays a crucial role in modulating such properties of nanotubes for their useful applications. In this talk, I will discuss on the rational design and synthesis of helical polycarbodiimides to stably and non-covalently encapsulate carbon nanotubes and modulate their properties. We showed that the polymer-cloaking of the nanotubes exhibited the unprecedented control over nanotube optical properties, surface potential, and interaction with biomolecules enabling development of new molecular imaging probes and optical biosensors. I will also discuss on polymer chemistry that facilitated nanosensor delivery into the nucleus in cancer cells.



POLY 391: Organometallic approach to bioactive dendrimers and dendrimer-derived magnetoceramics

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Interest in metallodendrimers remains intense, being driven by the opportunity to integrate the chemistry of the metal with the unique architecture of dendrimers. Indeed, an infinite suite of tunable properties is attainable by the rational insertion of metal with the desired chemistry within precise microstructures within the dendrimer scaffold. Our research program explores the unique chemistry of iron(II) to construct a new class of functional dendrimers facilely. The presence of the iron center endows these dendrimers with redox activity, enabling the in-situ formation of free radicals to induce oxidative stress, a chemical process with implication for diverse biological properties including antimicrobial activity. These dendrimers feature excellent activity against clinically relevant multi-drug resistant pathogens such as Methicillin-resistant *Staphylococcus aureus* and Vancomycin-resistant *Enterococcus faecium*. The fundamental chemistry of the dendrimers enables functionalization with bioactive moieties such as quaternary ammonium groups and thiazoles to potentiate the overall bioactivity without compromising biocompatibility to primary human epidermal keratinocytes. The biocompatibility is further supported by the lack of toxicity to red blood cells as revealed by *in vitro* hemolytic profile of these dendrimers. The chemistry of the iron center as well as the unique architecture of the dendrimers provide access to magnetoceramics. Indeed, pyrolysis of the dendrimers yields magnetoceramics that possess magnetic properties, which are tunable via dendritic effects and functionalization with organo-cobalt moieties. A switch from homometallic iron-containing dendrimers to heterometallic iron and cobalt-containing dendrimers tunes the crystallinity of the resulting magnetoceramics. Also, the dendrimer scaffold controls the formation of the crystalline domains, providing a template to separate the iron and cobalt domains.



Organometallic dendrimer-derived magnetoceramics

POLY 392: Stimuli-responsive dendronized polymeric hydrogels

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Stimuli-responsive hydrogels constructed from polymers of inherent stimuli-responsive units are capable of adapting or undergoing macroscopic changes (shrinking or expanding, sol-gel transitions) in response to external triggers, which are promising materials for various bio-related applications. We here report on an intriguing class of stimuli-responsive dendronized polymeric hydrogels constructed from either poly (methyl methacrylate) or chitosan carrying dendritic oligoethylene glycols (OEG) dendrons via dynamic covalent chemistry (Figure 1). These hydrogels exhibit responsive behavior upon various external stimulus including temperature, pH, and metal ions. The dynamic nature also affords the hydrogels adaptive self-healing property. By virtue of the enhanced dynamic covalent linkages through either thermally induced polymer aggregation or freezing polymer aqueous solutions, hydrogels were prepared under the conditions above the polymer's cloud point (T_{cp}) or below the freezing point (T_f) of the aqueous solutions, respectively, resulting in hydrogels with enhanced mechanical properties and porous structures, as well as different thermally induced shrinking behavior. More importantly, we note that the crowding and thickness effects from dendronized polymer architecture make significant contribution to hydrogel formation and enhancement of their mechanical performance. We further demonstrate that these hydrogels with good biocompatibility are promising candidates for drug delivery and 3D cell cultivation.

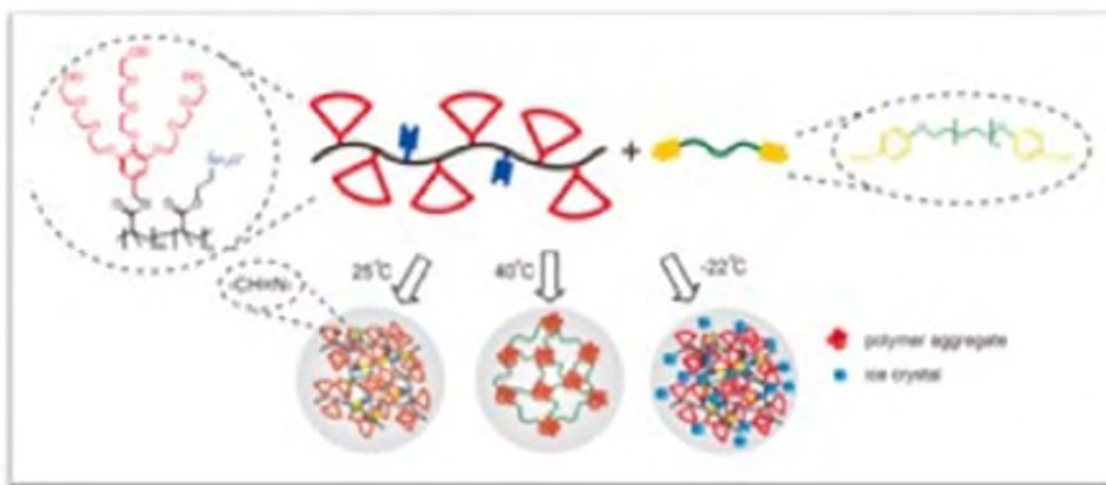


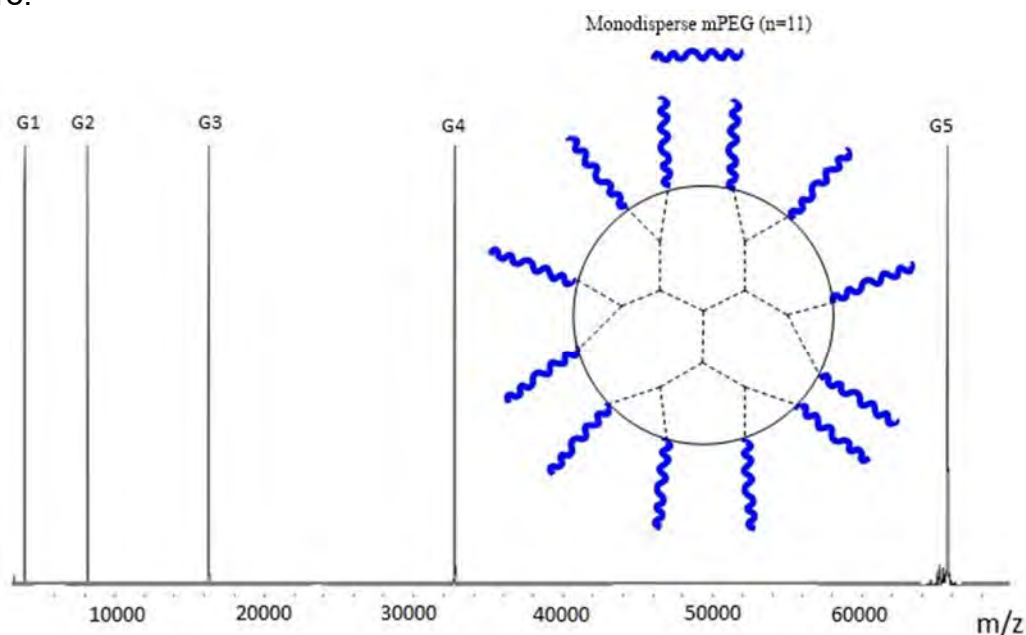
Figure 1. Cartoon presentation of stimuli-responsive dendronized polymeric hydrogels: morphology and mechanical properties dependent on fabrication temperature.

POLY 393: Synthesis of high molecular weight monodisperse pegylated dendrimeric structures

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Pegylation of drugs to improve their mobility and stealth behaviour inside the body has been in use for more than 20 years. However, the dispersity of the PEG chains plays an important role in that and other potential applications. The synthesis of monodisperse PEGs is a tedious and arduous process that relies on a cascade of purification steps. A newly reported synthetic procedure provided with monodisperse PEG up to 10000 Da. However, to get to even higher molecular weight PEGs it is apparent that the use of scaffolds with multiple anchoring sites is an attractive strategy. Our research has recently explored the use of a bis-MPA based polyester dendrimer to introduce a number of tetraethylene glycol (TEG) chains through amidation reactions. In the literature, it is possible to find longer PEGs introduced in dendritic structures through different linkages.

In this work, we describe a versatile synthetic strategy using hydroxyl functional bis-MPA based dendrimers of generations 1 to 5. Successful introduction of a monodisperse mPEG was accomplished *via* anhydride chemistry and full conversion of all generations resulted in monodisperse pegylated dendrimers with molecular weights in the protein region. For instance, a fifth generation pegylated dendrimer with an unprecedented molecular weight of 65 kDa containing approximately 83wt% mPEG was isolated and properly characterized using NMR and MALDI-TOF MS. To our knowledge this is the highest monodisperse pegylated dendritic structures described in the literature.

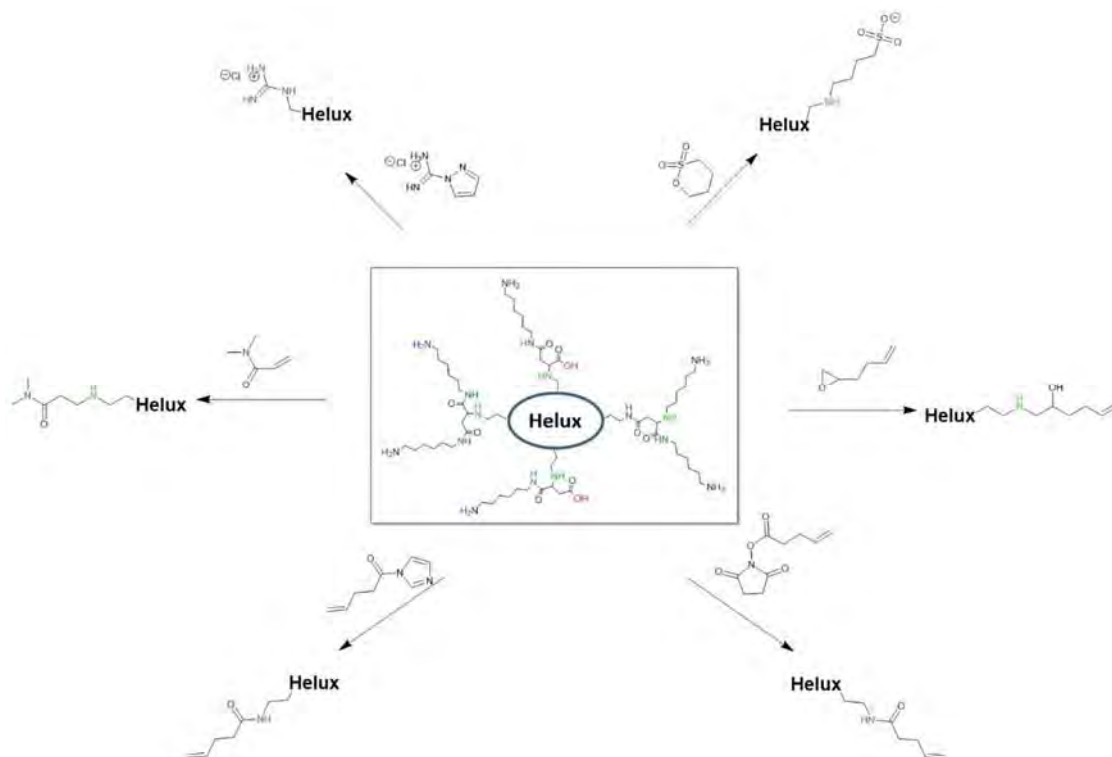


MALDI-TOF spectra of pegylated dendrimers from G1 to G5

POLY 394: Helux: Heterofunctional hyperbranched poly(amido amine) carboxylate

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The synthetic route to PAMAM dendrimers include Michael addition and subsequent amidation of acrylates and diamines, yielding a highly cationic and branched poly(amido amine) polymeric scaffolds. However, the absence of heterogeneity of the final dendrimers and tedious iterative chemistry required reduces the efficiency in their envisaged applications. For instance, partially degradation of PAMAM dendrimers, *via* hydrolysis of the amide bonds to carboxylic counterparts, results in more flexible, less cationic and degraded structures which are suitable for gene transfer applications. Consequently, the interest to introduce heterogeneity and utilizing scalable hyperbranched poly(amido amine) polymers could increase and facilitate a greater number of applications. An interesting candidate that captures such features is the currently available DSM product Helux, a hyperbranched poly(amido amine carboxylate). Helux is synthesized by Michael addition and amidation of diethyl maleate (DEM) and diamino-hexane (HMDA), similar to the PAMAM, however, it comprises an intrinsic heterofunctional characteristic, including amides, carboxylic acids, and, primary and secondary amines. The hyperbranched Helux is due to its heterofunctionality, water soluble and a prime candidate to be further functionalized and manipulated at our disposal. Herein, we describe, for the first time, the in-depth characteristics and properties, and as well, a series of successful postfunctionalizations of the Helux, being a promising multifunctional scaffolds.



POLY 395: UCST star polypeptides: Synthesis and solution behavior

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We report on star polypeptide polymers that exhibit upper critical solution temperature (UCST) behavior in aqueous solution. First, *star*-polyornithine (*star*-PO) was synthesized *via* ring opening polymerization of N- δ -Cbz-L-ornithine N-carboxyanhydride (L-ornithine(Z)-NCA) using a generation-four polyamidoamine dendrimer (G4-PAMAM) as a precursor. To endow UCST behavior to *star*-PO, the primary amines in the side chains were converted into ureido groups, making *star*-poly(ornithine-co-citrulline) (*star*-POC). Figure 1b shows AFM height image of the *star*-POC. The *star*-POC polymers exhibited UCST transitions in aqueous solutions which were sharper (occurring within a narrow temperature range of 5 °C) than those typically observed with linear UCST polymers. Importantly, individual star polymers and their aggregates in 150 mM NaCl solutions at pH 7.0 demonstrated transitions at close-to-ambient temperatures as quantified by dynamic light scattering. Moreover, the UCST of the star polypeptides could be tuned *via* both the length of POC branches and the degree of ureido modification. For a fixed degree of ureido modification, the UCST of *star*-POC polymers increased with the length of the *star*-polymer branches. For example, in the case of 96% ureido-modified *star*-POC, UCST changed from 17 °C to 24 °C for *star* polymers with 55-unit to 100-unit branches (*star*-POC₅₅ and *star*-POC₁₀₀ respectively, shown in Figure 1a). At the same time, for *star*-POC polymers with fixed branch length, higher degrees of ureido modification resulted in an increase of UCST. Specifically, *star*-POC₅₅ polymers with 93% and 96% modified units exhibited UCSTs of 14°C and 17°C, respectively. These results, taken together with potential biocompatibility and biodegradability, make *star*-POC polymers promising candidates for use as individually dispersed responsive containers or as building blocks for responsive assemblies.

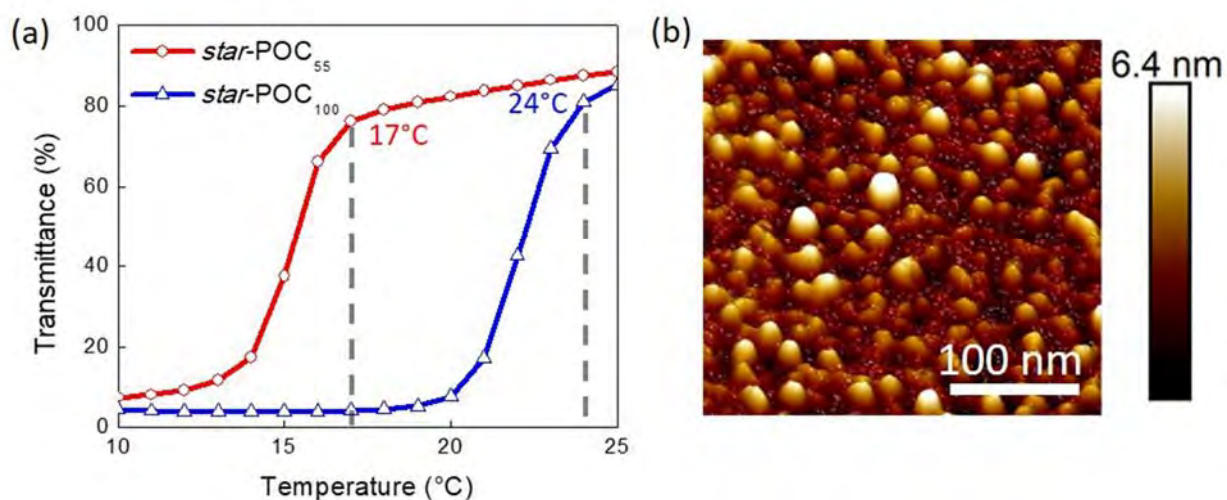


Figure 1. (a) The *star*-POC UCSTs as a function of degree of polymerization, (b) AFM height image of *star*-POC₅₅.

POLY 396: Stimuli-responsive supramolecular polymer adhesives exhibiting high toughness and stiffness

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Supramolecular polymers (SPs) consist of monomeric building blocks that associate via directional, non-covalent interactions such as hydrogen-bonding or metal-ligand complexation into macromolecular assemblies. Due to the transient, reversible nature of these bonds, SPs are susceptible to external stimulation and they can be (temporarily) disassembled back into the monomeric species via triggers such as heat or light. Changing the mechanical properties of SP materials by an external stimulus is particularly interesting in the context of healable materials or debonding-on-demand adhesives. However, the development of SP materials whose mechanical properties are comparable to their covalently linked counterparts has remained challenging. We here report the synthesis and characterization of a family of SP networks based on trifunctional building blocks carrying three quadruple hydrogen-bonding ureido-4-pyrimidinone (UPy) groups. Three monomers based on polypropylene oxide (PPO) cores of different molecular weights (ca. 440 – 5000 g/mol) were used. While the SP based on 440-PPO-UPy₃ formed a brittle glassy material with a glass transition temperature (T_g) at 84 °C, both 3000-PPO-UPy₃ and 5000-PPO-UPy₃ adopted phase separated morphologies, with a crystalline phase formed by the UPy-dimers melting around 95–113 °C, and a rubbery phase with a T_g around -60 °C. At room temperature, the latter two materials display Young's moduli of 28 and 14 MPa, a tensile strength of 1.6 and 0.7 MPa, and a strain at break of 9 and 6%, respectively. Moreover, the various building blocks can be combined to create blends with attractive property combinations. In particular, blending of 440-PPO-UPy₃ with higher molecular weight cores allowed a significant increase in both toughness and stiffness. Thus, the combination of these characteristics and the low melt-viscosity affords materials with promising mechanical performance, adhesive properties and attractive (de)bonding-on-demand capabilities that may be useful for a wide range of applications.

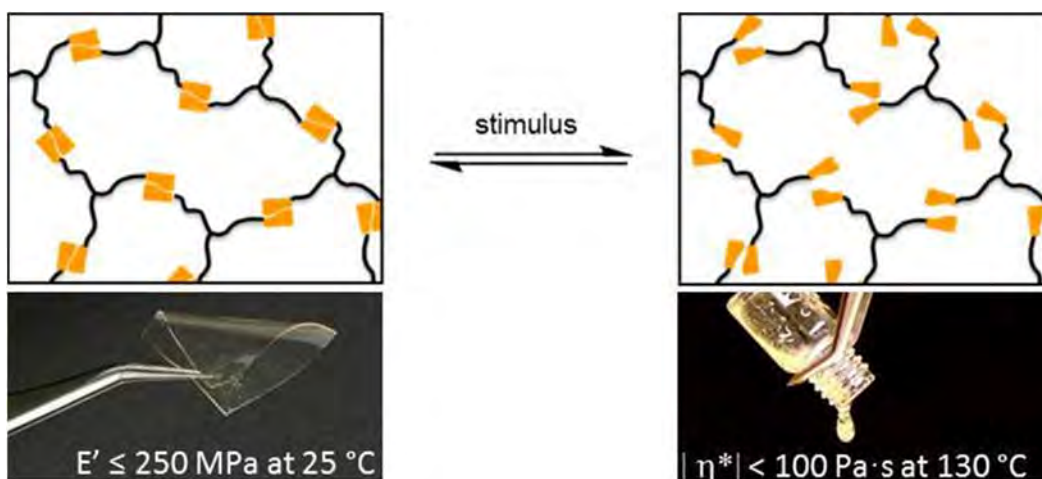


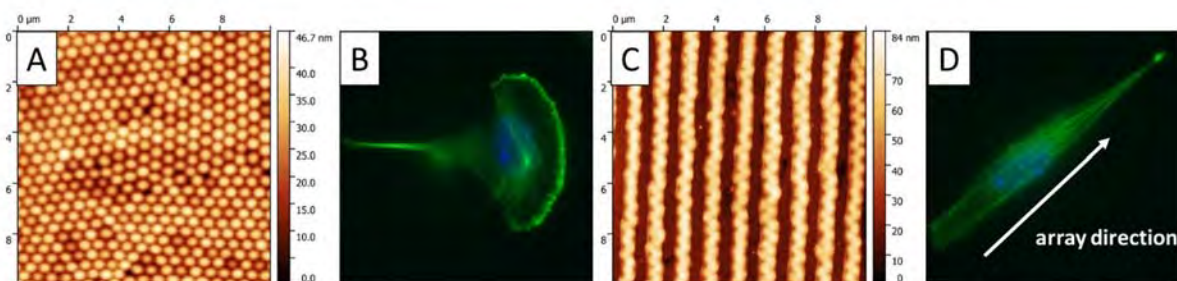
Fig. 1: Scheme of the stimuli-responsive trifunctional UPy-based SP network (top), and pictures of a PPO-UPy₃ material below and above its melting transition (bottom).

POLY 397: Printing of microgel arrays for regulation of cell motility and adhesion

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Microgels are 3D cross-linked polymer colloids which can react onto outer stimuli by a change of their size. These stimuli can be salt, temperature or light. Due to their swelling ability they can contain upto 90% water. This makes them an interesting polymeric material for interaction with biological systems. Topology and surface chemistry are powerful tools to affect cell adhesion and migration. We focused on use of microgels as building blocks for the decoration of biointerfaces. We developed recently a new technique that allows printing microgels on solid substrates.

By using wrinkled PDMS templates we successfully printed stimuli-responsive poly(N-Isopropylacrylamide) (pNIPAm) microgels in form of colloidal arrays on glass supports. By using low-pressure Argon plasma the microgels were chemically grafted onto the glass substrates. This process lead to highly stable microgel arrays in cell culture media. We could identify the influencing factors on the printing process and were able to print We demonstrated that our surface-grafted microgel arrays could serve as novel substrates for the analysis of cell adhesion and migration. Microgel arrays influenced size, speed and dynamics of focal adhesions as well as cell motility forcing cells to move along highly directional trajectories. Modulation of microgel state, spacing or cross-linking density served as an effective tool for regulation of cell motility.

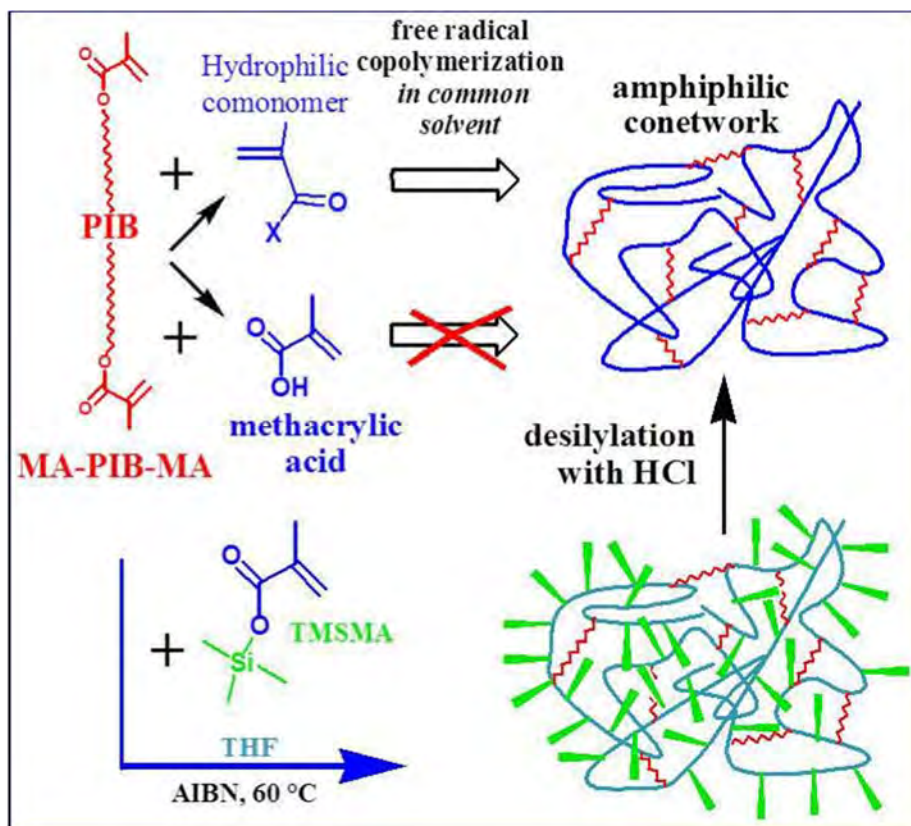


AFM image of pNIPAm microgel monolayer (A) and microgel array (C). Fluorescent microscopy image of a B16F1 (mice skin melanoma cells) on the monolayer (B) and the array (D). Cells were fixed and labelled with fluorescent phalloidin and nuclei were stained with DAPI (Blue). On the monolayer the cells form their typical fan like shape, however on the microgel array the cells change shape and stretch along the array direction (D).

POLY 398: Nanostructured pH-responsive polyelectrolyte amphiphilic polymer conetworks

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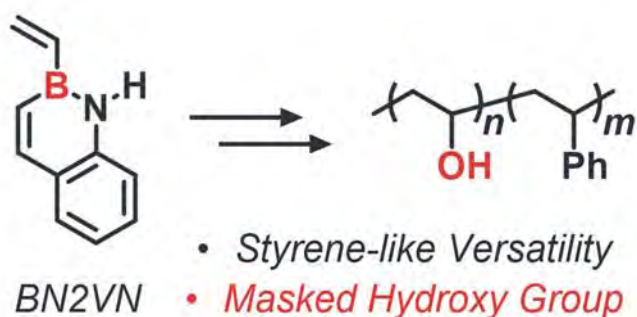
Amphiphilic conetworks composed of covalently linked immiscible hydrophobic and hydrophilic polymer chains provide a variety of unique properties and functions. In this presentation, the unusual synthesis routes, structure-property relations and unprecedented pH-responsive behavior of amphiphilic conetworks consisting of hydrophilic polyelectrolyte chains, with monomer units of either acidic or basic characters, such as (meth)acrylic acid or vinyl imidazole, respectively, cross-linked with polyisobutylene (PIB) or poly(tetrahydrofuran) chains will be reported.



POLY 399: BN aromatic ring strategy for tunable hydroxy content in polystyrene

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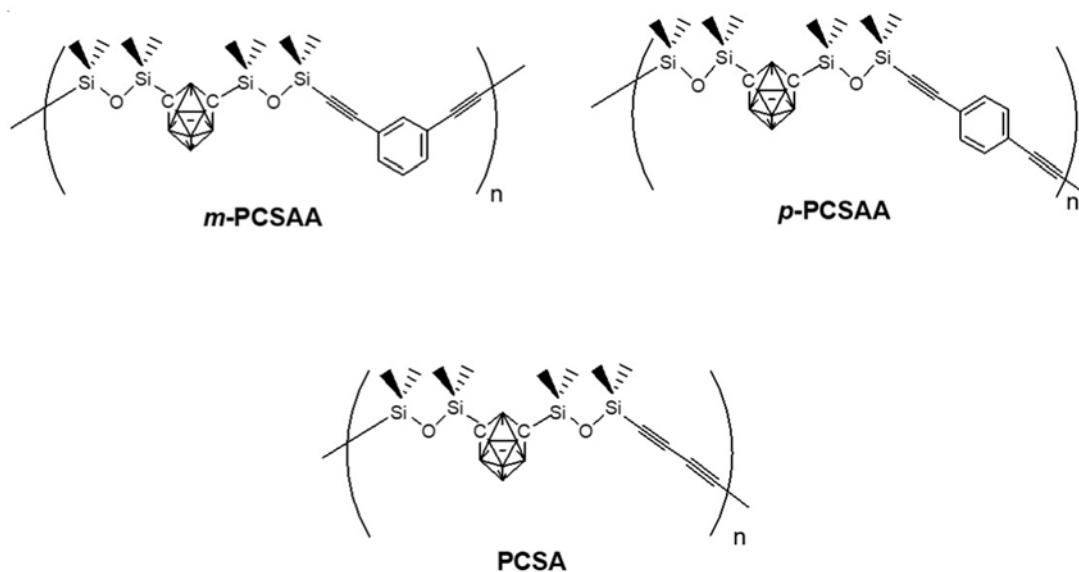
BN 2-vinylnaphthalene (BN2VN), a BN aromatic vinyl monomer, is copolymerized with styrene under free radical conditions. Experimental determination of the reactivity ratios of BN2VN and styrene is consistent with statistical copolymerization. Oxidation yields styrene–vinyl alcohol statistical copolymers with tunable hydroxy group content. BN aromatic polymers represent a platform for the preparation of diverse functional polymeric architectures via the remarkable reaction chemistry of C–B bonds.



POLY 400: Diffusion limited oxidation (DLO) in PCSA and PCSAA

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NRL-developed poly(carborane-siloxane-acetylenes) (PCSA) and poly(carborane-siloxane-arylacetylenes) (m-PCSAA and p-PCSAA) are two classes of high performance thermosetting functional polymers intended for use in advanced applications under extreme environmental conditions. While the anticipated temperature range of such applications is between 400C and 700C, results from previous thermo-oxidative stability analyses of these polymers up to 1000C are encouraging as they retain 80% of initial weight upon rapid exposure to such temperatures in both inert and oxidative environments. While such stabilities are quite remarkable, particularly, the oxidative stabilities are impressive and are believed to be the result of a dominantly operational diffusion limited oxidation (DLO) condition. Since previous oxidation studies up to 500C have established the initial generation of B₂O₃ and SiO₂ on the evolving thermosetted matrices, in this talk, we will examine the surface science of such polymers under inert and oxidative conditions up to 750C by both experiment and theory and provide fundamental insight into the DLO effect in these polymers at that temperature regime.



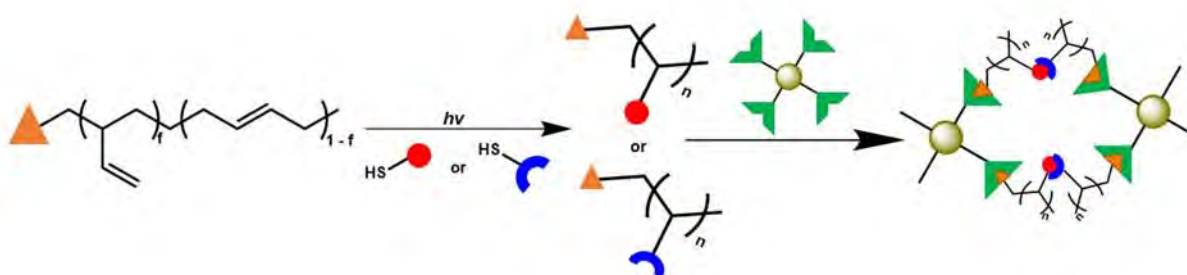
Structures of PCSAA, m-PCSAA and p-PCSAA

POLY 401: Modular functionalization of polybutadiene with dynamic bonds for matrix free nanocomposites

Andrew Tibbits^{1,2}, *TheyCallMeDrTibbs@gmail.com*, **Kyoungweon Park**^{1,2}, **Jason Streit**^{1,2}, **Lawrence F. Drummy**¹, **Richard A. Vaia**¹. (1) Air Force Research Lab, WPAFB, Ohio, United States (2) UES, Inc, Beavercreek, Ohio, United States

Polymer-grafted nanoparticles (PGNs) with dynamic bonds have been shown to assemble into precise arrays tunable with temperature and the intrinsic properties of the polymer canopy even without an additional polymer matrix. These matrix free materials have significant ramifications in the design of tough and stimulus-responsive coatings, flexible electronics, and functional inks. However, tuning properties for a specific application is often tedious due to challenging synthetic methods. Polybutadienes, containing both 1,2-butadiene and 1,4-butadiene units, are attractive polymers for post-synthesis modification with pendant supramolecular moieties. The reactive nature of the diene bonds permits superior control over pendant group functionality and degree of functionalization.

Herein we show that polybutadiene can be readily functionalized via thiol-ene chemistry. Careful manipulation of reaction conditions and mercaptan structure and composition enables preparation of rubbery and glassy polymer films with dynamic supramolecular interactions ranging from weak (e.g., single H-donor and single H-acceptor) to strong (e.g., guanine and cytosine associative nucleobase pair). Simultaneous modulation of covalent crosslink density with multifunctional thiols allows for further enhancement of energy dissipation under strain. PGNs are fabricated by grafting amine-terminated polybutadiene with the modified pendant groups to carboxy-functionalized nanoparticles. The nanoparticle spacing, self-assembled structure, and nanoscale mechanics of these matrix-free nanocomposites and arrays are readily tuned via simple manipulation of the pendant functional group, degree of functionalization, nanoparticle dimensions, and molecular weight as confirmed by X-ray scattering, microscopy, and atomic force microscopy. Overall, these approaches afford a versatile and scalable preparation of stimuli responsive and tough nanocomposites.

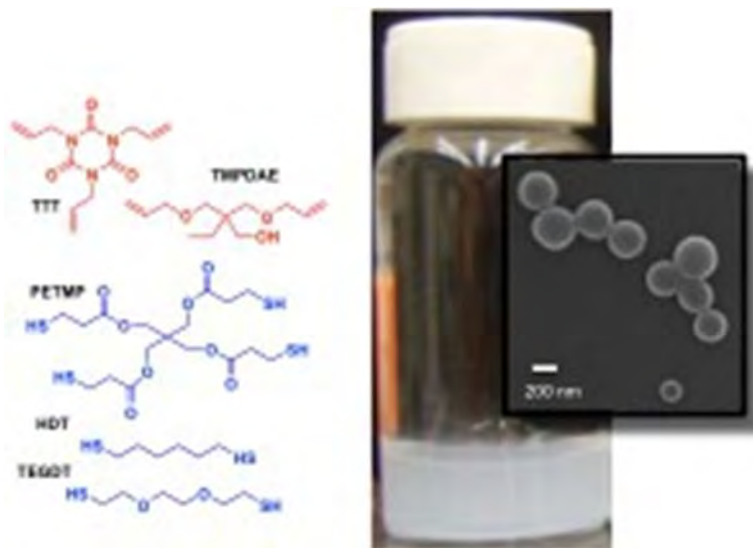


Schematic diagram showing design of PGNs interacting via associative dynamic bonds. Photoinitiated thiol-ene chemistry is used to functionalize pendant units of telechelic polybutadiene with supramolecular moieties. Modified polymers are subsequently grafted to the surface of silica and gold nanoparticles allowing for the synthesis of responsive and tough matrix free nanocomposites.

POLY 402: Radical-mediated thiol–ene emulsion polymerizations: formation of functional nanoparticles

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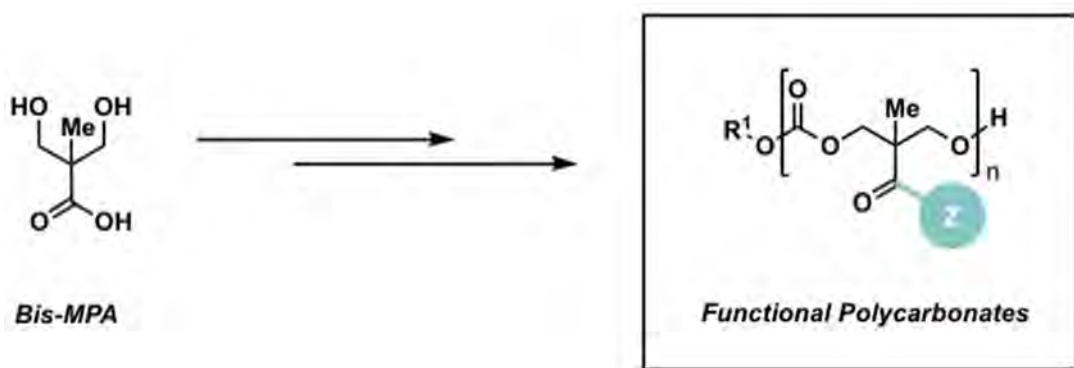
Thiol–ene “click” chemistry is highly efficient and has been utilized in recent decades for both bulk polymerization and polymer modification. More recently, radical-mediated thiol–ene chemistry has been applied to heterogeneous polymerizations for the production of polymer particles. One significant advance of this research focus was the development of emulsion polymerization of different thiol–ene polymer compositions to form functional nanoparticles. It has been shown that the average particle diameter can be pre-determined by appropriate choice of reaction conditions, and size homogeneity (monodispersity) can also be achieved. Another development has been the functionalization of the nanoparticles, either through addition of functional thiol or ene moieties, or through post-polymerization modification, such as thiol-X based chemistries (e.g., thiol-Michael, thiol-ene reactions), or oxidation of the thioether bonds present in the polymer particles to form sulfoxide bonds.



POLY 403: Development of new high performance functional materials and macromolecular therapeutic platforms

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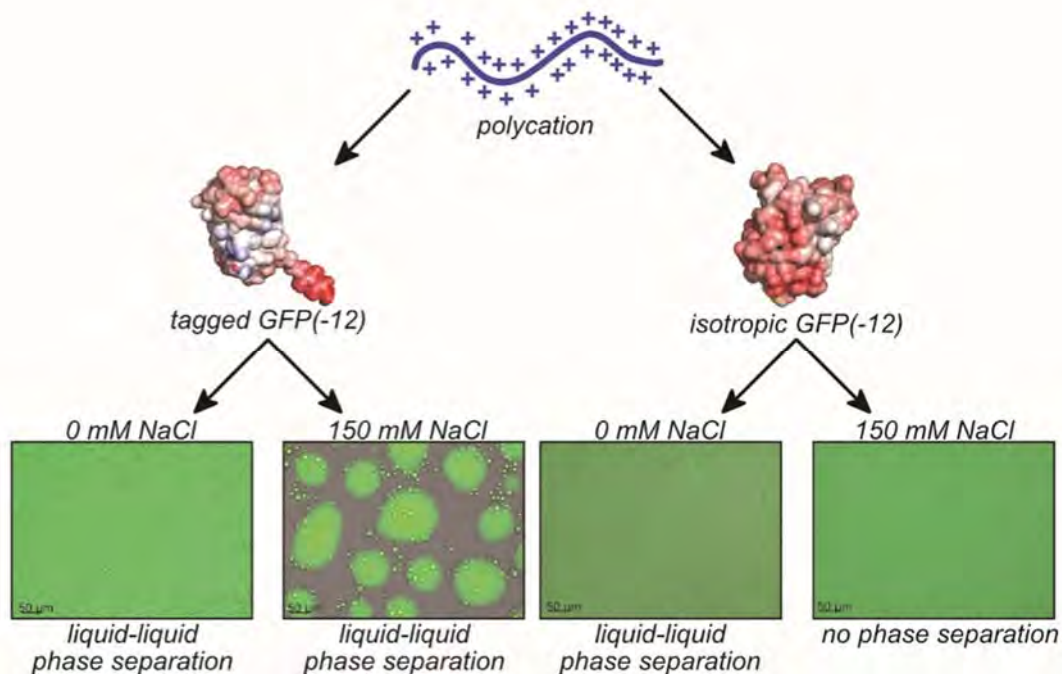
The development of new functional materials scaffolds with tailorable properties are critically important for a diverse array biomedical applications. In this context, polycarbonate based platforms stand out in terms of their biocompatibility, biodegradability, and breadth of functional groups that may be incorporated into the polymer backbone. These features have enabled the development of numerous polycarbonate based platforms for applications in drug delivery, injectable hydrogels, antimicrobials, and cancer therapy. In addition to polycarbonate materials, significant advances have been made in the area of repurposing and recycling PET into new, high value monomers. These can readily be incorporated into a diverse array of materials with applications as antifungal and antimicrobial compounds.



POLY 404: Effect of protein charge distribution on complex coacervation for the development of a polyionic coacervate tag

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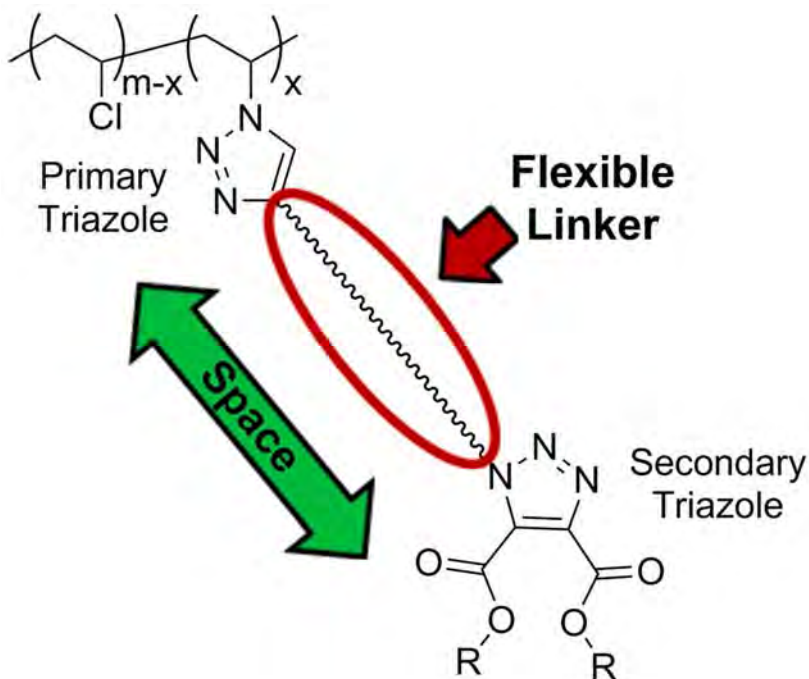
Polyelectrolytes of opposite charge in an aqueous solution can undergo a liquid-liquid phase separation known as complex coacervation. Complex coacervation of zwitterionic proteins with oppositely charged polyelectrolytes results in a protein rich phase, which has potential applications in protein therapeutics and purification. Many globular proteins, however, do not phase separate, and those that do phase separate over narrow pH and ionic strength ranges. The protein and polymer design factors that govern complex coacervation under varying conditions are still relatively unknown. Recent work indicates that proteins with an intrinsically disordered region, a higher net charge, and those with a patch of charged residues are more likely to undergo phase separation under varying conditions. This work looks to design a polyionic coacervate tag that can be appended to a protein of interest to facilitate complex coacervation with an oppositely charged polyelectrolyte. The addition of a polyelectrolyte tag to superfolder GFP results in a system that remains a phase separated liquid at physiologically relevant salt concentrations and pH indicating its potential for use in vivo.



POLY 405: Tailorable grafting moieties for non-migratory internal plasticization of poly(vinyl chloride)

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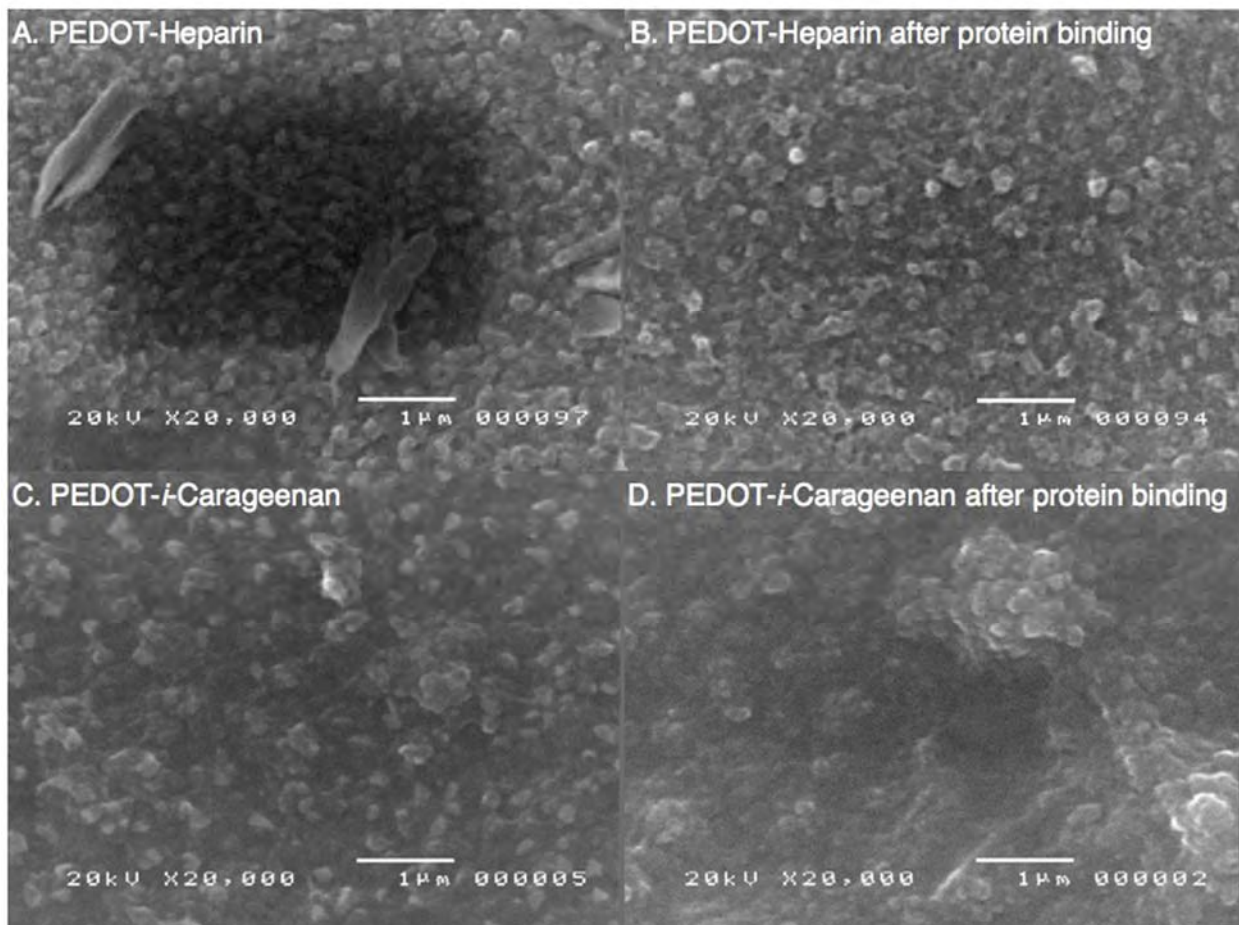
Branched and linear non-migratory internal plasticizers attached to PVC by a pendant triazole linkage were synthesized and investigated. Copper-free azide-alkyne thermal cycloaddition was employed to covalently bind triazole-based phthalate mimics to PVC. To systematically investigate the effect of plasticizer structure on glass transition temperature, several architectural motifs were explored. Free volume theory was considered when designing many of these internal plasticizers: flexible hexyl-tethers were utilized to generate additional space between the triazole-phthalate mimic and the polymer backbone. Compatibility of these triazole-plasticizers in PVC is important: variation of the ester moieties on the triazole possessing alkyl and/or poly(ethylene oxide) chains produced a wide range of glass transition temperatures (T_g): from anti-plasticizing 96 °C, to highly efficient plasticized materials exhibiting T_g values as low as -42 °C.



POLY 406: Synthesis and characterization of PEDOT-polysaccharide films for urokinase recognition

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Elevated expression of urokinase, a glycosyl-phosphatidylinositol-linked membrane protein, is associated with increased tumor leakiness and metastasis. In this study, poly(3,4-ethylenedioxythiophene) (PEDOT) was electropolymerized with electronegative multisulfated polysaccharide such as heparin or *i*-carrageenan to produce PEDOT-heparin or PEDOT-*i*-carrageenan polymer composite films *via* a fixed applied oxidative potential of 1.200V for 600 seconds. The surface morphologies of both films were rough and clustered, with cluster sizes ranging from 200 nm to 300 nm for PEDOT-heparin (A) and 250 nm to 400 nm for PEDOT-*i*-carrageenan (C), and the clusters became less prominent after protein binding (B PEDOT-heparin and D PEDOT-*i*-carrageenan). The films were characterized using cyclic voltammetry before and after protein binding. Binding studies were also carried out using impedance spectroscopy. The results obtained will be presented.



POLY 407: Shape-stable ultrasoft hydrogel microstructures

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Hydrogels and thin hydrogel coatings are interesting polymers to control the interaction of materials and surfaces with a biological environment. It has been shown for example that hydrogels can render a surface bioinert such that no proteins adsorb to this surface and no cells adhere there as well. A combination of hydrogels with cell attractive polymers or receptor motifs is hence important to spatially control cell adhesion on surfaces. One interesting architecture in this regard are surface reliefs such as pillar arrays. These may also be used for mechanical stimulation provided the pillars are soft enough so that a cell can interact mechanically.

Swollen hydrogels are materials that contain significant amounts of water and are very soft. However, typical microstructuring techniques such as photolithography or hot embossing require processing in the dry state. Subsequent exposure to water leads then to a strong volume increase due to the swelling and the microstructure is lost. In this contribution, we report on a novel pathway to generate shape stable ultrasoft hydrogel microstructures using C,H insertion crosslinking reactions in solution combined with embossing techniques. Figure 1 shows the method. The microstructures are generated in the swollen state during the UV induced crosslinking of polydimethyl acrylamide copolymers carrying benzophenone groups. The microstructures collapse upon drying but reswell and the shapes are recovered when the sample is again placed in water. We will report on the parameters and conditions for which such shape memory surface architectures can be generated. The resulting post arrays are very soft and modulus measurements by AFM have yielded values in the kPa range. The microstructuring process is not limited to shape. Additionally, the surfaces of the microstructures can be further modified. Other polymers can for example be inked to the post top faces and bound there, to generate surface properties in these regions that differ from those between the posts.

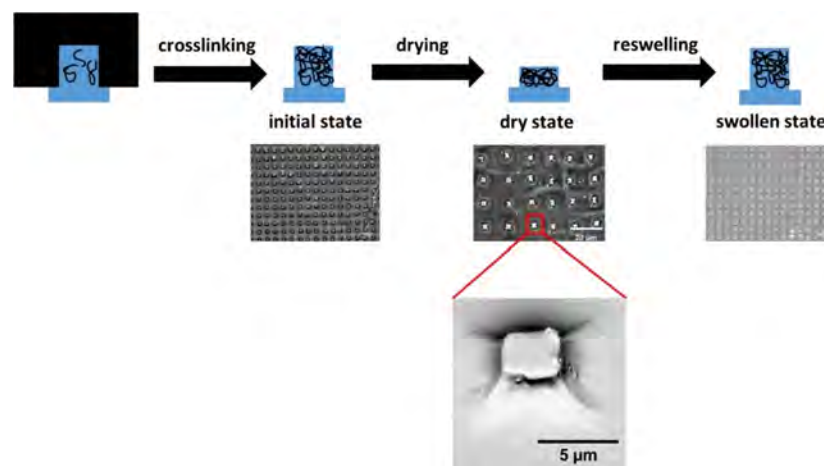
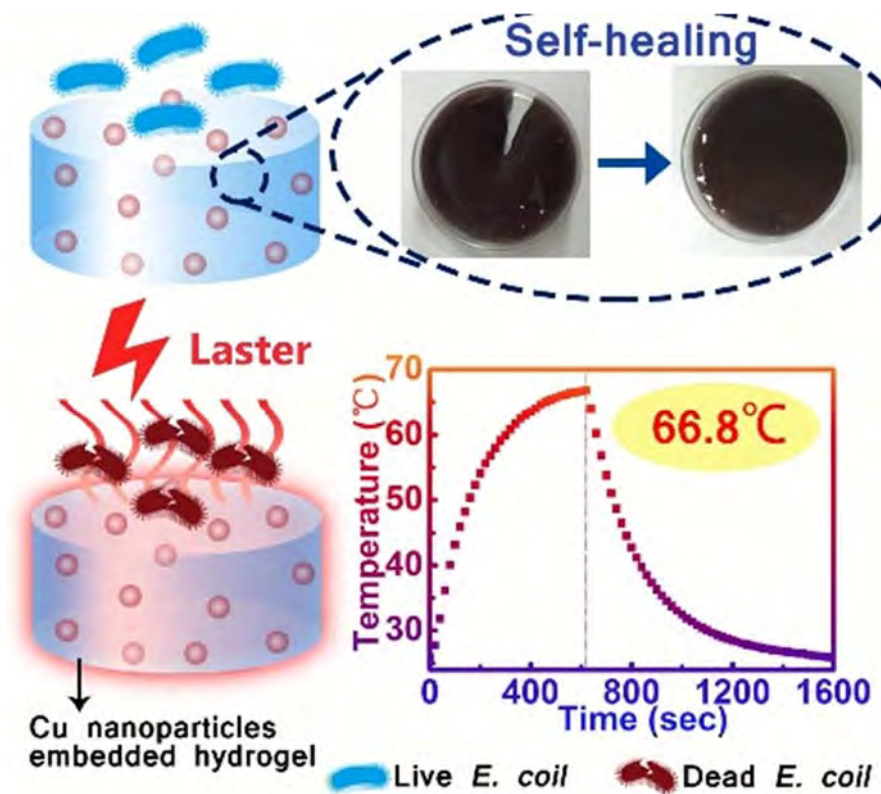


Figure 1: Process description for the generation of ultrasoft hydrogel pillars together with images of the structures in the different swelling states.

POLY 408: Copper nanoparticles-contained hydrogel with self-healing and photothermal properties

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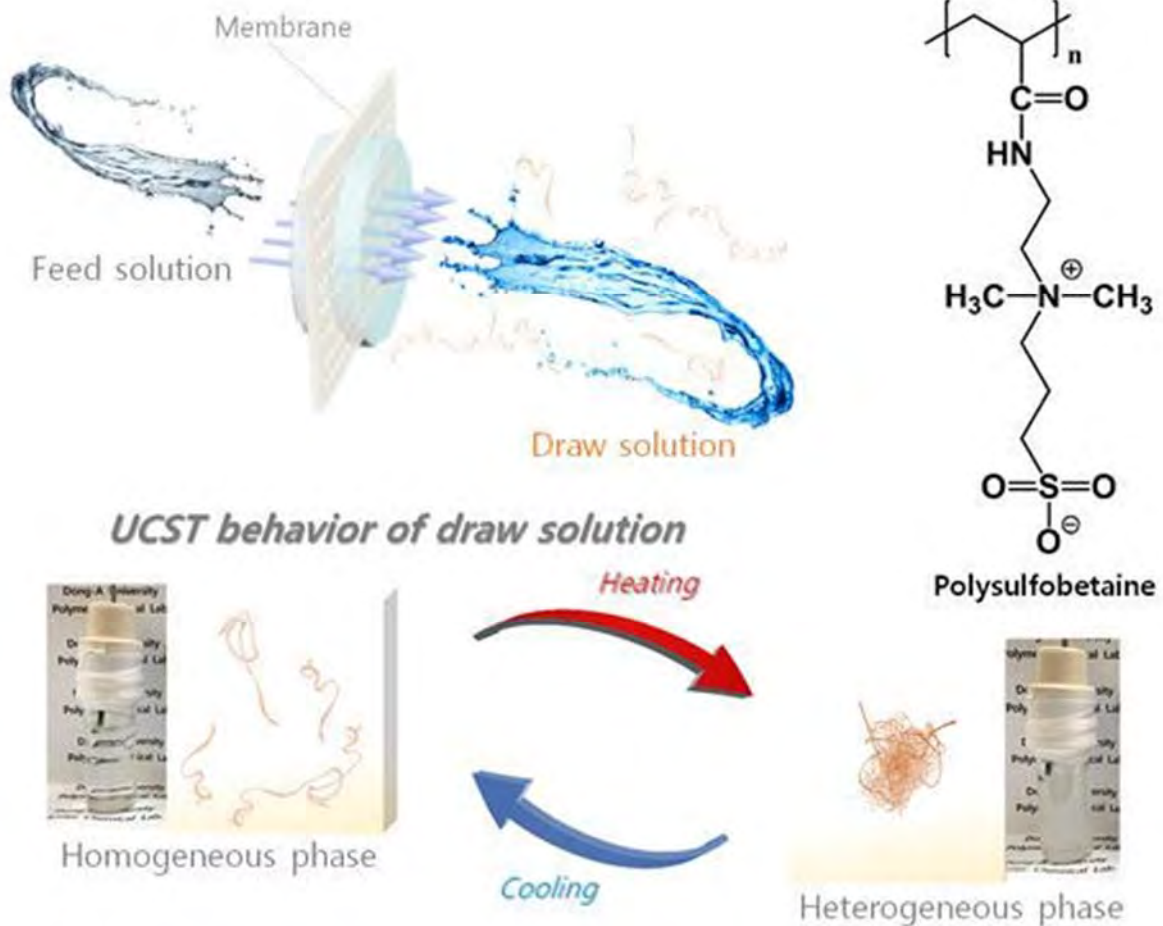
Copper (Cu) nanoparticles possess unusual electrical, thermal, and optical properties. However, applications of these materials are often limited by their tendency to oxidize. In this work, we present the use of a simple polyol method to prepare Cu nanoparticles with controllable sizes. The reaction required no inert atmosphere or surfactant agents, and was completed in 30 min. The as-prepared Cu nanoparticles showed good resistance to oxidation in solution. Then, they were incorporated into a biocompatible polysaccharide hydrogel which further stabilized the nanoparticles. The resulting hybrid hydrogel exhibited a rapid self-healing ability upon external damage. Moreover, it showed rapid temperature elevation under laser irradiation, which could be ascribed to the excellent photothermal conversion properties of the embedded Cu nanoparticles. The hybrid hydrogel showed limited cytotoxicity. However, under laser irradiation, it displayed good antibacterial properties owing to the heating effects. This hybrid hydrogel shows a good promise as a material for applications in biomedical fields and photothermal therapy.



POLY 409: Polymeric materials having upper critical solution temperature characteristics as osmotic agents for forward osmosis process

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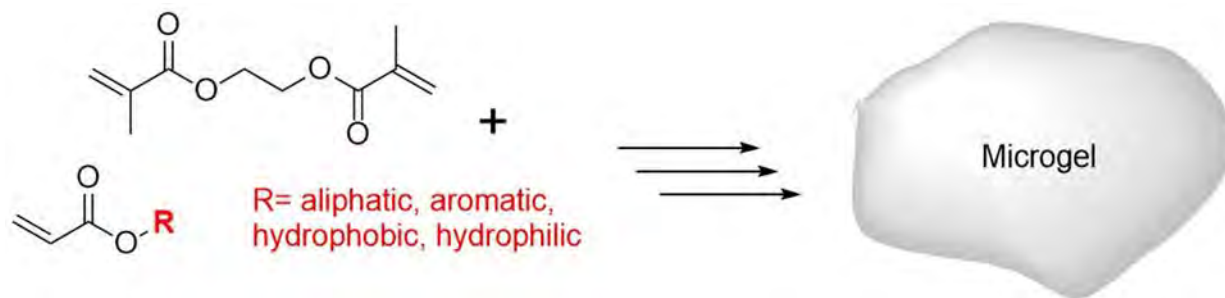
We synthesized the zwitterionic polysulfobetaine, which has upper critical solution temperature (UCST) behaviors, via conventional free radical polymerization in order to confirm its suitability as an osmotic agent for the forward osmosis process. The forward osmosis and recovery properties of zwitterionic polysulfobetaine were systematically studied. The UCST behaviors of the monomer sulfobetaine were not confirmed, while the UCST of polysulfobetaine was observed to be about 40 °C. These results suggest that zwitterionic polysulfobetaine can be easily reused from permeated solution by cooling them to below the UCST. In an active layer facing feed solution system containing 20 wt% zwitterionic polysulfobetaine at a temperature of 50 °C, the water flux and reverse solute flux of polysulfobetaine were found to be approximately 3.22 LMH and 0.36 gMH, respectively. Therefore, we investigated the suitability of homopolymer systems having UCST characteristics as osmotic agents for the forward osmosis process for the first time.



POLY 410: Designing matrix effects in polyacrylate microgels

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Synthesis of microgels that immobilize a catalyst to enhance its performance institutes a large world of opportunities for polymers in the biochemistry field. A crucial aspect of the microgel is its matrix; therefore, matrix alterations will affect the catalytic activity of an immobilized catalyst. Accordingly, the polymerization proceedings of microgels derived from acrylate monomers with large structural diversity were documented by gravimetric analysis. The influence of matrix effects on the particle diameters was recorded in addition and will be described.



Synthesis of crosslinked microgels using substituted acrylates

POLY 411: Stereoselective photoredox ring-opening polymerization of *O*-carboxyanhydrides

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Biodegradable polyesters with various tacticities have been synthesized by means of stereoselective ring-opening polymerization of racemic lactide and β -lactones but with limited side-chain groups. However, stereoselective synthesis of functional polyesters remains challenging from *O*-carboxyanhydrides that have abundant pendant side-chain functional groups. Herein we report a powerful strategy to synthesize stereoblock polyesters by stereoselective ring-opening polymerization of racemic *O*-carboxyanhydrides with the use of photoredox Ni / Ir catalysts and a selected Zn complex with an achiral ligand. The obtained stereoblock copolymers are highly isotactic with high molecular weights (>70 kDa) and narrow molecular weight distributions ($M_w/M_n < 1.1$), and they display distinct melting temperatures that are similar to their stereocomplex counterparts. Furthermore, in one-pot photoredox copolymerization of two different *O*-carboxyanhydrides, the use of such Zn complex mediates kinetic resolution of the co-monomers during enchainment and shows a chirality preference that allows for the synthesis of gradient copolymers.

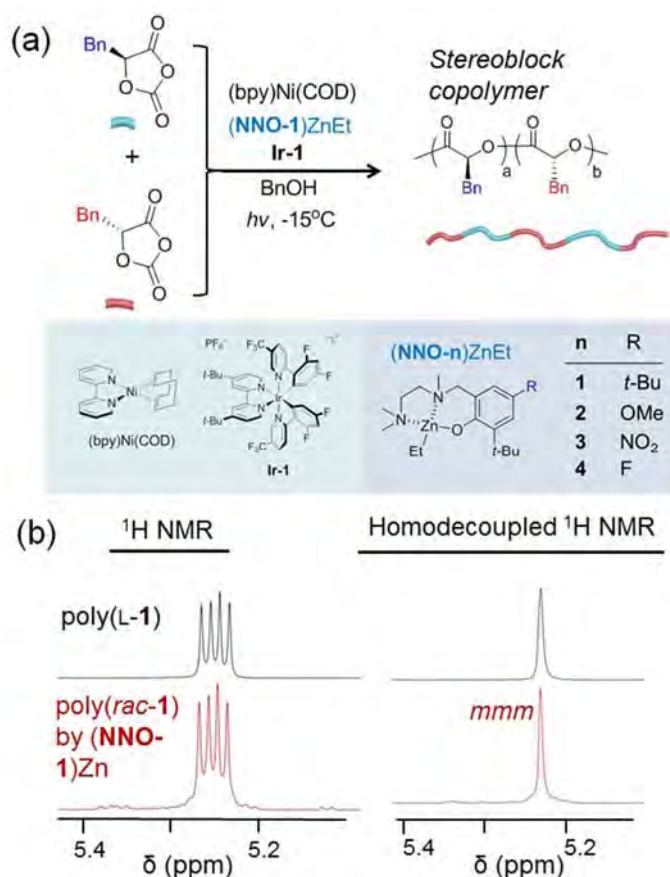
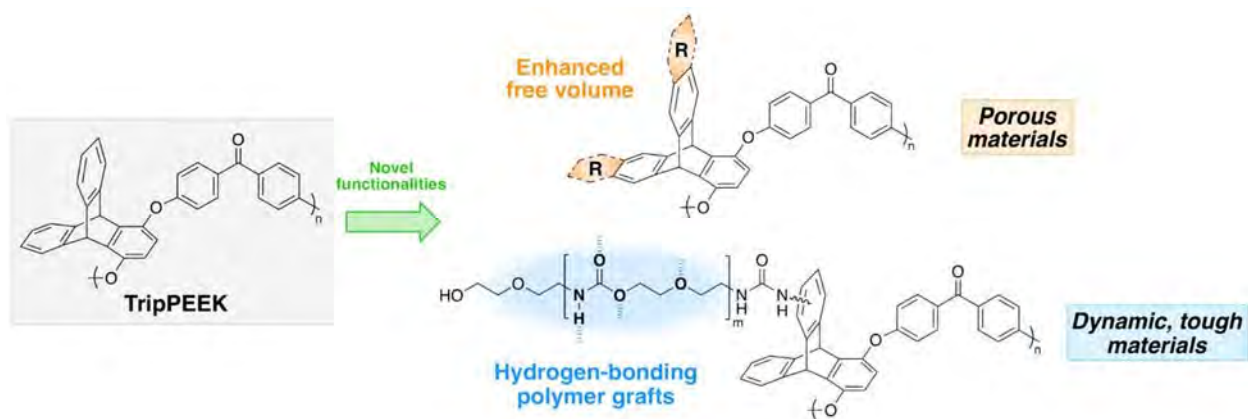


Fig 1. (a) Stereoblock polymerization scheme. (b) ^1H NMR of poly(sb-1).

POLY 412: Functional triptycene-based poly(ether ether ketone)s for porous and impact-protective materials

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Poly(ether ether ketone)s (PEEKs) exhibit high strength and inertness, and have found use in demanding applications such as medical implants and precision mechanical parts. Triptycene-based PEEKs (TripPEEKs) combine the structural rigidity and free volume of triptycene with the exceptional thermal and chemical stability of PEEK. Using TripPEEK derivatives, our group has previously demonstrated that these properties lead to enhanced performances in ion-exchange membranes. In order to expand the potential for further applications, we have developed novel synthetic routes to TripPEEKs with diverse and well-defined functionalities. Several applications that leverage the free volume and rigidity of TripPEEK will be discussed. We have explored the augmentation of free volume elements in order to create porous materials towards gas separation membranes, as well as the incorporation of pendant groups and polymer grafts with complex hydrogen-bonding behavior in order to construct tough, dynamically stiffening materials for impact protection.



POLY 413: Fluorescent labeling method reveals the functional mechanism of poly(acrylamide-co-acrylonitrile)s with upper critical solution temperatures

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Stimulus-responsive polymers can be utilized as highly-functionalized materials in cosmetics. In order to make products that can be easily washed out by hot water, we focus on thermo-responsive polymers with upper critical solution temperatures (UCSTs). Poly(acrylamide-co-acrylonitrile) (poly(AAm-co-AN), Fig. 1a) was selected as a model polymer due to its simple chemical structure without permanent charges. First, we synthesized poly(AAm-co-AN)s with a different AAm/AN ratio. When AN was added immediately prior to the polymerization (to prevent its volatilization), the amount of AN units in the copolymer corresponded to the molar ratio of AN in feed. Poly(AAm-co-AN) containing a higher amount of AN units showed a higher UCST in water, which was in accordance with a previous report by Agewal et al. (*Macromolecules*, **2012**, *45*, 3910)

Next, the functional mechanism of poly(AAm-co-AN) was investigated by fluorometry. The environment-sensitive DBD (*N*-{2-[(7-*N,N*-dimethylaminosulfonyl)-2,1,3-benzoxadiazol-4-yl](methyl)amino}ethyl-*N*-methylacrylamide, *J. Phys. Chem. B*, **2008**, *112*, 2829) was used as a labelling fluorophore. The maximum emission wavelength of DBD units hypsochromically shifts in a more hydrophobic environment. In our previous study on poly(*N*-isopropylacrylamide) with a lower critical solution temperature (*ca* 32 °C), we observed a drastic shift in the maximum emission wavelength from 577 to 550 nm along with the thermal response (*J. Phys. Chem. B*, **2008**). In contrast, only a slight change in the maximum emission wavelength from 580 to 576 nm was observed in the response of DBD-labeled poly(AAm-co-AN) (poly(AAm-co-AN-co-DBD), Fig. 1a), suggesting that the microenvironment around the DBD units in the copolymer did not change around UCST (Fig. 1b). In fluorescence quenching titration using potassium iodide as a quencher, the DBD units in poly(AAm-co-AN-co-DBD) were quenched even below UCST. This result indicated that the iodide ion was accessible to the DBD units in the aggregates of the copolymer, indicating that poly(AAm-co-AN) aggregated loosely below UCST (Fig. 1c). In the aggregated form, it is likely that the dipole-dipole interactions between the cyano groups in AN units dominantly work as crosslinkers.

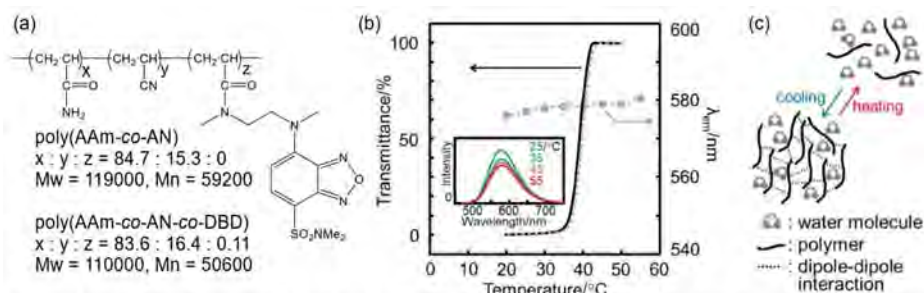
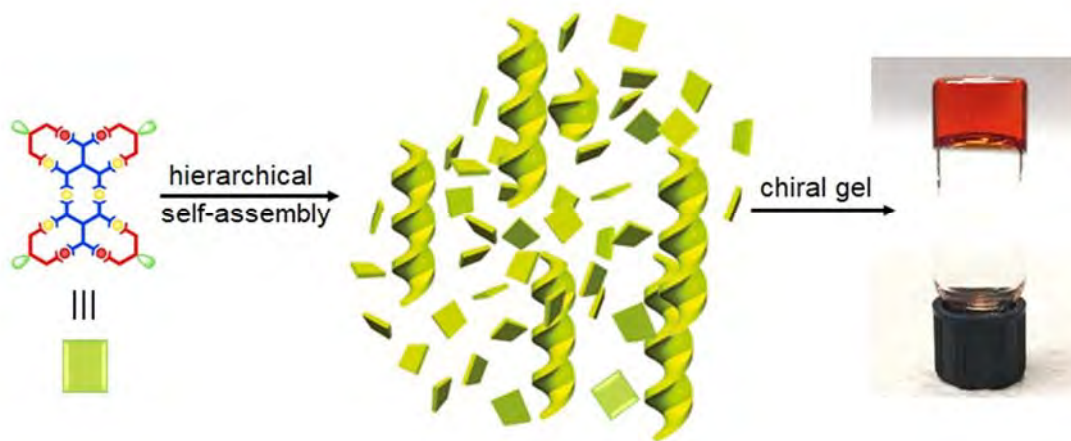


Figure 1. (a) Chemical structure of the synthesized polymers. (b) Change in the transmittances (at 670 nm, left axes) of poly(AAm-co-AN) and poly(AAm-co-AN-co-DBD), and change in λ_{em} (right axes) of poly(AAm-co-AN-co-DBD) in aqueous solution (1 w/v%). Inset: fluorescence spectra. The sample was excited at 456 nm. (c) Proposed functional mechanism of poly(AAm-co-AN) in aqueous solution.

POLY 414: Self-assembly of chiral helical nanostructures based on cholesterol-aided metallomacrocyclic

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Chirality is very common in nature and can occur at different scales such as molecular, macromolecular, supramolecular and material level. In supramolecular assembly, the chirality is not only determined by the molecule component itself, but also largely relies on the spatial arrangement of the component molecules through non-covalent interactions. Here, we designed a square-like metallomacrocyclic which tended to form twisted helical nanoarchitectures through hierarchical self-assembly. When cholesterol was introduced as chiral component, the helical nanoarchitectures displayed one-handed arrangement, followed by the gelation process. Both 1D and 2D NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), traveling-wave ion mobility mass spectrometry (TWIM-MS) have been used to characterize the supramolecules. And scanning electron microscopy (SEM), transmission electron microscopy (TEM), circular dichroism (CD) microscopy are utilized to characterize the helical nanostructures.

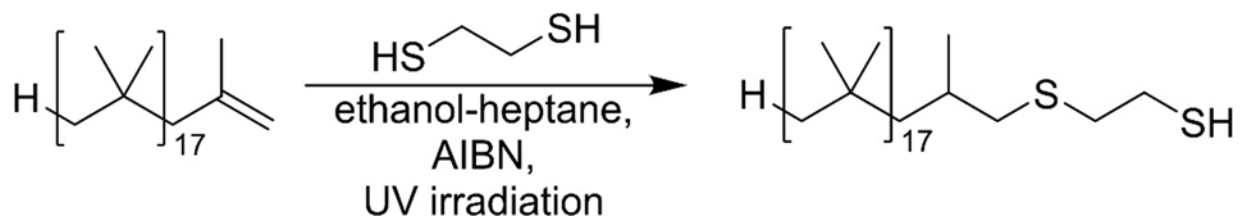


POLY 415: Ethanedithiol-functionalized polyisobutylene for biphasic extraction of transition metal catalysts

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Separation of the transition metals routinely used in homogeneous catalysts from the reaction mixtures is a long-standing problem. Recently our group have proposed functionalized polyisobutylene (PIB) oligomers as a highly hydrocarbon selectively soluble support for the homogeneous catalysts. They can be quite effective at separating catalysts from reaction mixtures by simple liquid-liquid separation with negligible metal leaching. In the best example to date, the Pd content in the product solution is reduced by nearly five orders of magnitude to 2 ppb. At the same time, in case of the catalyst decomposition, selectively soluble ligands can facilitate phase separation of catalyst residues from products. Based on this concept, these PIB-bound ligands can be used also as an advantageous agents for metals sequestration. This approach would be especially attractive if the sequestrants can be prepared with minimal synthetic effort.

Here we report a relatively simple ethanedithiol-functionalized PIB as an excellent sequesterant for Cu and Pd metal catalysts. It can be prepared via single step photoinitiated thiol-ene "click" reaction starting from inexpensive vinyl-terminated PIB and 1,2-ethanedithiol. Heptane solution of this sequesterant was used for efficient (>99%) extraction of Cu, Pd and some other transition metal cations (Co²⁺, Ni²⁺, Zn²⁺, Ru³⁺ and Pd²⁺) from model solutions as well as from crude products obtained in Pd and Cu catalyzed reactions.

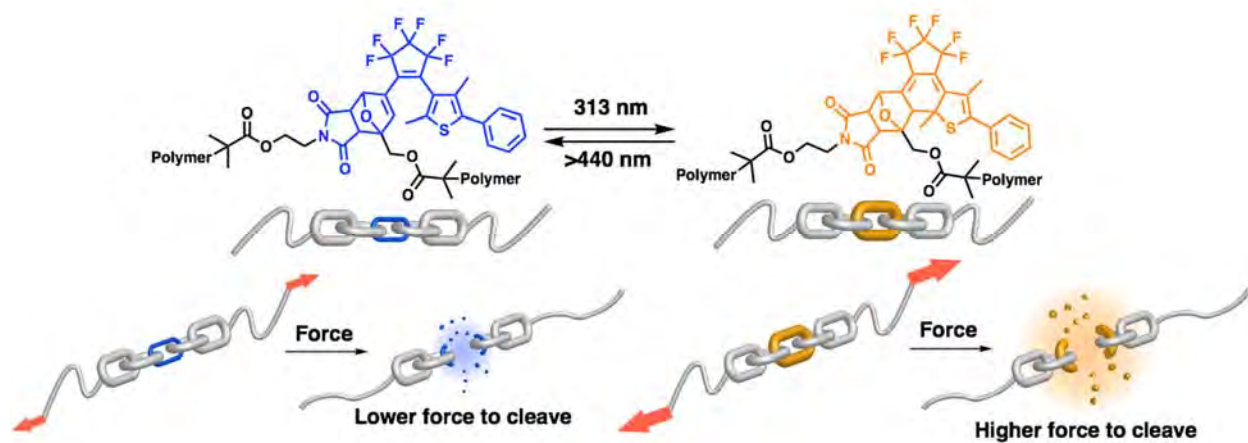


Scheme 1. Synthesis of ethanedithiol-functionalized polyisobutylene

POLY 416: Photoregulation of mechanochemical scission in polymers with a diarylethene-conjugated Diels–Alder adduct

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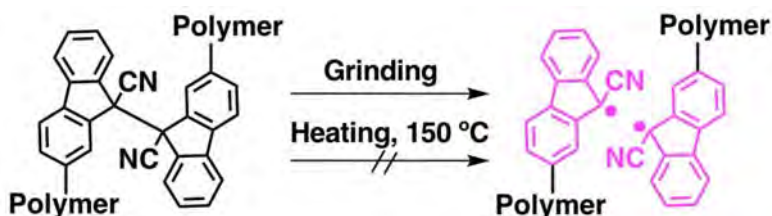
Control over mechanochemical polymer scission by another external stimulus may offer a new avenue to further advance the fields of polymer chemistry, mechanochemistry, and materials science. Herein, we demonstrate that light can regulate the mechanochemical behavior of a designed diarylethene-conjugated Diels–Alder adduct (DAE/DA) that reversibly isomerizes from a weaker open-form to a stronger closed-form under photoirradiation. Pulsed ultrasonication experiments, spectroscopic analyses, and density functional theory calculations support the successful photoregulation of the reactivity of the designed DAE/DA mechanophore, which was incorporated at the mid-chain of a polymer, and indicate that higher force and energy are required to cleave the closed form of the DAE/DA mechanophore relative to the open form. The present photoregulation concept provides an attractive approach toward a new generation of mechanofunctional polymers.



POLY 417: Thermally stable mechanochromic polymers having difluorenylsuccinonitrile

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Mechanochromic polymers, which change their colors under mechanical stress, have attracted much attention in materials science. The main strategy for building mechanochromic polymers involves incorporation of mechanochromophores into polymer chains. Recently, we have reported that the central carbon–carbon bond in tetraarylsuccinonitrile (TASN), can be cleaved to afford pink-colored radical by either thermal or mechanical stimuli. The generated carbon-centered radical species are tolerant of oxygen and detectable by electron paramagnetic resonance (EPR) spectroscopy, resulting in quantitative evaluation of the mechanical stress in air. However, the thermo-responsiveness of TASN limits its application as a mechanochromophore under heating conditions. Herein, we report the design and synthesis of a novel mechanochromophore, difluorenylsuccinonitrile (DFSN), whose central carbon–carbon bond is more tolerant of thermal stimulus, and mechanochromic polymers with a DFSN skeleton at their mid-chains. A DFSN derivative with two hydroxyl groups was synthesized from commercially available 2-fluorencarboxaldehyde in 7 steps. Thermal properties of the obtained DFSN derivative were evaluated by EPR measurements, which revealed that the cleavage ratio of central carbon–carbon bond in DFSN at 373 K was suppressed to less than 1/2000 in comparison with counterpart TASN. In addition, DFSN derivatives bearing two initiator moieties for atom transfer radical polymerization (ATRP) was synthesized and applied to ATRP of methyl methacrylate, affording DFSN-containing poly(methyl methacrylate) (PMMA-DFSN-PMMA). PMMA-DFSN-PMMA exhibited a remarkable color change from white to pink upon grinding. EPR measurement supported that this color change is originated from dissociation of a DFSN moiety at the middle of a PMMA chain. It is concluded that DFSN works as a thermally stable mechanochromophore but sufficiently sensitive to mechanical stress.



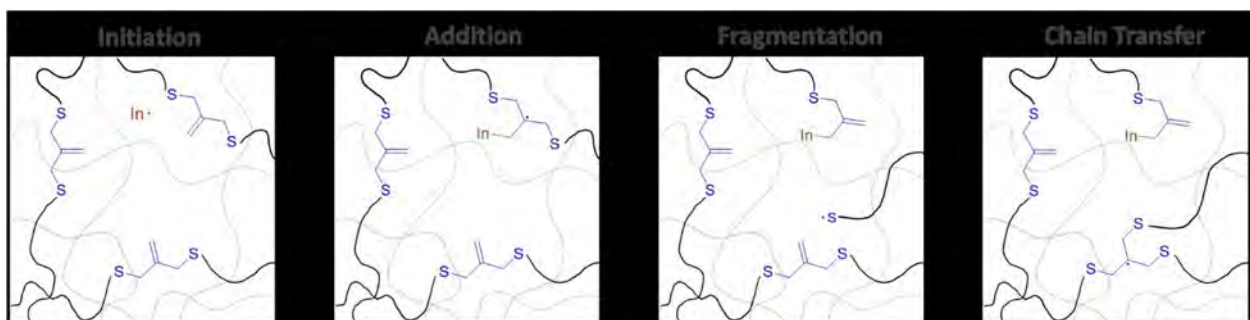
DFSN skelton in a polymer

POLY 418: Reducing volumetric shrinkage stress in composites via addition-fragmentation functionalized microparticles

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Composite materials are an ever-growing area of academic and industrial interest. Rational design of composites results in materials with unique/useful properties derived from the combination of the constituent materials. As just one example, polymeric dental restorative composites are of great interest because millions of these restorations are performed annually, with a complex interplay between the polymer and filler controlling much of the composite behavior. Particularly, effective implementation of and the longevity of these composites is often limited by stresses that build up during polymerization due to volumetric shrinkage, leading to material failure or delamination. Due to modulus and thermal expansion mismatches, polymerization shrinkage and thermal expansion stresses are amplified at the interface between the polymer matrix and the filler particles. There has been significant work to address shrinkage stress in the matrix phase, but little has been done to mitigate the high stress concentration at the interface of the matrix with the filler, that often leads to failure and cracking.

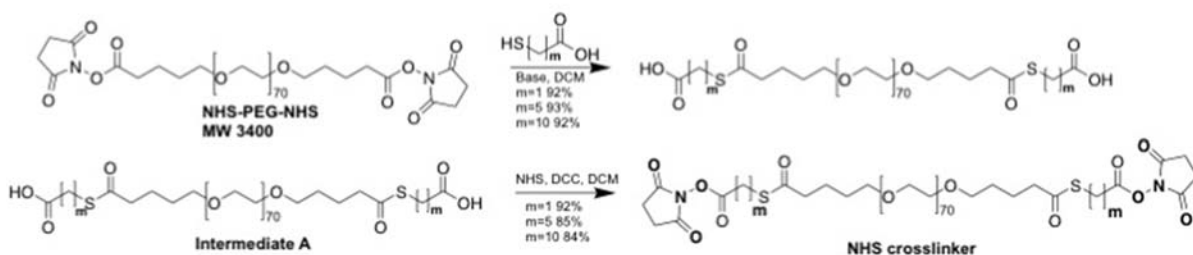
To address this shortcoming, polymeric microspheres were synthesized from monomers that contain moieties capable of radical mediated addition-fragmentation chain transfer (AFT) in their core structure in the form of allyl sulfides. When incorporated into a matrix resin that is polymerized via a radical mediated mechanism, these AFT moieties enable bond exchange both in the particles and between the particles and the matrix as shown. This dynamic bond exchange during polymerization reduces the internal stresses that develop during the polymerization and as a result of thermal expansion differences.



POLY 419: Insertion of methylene groups into PEG crosslinkers allows for control of hydrogel swelling and mechanical properties

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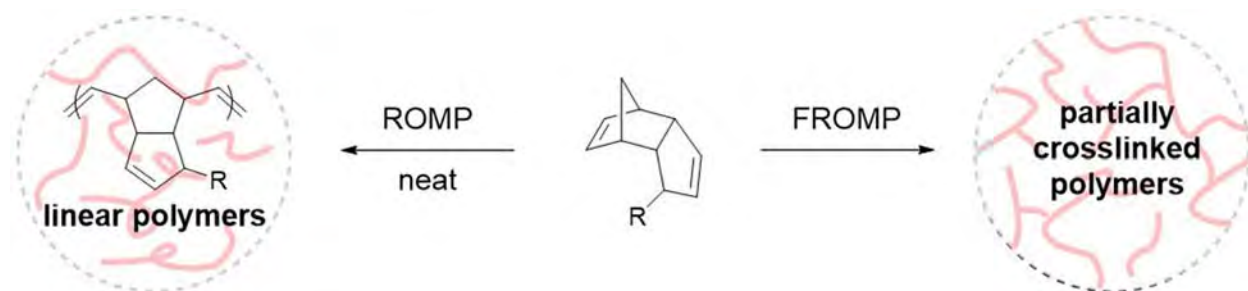
Hydrogels are used in many biomedical applications such as tissue engineering, drug delivery and wound healing. Controlling the mechanical and swelling properties of hydrogels is a critical component to determining appropriate applications for these materials. We hypothesized that introduction of methylene groups within a PEG crosslinker containing terminal NHS active esters will provide additional control of these properties when crosslinked with a multifunctional amine, such as a tri-lysine Dendron. The general synthetic route to the PEG crosslinkers is as follows: NHS-PEG-NHS is reacted with a thiol and base in dry methylene chloride to afford intermediate A. The crosslinker was obtained by reacting intermediate A with N,N'-dicyclohexylcarbodiimide and N-hydroxysuccinimide in dry methylene chloride. Three different PEG crosslinkers were synthesized and characterized by NMR, MALDI, TGA and DSC. The mechanical properties and swelling properties of the resulting hydrogels are dependent on added weight percent and on the number of methylenes present in the crosslinker. In addition, these hydrogels can be controllably dissolved on-demand via a thiol-thioester exchange reaction as an internal thioester is present within the PEG crosslinker. Finally, these hydrogels are non-toxic, biocompatible, and biodegradable.



POLY 420: Investigation of crosslinking mechanism in ring-opening metathesis polymerization of functionalized dicyclopentadienes

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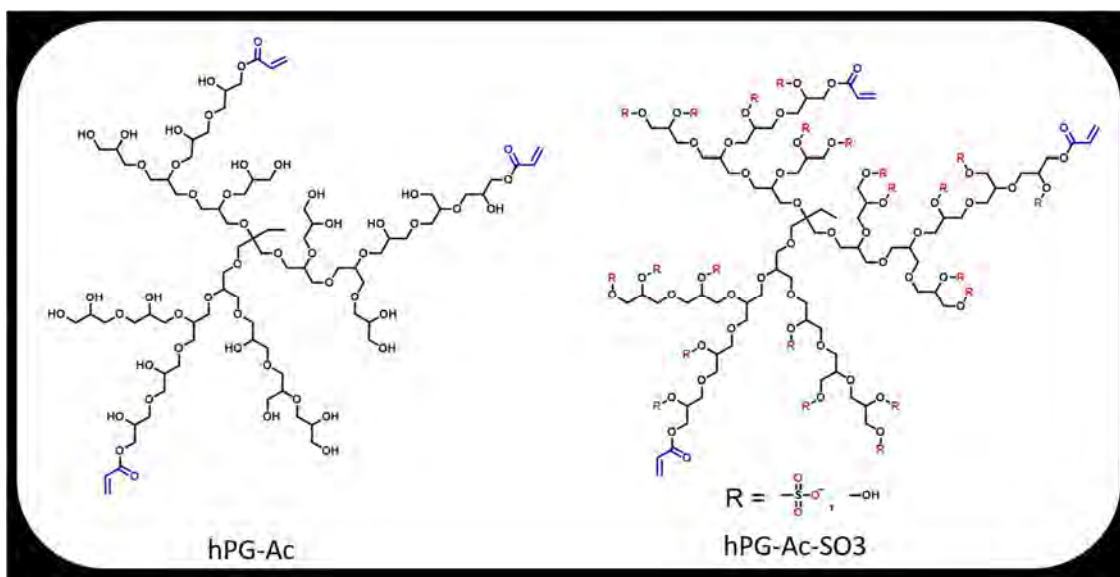
Polydicyclopentadiene (PDCPD) is a thermoset polymer of growing importance in the production of durable parts in the automotive industry due to its low cost, high stiffness and high impact resistance. PDCPD is formed through ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD). The majority of PDCPD materials are densely crosslinked, which leads to enhanced mechanical properties. However, the crosslinking mechanism remains debatable in the literature. Metathesis of both olefins within the DCPD monomer and thermally initiated olefin addition reaction are both proposed as the principle mode of crosslinking. Recently, our group reported synthesis of PDCPD by frontal ring-opening metathesis polymerization (FROMP) that allows rapid materials fabrication with minimal external energy. We observed that FROMP of allylic-substituted DCPD using Grubbs' catalysts afforded both partially crosslinked and linear polymers. However, under ROMP conditions, only linear structures were obtained at various temperatures since ROMP of much less strained cyclopentene ring is not favored. Characterized by DSC, NMR and Raman spectroscopy, we systematically studied a series of DCPD monomers and investigated different mechanisms of crosslinking in ROMP and FROMP. This study not only contributes to mechanistic understanding of PDCPD crosslinking, but also provides insights into rational development of functionalized PDCPD for broader applications.



POLY 421: Multifunctional hyperbranched polyglycerol as building blocks for the synthesis of cell-instructive hydrogels

Eric W. Fowler, *fowlere@udel.edu*, Xinqiao Jia. *Materials Science and Engineering, University of Delaware, Newark, Delaware, United States*

Hyperbranched polyglycerols (hPGs) with abundant terminal hydroxyls (hPG-OH) were synthesized by ring opening multibranching polymerization of glycidol via slow monomer addition using dioxane as an emulsifying agent. Characterizations of the polymerization products by quasi-elastic light scattering and multiangle laser light scattering gel permeation chromatography revealed a hydrodynamic radius > 8 nm and a molecular weight > 500 kDa (with a PDI of 1.10). Acrylated hPGs (hPG-AC) were prepared via the reaction of terminal hydroxyls with acryloyl chloride. Treatment of hPG-AC with DMF-SO₃ produced sulfated hPG (hPG-AC-SO₃). Differential scanning fluorescence confirmed the ability of hPG-AC-SO₃ to bind and stabilize fibroblast growth factor 10 (FGF10). Hydrogels were prepared using hPG-AC, hPG-AC-SO₃, and thiolated hyaluronic acid (HA-SH) via Michael addition. Synthetic peptides derived from proteins found in the basement membrane were covalently incorporated into the hydrogel to promote cell-matrix interactions. Primary salivary human stem/progenitor cells (hS/PCs), isolated from human salivary parotid glands, remained viable following encapsulation in the synthetic matrix and formed multicellular spheroid assemblies reminiscent of the acini found in the native glands by day 7. Hydrogels containing sulfated moieties moderated proliferation and spheroid development over the 14-day culture period to a greater extent than unsulfated formulations. In conclusion, multifunctional hPGs were synthesized for the construction of biomimetic hydrogels with sequestered growth factors to promote the growth and assembly of hS/PCs in vitro. Moving forward, these hydrogel will be utilized to study FGF10 delivery and its impact on branching morphogenesis.

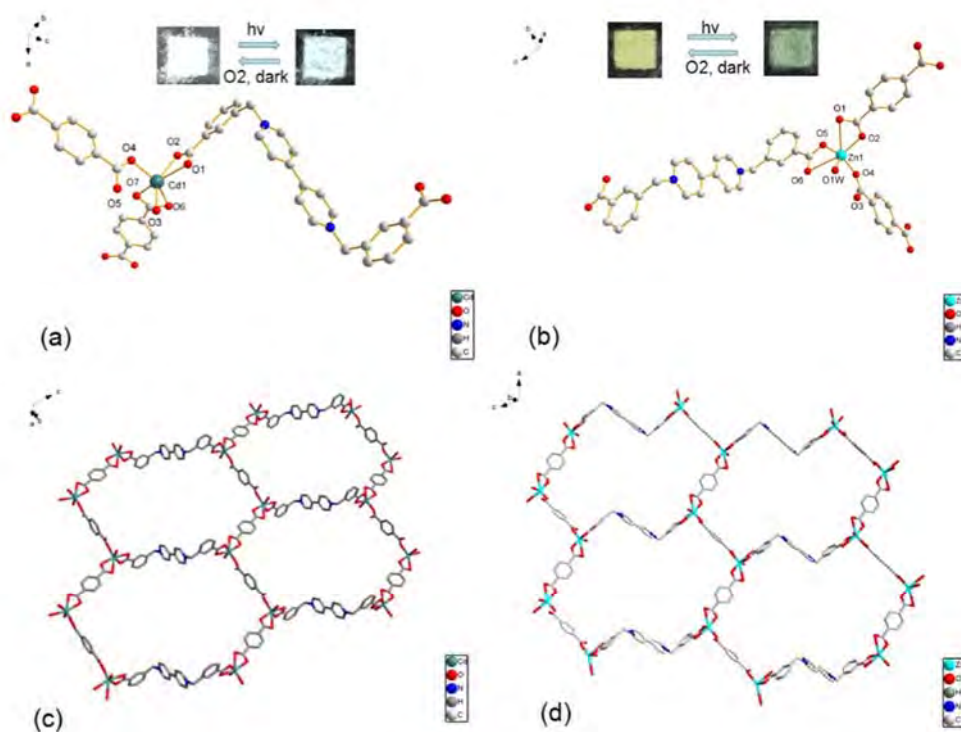


Truncated chemical structures of the hyperbranched polyglycerol derivatives hPG-Ac and hPG-Ac-SO₃.

POLY 422: Flexible viologen- based porous coordination polymers showing fast-responsive photochromism and photomodulated fluorescence properties

Hong Zhang, *zhangh@nenu.edu.cn*. Department of Chemistry, Northeast Normal University, Changchun, Jilin, China

1,4-benzenedicarboxylic acid, $L_2 = 1,1'$ -bis(3-carboxybenzyl)-4,4'-bipyridinium dichloride) based flexible viologen have been synthesized. Single crystal X-Ray diffraction analysis shows that the two compounds have similar two - dimensional coordination chain and central symmetry packing patterns. Compound **1** and **2** show fast- responsive photochromism behavior within one second under Xenon lamp and transformations from yellow to blue due to the same viologen units and carboxylate ligand. The discolourization time both **1** and **2** is more than three months due to the stability of the viologen radicals but can be discoloured by heat. Therefore, compound **1** and **2** can be applied in electrochemistry. The fluorescent properties of the two complexes have been studied with 365nm wavelength emission and show well photomodulated fluorescent properties.



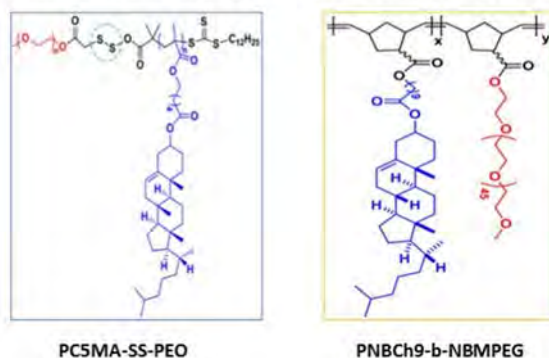
(a) the coordination environment of Cd(II) in compound **1**. (b) the two - dimensional layer in compound **1**.
(c) the coordination environment of Zn(II) in compound **2**. (d) the two - dimensional layer in compound **2**.

POLY 423: Biodegradable liquid crystalline polymeric nanoparticles for drug delivery

Dennis Ndaya¹, dennis.ndaya@uconn.edu, **Reuben Bosire**², **Laura Gonzalez_fajardo**³, **Andre Beringsh**⁴, **Xiuling Lu**⁵, **Rajeswari Kasir**⁶. (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (3) Pharmaceutical Sciences, University of Connecticut, Storrs, Connecticut, United States (6) Chemistry and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States

Amphiphilic liquid crystalline brush-like copolymers designed from biologically compatible cholesterol and methoxy polyethylene oxide components achieve optimized polymeric micellar delivery system for the solubilization and controlled delivery of cancer drugs. In this study, we synthesized stimuli responsive and well-defined core-structure block copolymers, Polynorbonene-cholesterol/ methoxy Polyethylene oxide (PNBCh9-b-NBMPEG) and Polymethacrylate-cholesterol-SS-Polyethylene oxide (PC5MA-SS-PEO). The disulfide bond in PC5MA-SS-PEO are easily reduced by the high glutathione concentration in cancer cells achieving high drug delivery efficiency while the stable and compact core-hydrophilic shell in PNBCh9-b-NBMPEG copolymer leads to a high encapsulation efficiency and drug loading capacity. The copolymers are uniquely designed to increase the degree of chemical compatibility between drugs and their core structure for lower rate of drug release from polymeric micelles. In water all these copolymers self-assemble into particles incorporating drugs hence achieving key characteristics of the carrier-like particle size and drug loading for nanoparticles (NPs) mediated drug delivery systems for cancer. The Doxorubicin (Dox) encapsulated NPs were characterized for their size, morphology and critical micellar concentration, in which they displayed spherical shapes, optimal sizes and surface charges suitable for tumor tissues targeting. For instance, biodistribution studies in tumor-bearing severe combined immunodeficiency (SCID) mice showed that the polymer (PNBCh9-b-NBMPEG)-drug nanoparticles preferentially accumulated in tumor tissues with markedly reduced accumulation in non-target healthy organs like the heart, kidneys and liver. The interesting results shows the potential all these copolymers have for the solubilization, nanocarriers and delivery of polyethylene oxide-cholesterol compatible drugs.

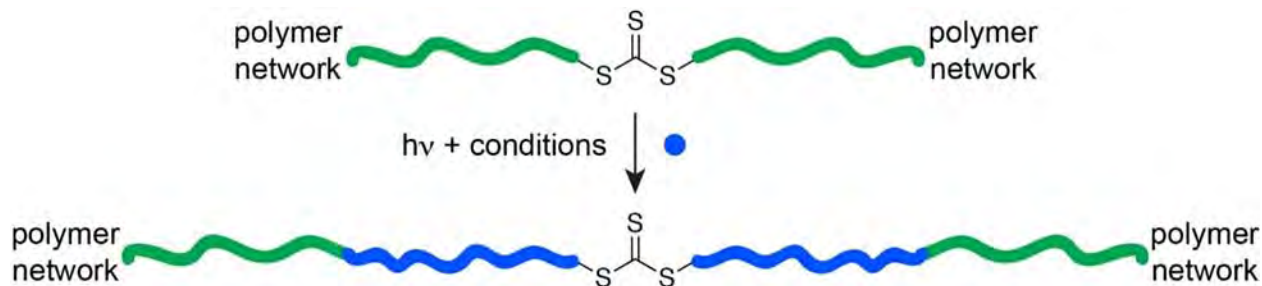
The chemical structures of the Liquid Crystalline Brush-like Copolymers



POLY 424: Living additive manufacturing for complex gel formation via photo-controlled radical polymerization under ambient conditions

Jessica R. Lamb, *jrlamb@mit.edu*, Jeremiah A. Johnson. Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

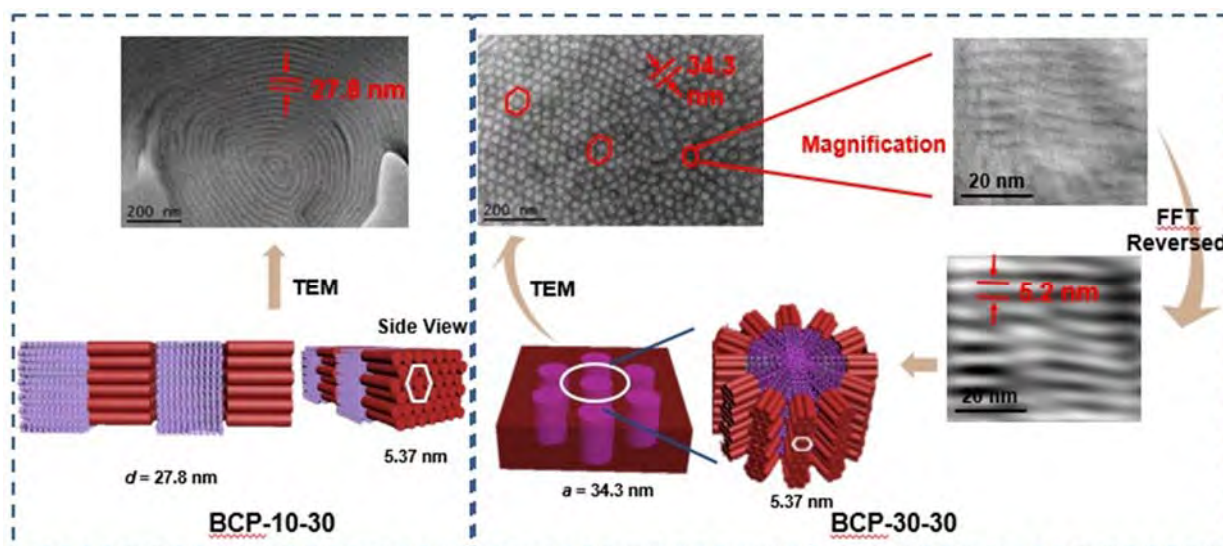
Photo-initiated additive manufacturing is a robust material-fabrication technique with numerous applications in coatings, adhesives, microelectronics, and biomaterials. Classical methods rely on irreversibly-initiated free radical polymerizations which create materials with “dead” chain ends. Such processes eliminate the possibility for chain extension that could introduce new monomers and functionality into the material in a living fashion. Recent work from our group demonstrated the first “living” additive manufacturing to transform parent gels into complex daughter gels with spatiotemporal control. While a significant advance, the air-free conditions and synthetically challenging end-linked gels used in the previous study make this method impractical in an industrial setting. In this work, recent results toward living additive manufacturing of randomly crosslinked gels under ambient conditions are presented, and the implications on future directions are discussed.



POLY 425: Synthesis and sub-10 nm supramolecular self-assembly of MJLCPs containing three-dimensional nanobuilding blocks

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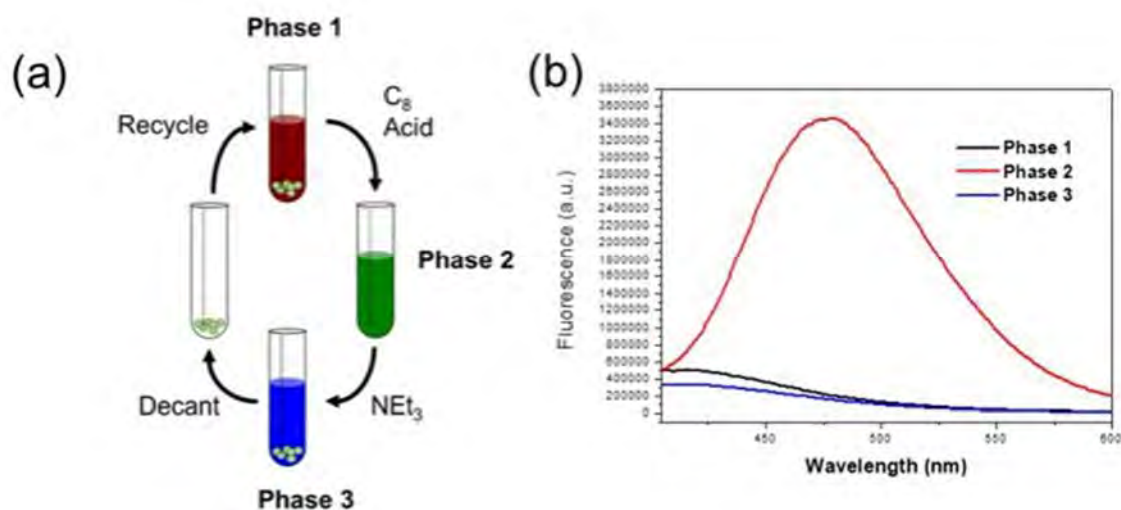
The work is focused on synthesis and self-assembly of rod-rod block copolymers (BCPs) **PNb12POSS-*b*-PNb10PP**. The BCPs were obtained through ROMP with the third-generation Grubbs' catalyst. The BCPs are denoted as **S_mP_n**, in which S and P refer to the **PNb12POSS** and **PNb10PP** segments, while *m* and *n* refer to the degrees of polymerization of **PNb12POSS** and **PNb10PP**, respectively. Molecular characterizations and thermal properties of the BCPs were performed with ¹H/¹³C NMR, GPC, TGA, and DSC. With a combination of DSC, PLM, WAXS, SAXS, and TEM, the phase structures and behaviors of **S_mP_n** were investigated. Results reveal that **S₂₀P₃₀** and **S₃₀P₃₀**, of which the volume fractions of **PNb12POSS** (*f*_{PNb12POSS}) are 62% and 54%, respectively, form hierarchically ordered structures as follows: hexagonal columnar (HEX) phase owing to BCPs microphase separation with lattice parameters *a* ~ 30 nm; Col_h and SmA phases of the MJLCPs with a *d*-spacing value of ~ 5 nm; Cr of POSS units and the π-π stacking of the 1D rod-like mesogens on angstrom scale. Similarly, in the BCP sample **S₁₀P₃₀** (*f*_{PNb12POSS} = 40%), the **PNb10PP** segment forms hierarchically ordered structures of SmA phase of the segment as a whole on the sub-10 nm length scale and the ordered packing of the 1D rod-like mesogen in the side chains on the angstrom length scale. However, the **PNb12POSS** segment and the POSS units in **S₁₀P₃₀** are both amorphous due to low degree of polymerization and content of POSS units. On the other hand, **S₁₀P₃₀** forms a lamellar (LAM) structure, rather than the HEX structure, through BCP microphase separation with a *d*-spacing value of ~ 30 nm. BCP sample **S₃₀P₁₂₀** and **S₈₀P₁₂₀** with high molecular weights (MWs) form similar hierarchically ordered structures on the sub-10 nm and angstrom length scales, to those of low MW BCPs, such as **S₃₀P₃₀**. However, the difference is that no ordered microphase-separated structures are formed by **S₃₀P₁₂₀**, while **S₈₀P₁₂₀** forms a spherical phase with a size of 100 – 200 nm.



POLY 426: Stimuli-responsive solubility of poly(*N*-isopropylacrylamide) in nonpolar solvents

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Polymers exhibit stimuli responsive solubility that depends on the polymer microstructure, the solvent, and a chemical or physical stimulus. For example, poly(*N*-isopropylacrylamide) (PNIPAM) is a common thermoresponsive polymers whose lower critical solution temperature derives from a favorable DH due to hydrogen bonding with water and an unfavorable DS due to the organization of solvents on the polymer. This work describes how H-bond solubilization can be used to generate chemically-reversible responsive solubility of a polar polymer like PNIPAM in nonpolar alkane solvents. The acid-assisted solubilization of PNIPAM was explored using carboxylic acids like acetic, valeric, octanoic and oleic acids. The results showed that the longer aliphatic acids are more effective on a mole:mole bases at effecting PNIPAM solubilization in hexane. Similar trend are seen for solubilization of PNIPAM in hydrocarbon oligomer solvents like poly(α -olefin)s (PAOs). In both cases, the PNIPAM that dissolves in the alkane solvents can be recovered by addition of base. Using dansyl-labelled PNIPAM with octanoic acid as a solubilization agent with NEt_3 as the chemical agent for PNIPAM precipitation, we have shown that the process of solubilization/precipitation can be repeated through at least three cycles (Figure 1a). Ongoing studies are exploring this molecular recognition based solubilization with other solubilizing agents, other precipitation agents and exploring the use of this chemically responsive solubility both as a tool to prepare new solvent systems and new sorts of recyclable catalysts.



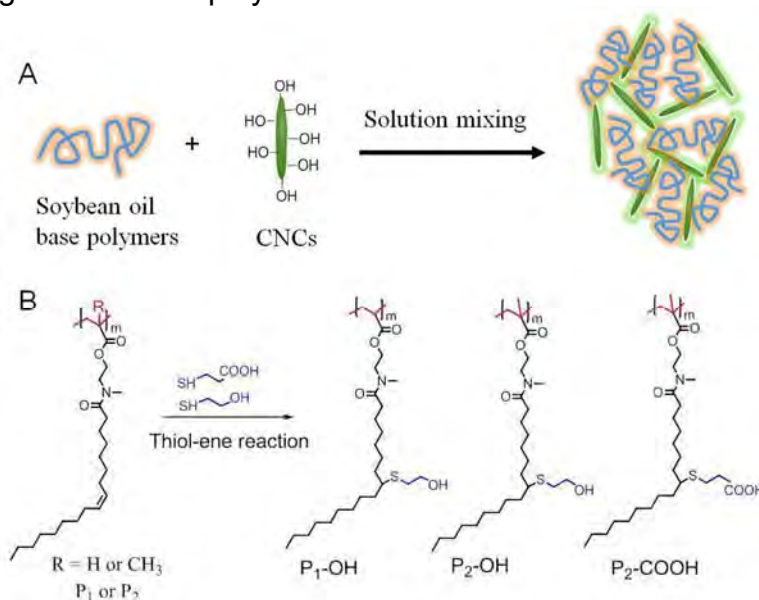
(a) The process of solubilization/precipitation of PNIPAM in hexane or alkane solvents (b) The fluorescence spectrum of phase 1, 2 and 3.

POLY 427: High-strength, stimuli-responsive polymer nanocomposites derived from soybean oil and cellulose nanocrystals

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Abstract

Polymer nanocomposites incorporate various fillers such as silica nanoparticles, nanoclay, carbon nanotubes, and many other stiff nanomaterials for property enhancement of polymer matrix. A burgeoning research direction is on the use of biomass derived cellulose nanocrystals (CNCs or nanowiskers), which have ultrahigh tensile stiffness (up to 150 GPa), for making mechanically reinforced polymer nanocomposites. We hypothesized that biomass-derived CNCs could improve the mechanical properties of soybean oil based (meth)acrylate polymers, given that good compatibility is achieved between the matrix and nanofillers. Herein we report the preparation of high mechanical strength polymer nanocomposites using soybean oil and CNCs as renewable biomass materials. As the surfaces of CNCs are covered with hydroxyl groups, polymers that can facilitate the formation of hydrogen bonding with CNCs would be good candidates for enhancing compatibility between fillers and matrix. As shown in **Scheme 1B**, two polymers (P1-OH and P2-OH) with hydroxyl groups and one polymer with carboxyl groups (P2-COOH) were prepared by thiol-ene chemistry with poly(soybean acrylate) (P1) and poly(soybean methacrylate) (P2). A homogeneous dispersion of CNCs in the modified polymers was observed by SEM. We also studied the effects of the polymer structure and the content of CNCs on the mechanical properties of polymer nanocomposites. Nanocomposite materials with tensile strength up to 23 MPa were obtained. The nanocomposites exhibited a fast switch on modulus with the presence and absence of water, since the enhancing mechanism is based on hydrogen bonding between the polymer and CNCs.

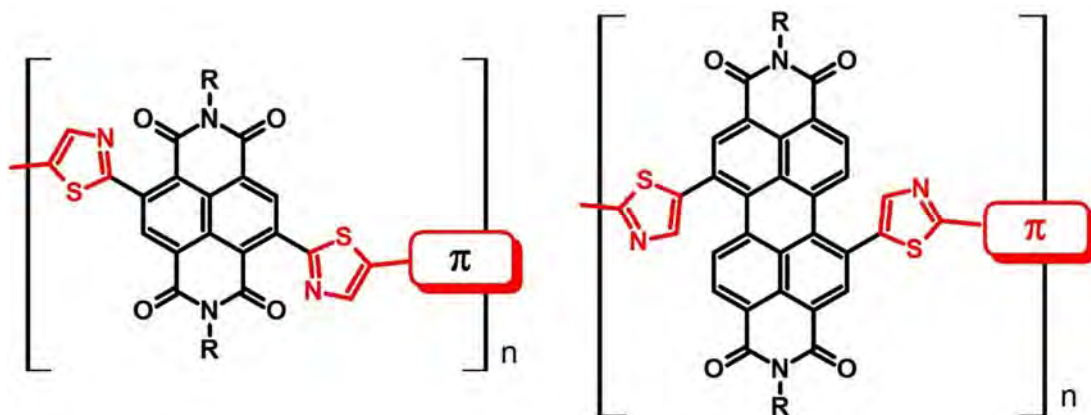


Scheme 1. (A) Preparation of nanocomposites from soy-derived polymers and CNCs; (B) chemical modification of soy polymers with -OH or -COOH groups via thiol-ene click chemistry.

POLY 428: Thiazole coupled NDI-PDI based polymers as n-type semiconductors

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Conjugated polymers displaying broad absorption in visible region, tunable electron energy levels, process able in form of thin flexible films are ideally required for applications in organic electronics. In recent years, mostly p-type materials have been widely developed globally therefore, n-type conjugated electron deficient semiconducting polymeric materials are in high demand for advancement in the field of organic electronics. Rylene dyes of Naphthalene diimides (NDI) and Perylene diimides (PDI) diimides are among the most promising n-type organic semiconductors because they exhibit high electron affinity, high electron mobilities, and ambient stability. In order to increase the n-type character in monomers the dibromo substituted NDI and PDI were coupled with electron withdrawing thiazole ring via Stille coupling reaction. Innovative n-type polymers of potentially tuneable optical and electronic properties comprising of individual donor-acceptor units are under progress by polymerization reaction of the thiazole flanked NDI-PDI monomers with different π -donors bridges.

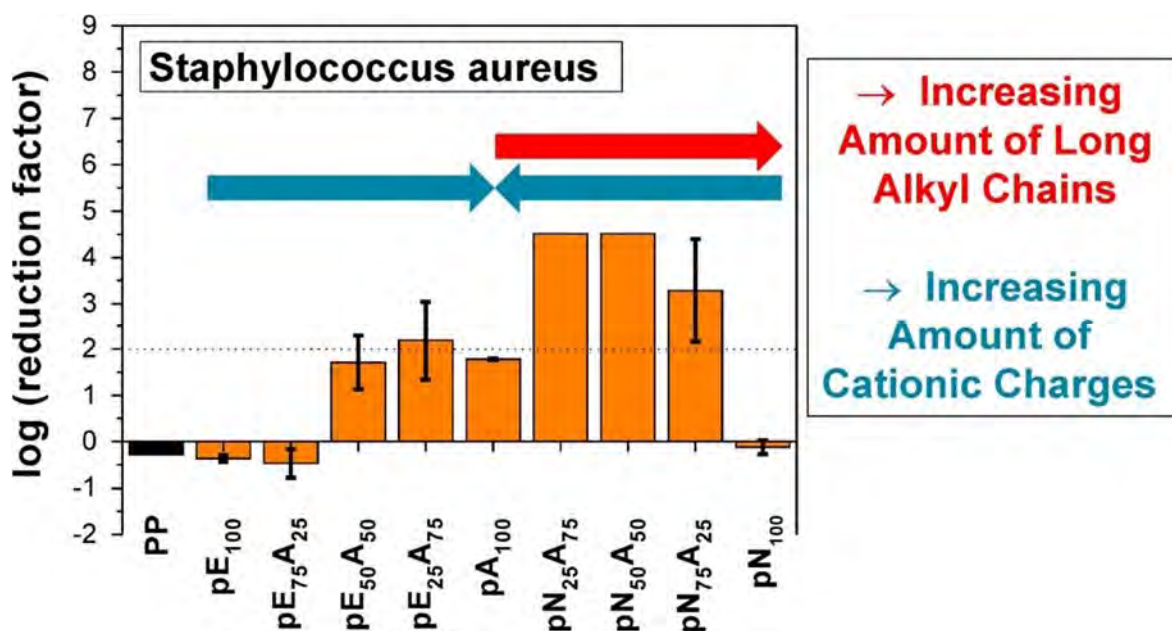


Thiazole coupled conjugated D-A polymers

POLY 429: Maintenance-free polymer-based contact poly(2-oxazoline)-based biocides in polyolefin blends

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Antimicrobial activity has its prominent role model in nature: Peptides with a high amount of cationic amino acids provide antimicrobial activity against bacteria and fungi. The cationic charge of the peptide provides competition interaction with the microbes' membranes while hydrophobic side-chains synergistically enhance this effect. Contact biocides are cationic polymers that kill microbial organisms by mere contact. In contrast to disinfectants with comparably high vapor pressure at room temperature, which have to be refilled or reapplied on a regular basis, contact biocides need little to no (regular) maintenance. In this study, the use of partially hydrolyzed poly(2-oxazoline)s as antimicrobial contact biocides was investigated, and the next generation of contact biocides in the form of partially hydrolyzed poly(2-oxazoline)s and poly(2-oxazine)s have been developed via synthesis and acid-mediated partial hydrolysis of the polymers. An important aspect was the reduction of the water solubility of those compounds as well as the amount needed to prepare polyolefin composites with surficial antimicrobial activity. Two approaches were followed, namely (i) the crosslinking of copoly(2-oxazoline)s by means of the UV-induced thiol-ene reactions, and (ii) the synthesis and partial hydrolysis of higher homologues of poly(2-oxazoline)s, namely the poly(2-oxazine)s. The antimicrobial activity was tested against *E. coli*, *P. aeruginosa*, *S. aureus*, and *C. albicans*. In addition, the correlation of the structures and the water solubility of the copolymers were investigated due to potential negative impact on the longevity of the antimicrobial properties.

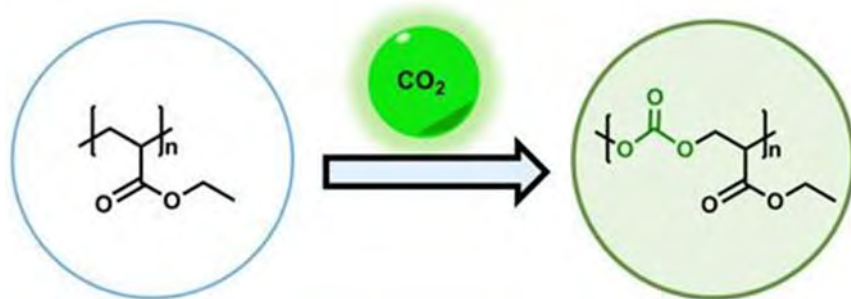


Correlation of the amount of cationic charges and/or hydrophobic alkyl chains (present in the polymeric contact biocides) on the antimicrobial activity.

POLY 430: Poly(alkyl glycidate carbonate)s as degradable poly(alkyl acrylates) analogues

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Polyacrylates are widely used polymers in industry, however their all aliphatic backbone leads to minimal degradability with challenges in recovery and recyclability. Insertion of a CO₂ into the backbone, forming polycarbonate analogues of polyacrylates provides for an environmentally friendly alternative polymer. The synthesis of five polycarbonate analogues of poly(methyl acrylate), poly(ethyl acrylate), and poly(butyl acrylate) is described. The polymers are synthesized via the copolymerization of CO₂ and an oxirane catalyzed by a salen cobalt complex. All of the carbonate acrylate analogues possess higher glass transition temperatures (T_g = 32 to -4.7 °C) than alkyl acrylates (T_g = 10 to -55 °C), however, the carbonate analogues undergo thermal decomposition at lower temperatures (>100 °C difference). Additionally, we synthesized constitutionally isomeric polycarbonates where the pendant ester group is in the reverse orientation to the backbone to investigate how this electronic and steric change affects the bulk properties. Compared to the acrylate derivative, the reverse analogues possess lower thermal properties (T_g = 24 to 0 °C). However, the polymerization reactions are 10X more efficient and with more polymer product produced than the cyclic carbonate byproduct. Finally, the polycarbonate analogues degrade into glycerol, alcohol, and CO₂ in a time and pH dependent manner with the rate of degradation accelerated at higher pH conditions. Both polycarbonate analogues degrade within an appreciable time span (3 to >30 days) while the polyacrylate shows no degradation. Cytotoxicity studies indicate that all of the carbonate and acrylate polymers are non-toxic to NIH 3T3 fibroblast cells at 2.5 mg/mL concentration for 24 hours (ANOVA, p >0.05).



POLY 431: Enhancing mechanical and thermal properties of 3D printed PLA by graphene reinforcement

Sahar Rostom², *srostom@vols.utk.edu*, **Brian Edwards**¹, **Mark D. Dadmun**². (1) *Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, United States* (2) *Chemistry, Univ of Tennessee, Knoxville, Tennessee, United States*

Fused Deposition Modeling (FDM) is a fast-growing 3D printing technology that may revolutionize manufacturing; however, the spread of the technology is limited by the lack of new specific functional materials and poor mechanical properties of the printed parts. During deposition, a thermoplastic filament is heated above its glass transition temperature inside a hot end and deposited onto a heated bed, where it cools and solidifies. These results in rapid heating and cooling cycles that produce a thermal gradient within the sample, creating residual stresses inside the printed object. A more complete understanding of the role of the thermal properties of the deposited material and thermal evolution during the printing process on the evolution of residual stresses and the mechanical properties of the part is needed to optimize the process. In the present work, we investigate the impact of adding graphene to polylactic acid (PLA) on the thermal conductivity of the material and its bearing on the mechanical properties of the printed part. Infrared (IR) Imaging is used to monitor in real time the thermal evolution in the printed PLA and graphene composites. All printed specimens are mechanically tested and scanning electron microscopy (SEM) is used to examine fracture surfaces. Our results show that the addition of graphene leads to enhancement in the thermal diffusivity. The graphene composites show significant improvement in ultimate strength and smaller voids between filaments and enhancement in inter-filament bonding. The effect of bed temperature on mechanical properties has also been investigated where an increase in bed temperature leads to a dramatic improvement in z direction strength and more isotropic samples.

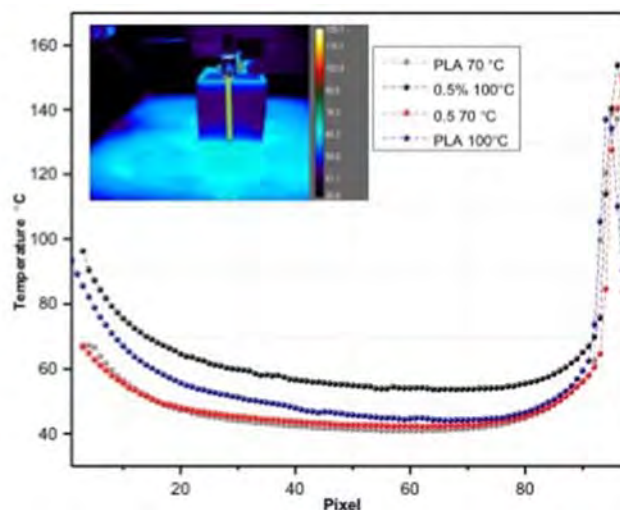


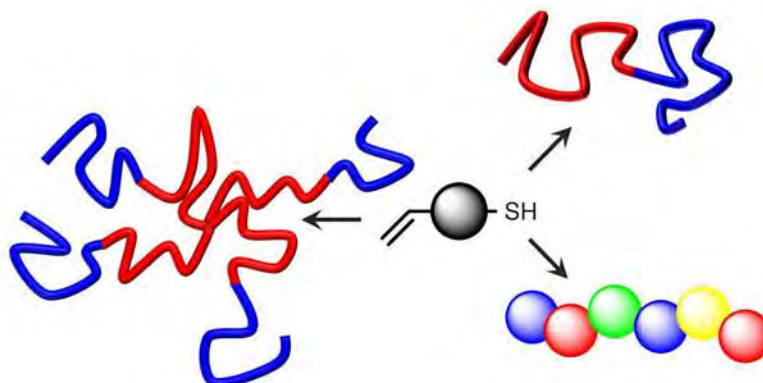
Figure1: Thermal profiles of PLA and 0.5% graphene composite at 70 and 100 °C bed temperature

POLY 432: Strategies for the assembly of sequence controlled polymers via thiol-click reactions

Benjamin Fairbanks¹, fairbanb@colorado.edu, Xun Han³, Heidi Culver⁴, Sudheendran Mavila², Christopher Bowman⁵. (1) University of Colorado, Boulder, Colorado, United States (2) Department of Chemical and Biological Engineering, University of Colorado-Boulder, Boulder, Colorado, United States (3) University of Colorado Boulder, Boulder, Colorado, United States (4) Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States (5) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

The varied functions of biopolymers, such as proteins and nucleic acids, are derived from the specific sequences of monomeric residues, which determine the adopted shapes of those polymers and their interactions with their environment. In order to approach the versatility and variety of the biomacromolecular library, polymer scientists require a synthetic toolbox that will allow for the precise control of not only polymer length, but monomer sequence as well. While advances have been made in recent years, the capability to perform such polymerizations in a scalable manner has remained elusive. The consecutive addition of single residues via sequential deprotection and addition reactions to a growing polymer on solid supports has, so far, proven the most effective strategy. This method, however, is constrained by the inefficiencies of the coupling and deprotection reactions as well as by the limited surface area of the solid support.

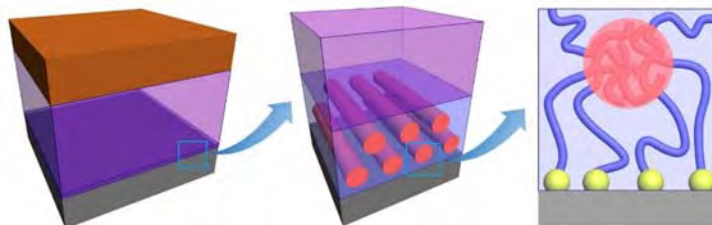
Because of their atom economy, high efficiency, orthogonality and mild reactions conditions, thiol-click chemistries are proving a useful tool in furthering the goal of polymer sequence control. Here, radical thiol-ene reactions were used to generate oligomers of thiol-ene monomers including those bearing pendant nucleobases. The versatility of the heterobifunctional compounds, containing both a thiol and an alkene moiety, permit a variety of polymerization and copolymerization strategies to manipulate the resulting sequence and structure of the polymeric product. The rapid click reaction was triggered via radical photoinitiation and reached high conversion in a matter of seconds making this strategy amenable to automation and the production of significant quantities of oligomer in a relatively short period of time. These approaches represent progress toward the goal of a scalable, solution phase, sequence controlled polymerization.



POLY 433: Dendrite-free lithium metal batteries based on single-ion polymers

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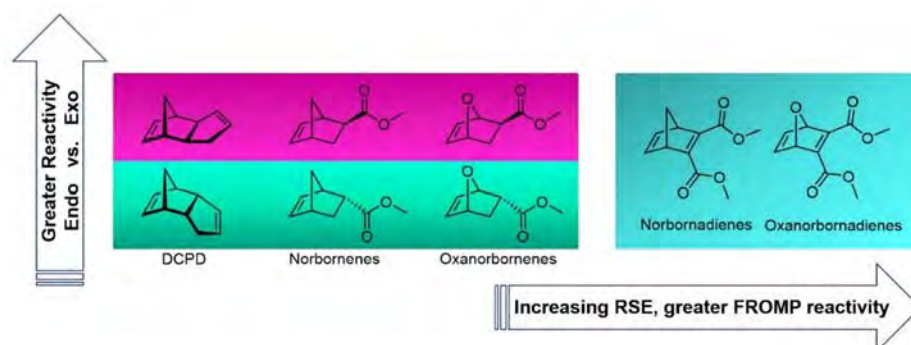
As the demand for energy storage devices with high energy densities increases, lithium metal batteries have emerged as the most promising candidates owing to their high theoretical capacity (3,860 mAh/g) and the lowest redox potential (-3.04 V vs. SHE). However, the safety issue of lithium metal batteries remain a major challenge, caused by short-circuit of the cells with lithium dendrite formation. Given that lithium dendrite is formed at the interfaces between lithium metal and electrolyte and makes a growth across polymeric separator, coating of lithium metal surfaces has been considered to be an effective means of preventing and/or retarding the lithium dendrite growth. Here, we investigate single-ion conducting polymers as a new coating material of lithium metal batteries by taking advantages of high mechanical stability and high lithium transference number of single-ion polymers. With the variation of morphology of the surface coating layers, interfacial resistance of the cells and the diffusivity of lithium ion were controlled. This enabled the improvement of discharge capacity and rate capability of the resultant lithium metal batteries.



POLY 434: Hotter monomers with better adhesion: 7-Oxanorbornene and 7-oxanorbornadiene derivatives for improved frontal ring-opening metathesis polymerization

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Frontal ring-opening metathesis polymerization (FROMP) is a promising system for rapidly cured cross-linked polymer composites. The current FROMP formulation utilizes endo-dicyclopentadiene (DCPD) with 5 wt% added ethylidene norbornene, giving a liquid monomer “pot” at room temperature. However, this system is not perfect as frontal velocities are slower than ideal and the poly(DCPD) chemical structure has inferior adhesion in carbon fiber composites compared with standard epoxy systems. Thus, new chemistry is needed to extend FROMP viability. We propose 7-oxanorbornene and 7-oxanorbornadiene monomers to allow us to correlate increasing ring strain energy (RSE) with “hotter” more reactive FROMP monomers. Calculated RSE is higher for oxanorbornene relative to norbornene and for oxanorbornadiene relative to oxanorbornene. These monomers, when mixed as additives with DCPD, should have improved curing *and* better adhesion due to the oxygen heteroatom. Incorporated ester groups in the monomers will raise the monomer boiling point (unmodified norbornene and norbornadiene boil at the front temperature ca. 150 °C) and provide another handle on reactivity via comparison of exo and endo derivatives as exo-DCPD is known to react much faster and with lower catalyst loadings than endo-DCPD. This study will be driven by synthetic chemistry in tandem with computational modeling of the new FROMP monomers. A continuum-level multi-physics model will be used to investigate the applications of frontal polymerization in the improved chemistry by solving coupled nonlinear reaction-diffusion equations. This numerical study will shed light on the underlying physics of the polymerization process including speed, maximum temperature, and characteristic length scales of the front. It will provide suggestions to make the chemistry of interest more efficient and allow us to determine the best candidates for the development of FROMP chemistry and engineering.



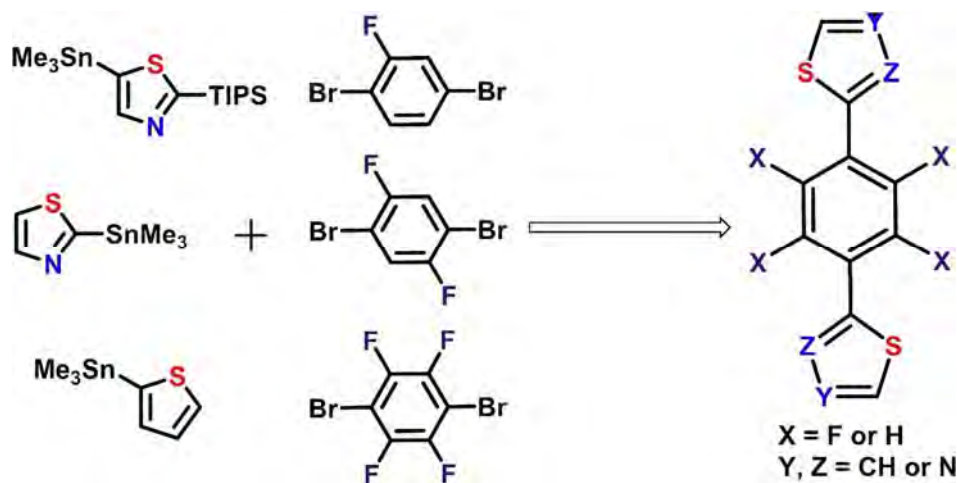
POLY 435: Design and structural study of fluorinated 1,4-di(thiazolyl)benzenes as monomers for π -conjugated polymers with enhanced coplanarity

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Polymer structures are defined by three basic characteristics: constitution, configuration and conformation. Whereas first two of them apply mostly to monomer units, the molecular conformation defines the ability of the macromolecules to form superstructures with unique physical and chemical properties. In particular, coplanar conformation of the backbone of conjugated polymers facilitates their π -stacking with formation of ordered packing in the solid state. These structures are extensively used in “plastic electronics” such as thin-film transistors (TFTs), organic light-emitting diodes (OLEDs), and photovoltaics.

Most of the known π -conjugated oligomers and polymers are composed of multiple aromatic rings connected by one single bond each with other. Steric repulsion and thermodynamic fluctuations prevent formation of coplanar structures due to low activation energy for dynamic torsional motion of a single bond. Some recent papers report applications of dynamic bridging intramolecular interactions for conformational control of the conjugated molecules. These interactions include hydrogen bonds, acid-base and metal coordination and heteroatom non-covalent interactions.

Here we report the design and crystallographical characterization of series of twelve novel three ring fluorinated compounds with S-F and N-F non-bonding intramolecular interactions. In addition to previously described bis-thiophene-phenylene system, a library of its thiazole analogues with different degree of fluorination of the central phenylene ring were prepared. Their solid state structures were studied with X-ray crystallography and compared with reported analogues. Introduction of electron poor thiazole (in contrast with electron rich thiophene) allows to enhance π - π stacking in solid state with significantly shorter interplanar distances.

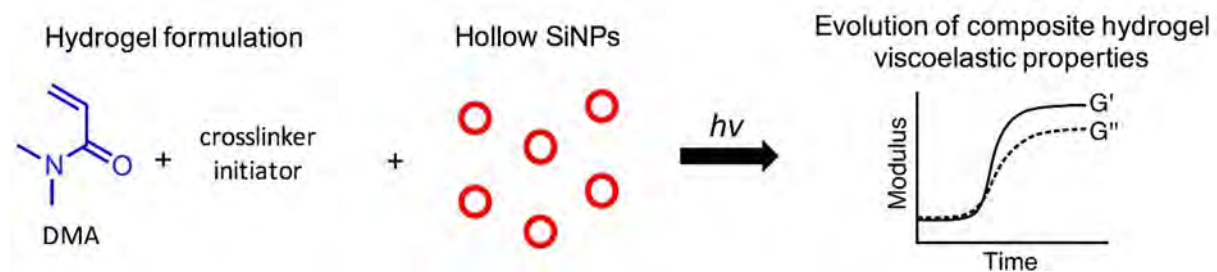


Scheme 1. Preparation of the title compounds.

POLY 436: Rheological and diffusional characteristics of dimethylacrylamide-based hydrogel networks containing hollow silicone nanoparticles

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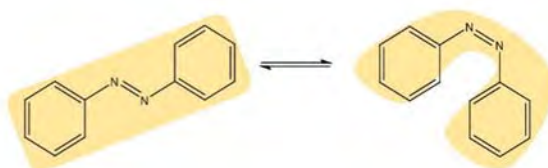
Composite hydrogels containing hollow nanoparticles are of special interest due to the encapsulation potential for drug delivery and contact lens applications. Previous work established the effect of synthetic parameters on surface-modified hollow silicone nanoparticle (SiNPs) dimensions, specifically particle diameter distribution, prepared using micro-emulsion polymerization. Hollow SiNPs were characterized by atomic force microscopy, scanning electron microscopy, and dynamic light scattering to clarify the reaction conditions needed to synthesize particles with 100-200nm diameter. In this work, SiNPs were dispersed into dimethylacrylamide-based hydrogel formulations to elucidate how hydrophobic particles containing specific functionality affects the evolution of viscoelastic properties within the composite networks. Diffusional experiments were performed to determine the effect of hydrophobic nanoparticle loading on water diffusivity through the composite hydrogel networks.



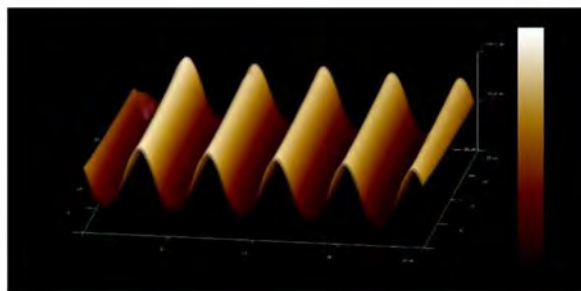
POLY 437: Probing the hydrogen bond in photoresponsive supramolecular azobenzene-polymer films

Kyra Herman¹, hermank3@tcnj.edu, **Celine Mileham**¹, milehac2@tcnj.edu, Jan Krüger², Nicolas Bolle², David McGee², Heba Abourahma¹. (1) Department of Chemistry, The College of New Jersey, Ewing, New Jersey, United States (2) Department of Physics, The College of New Jersey, Ewing, New Jersey, United States

Azobenzene-polymer films are a class of photoresponsive polymers that can undergo mass transport when irradiated with a laser interference pattern. Azobenzene molecules are known to undergo photoinduced *trans-cis* isomerization which changes their geometry from linear to bent, respectively. When coupled to a polymer, this molecular motion leads to mass redistribution of the film over macroscopic distances, typically resulting in the formation of topographical surface relief gratings (SRG). Such a phenomenon is of great interest because of its application in diffractive optics, optical nanomanipulation, and photonic signal processing. Research suggests that the azobenzene-polymer coupling interaction is a major influence in this phenomenon and therefore a better understanding of the relationship between the strength of the interaction and the magnitude of the observed mass transport is important. In our contribution to this area, we exploited the hydrogen bond to modulate the strength of the interaction and examine its effect on the observed mass transport. A series of three related thin films based on poly(4-vinylpyridine), P4VP, and hydroxyazobenzene derivatives with electron donating and withdrawing groups to modulate the strength of the hydrogen bond were synthesized. The light-induced mass transport of these films was determined by irradiating the films with a laser interference pattern and measuring the resulting SRG amplitude via atomic force microscopy. The films were also characterized by IR, UV-vis, DSC and TGA.



trans-cis isomerization of azobenzene changes its change from linear to bent



Atomic Force Microscope (AFM) image of supramolecular P4VP-azobenzene film showing surface modulation

POLY 438: Synthesis, photophysics and fluorescence phosphate sensing by a poly(phenylene ethynylene)-type cationic conjugated polyelectrolyte

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Conjugated polyelectrolytes (CPEs) are an important class of materials that have been developed for a variety of applications including chemical/bio-sensing. A poly(phenylene ethynylene) (PPE) type cationic water soluble CPE was synthesized and its biological important phosphate sensing properties were investigated. The organic soluble precursor of the CPE was synthesized via AABB-type step growth polymerization. This CPE is substituted with cationic groups consisting of polyammonium units in a linear chain. This CPE displays photophysical properties similar to the previously reported PPE type CPEs and exhibit amplified fluorescence quenching property in the presence of various diphosphates. The amplified fluorescence quenching of CPE observed in the presence of diphosphates is due to the aggregate of the polymers as a result of electrostatic interactions between dianions and the cationic CPEs. Addition of monophosphates did not quench the CPE fluorescence.

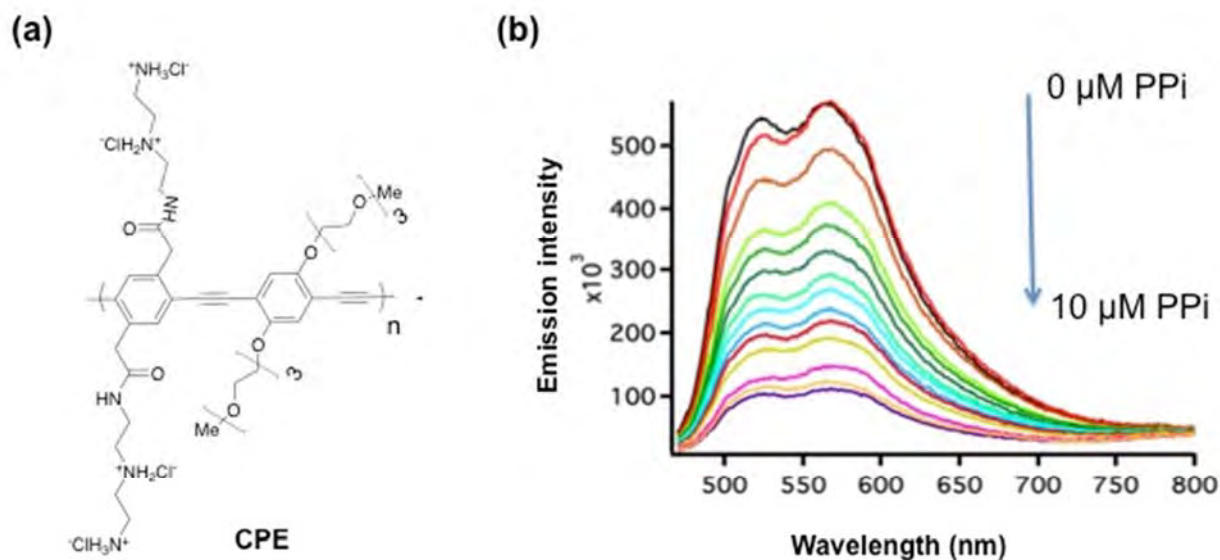
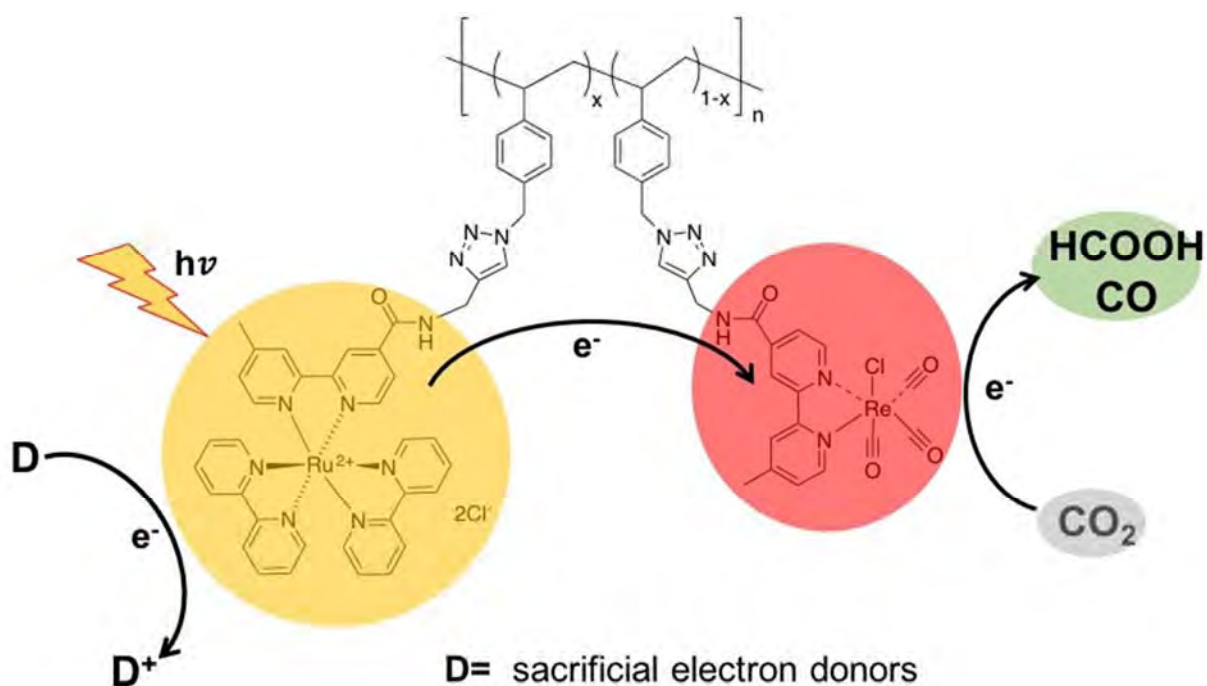


Figure 1. (a) Structure of water soluble CPE and (b) Fluorescence spectra of CPE in water with increasing pyrophosphate PPi concentration.

POLY 439: Polymeric chromophore-catalyst assembly for the photocatalytic CO₂ reduction

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The conversion of solar energy to the chemical energy by using the CO₂ reduction catalysts has been of great interest in solving global warming and shortage of energy. A polystyrene-based chromophore-catalyst assembly, used for photocatalytic CO₂ reduction, has been synthesized and characterized. The polystyrene backbone, synthesized by nitroxide mediated radical polymerization, was used as the scaffold to construct the chromophore-catalyst assembly. The CO₂ reduction catalyst centers based on Re(bpy)(CO)₃Cl and [Ru(bpy)₃]²⁺ derivatives as the chromophores were connected to the polystyrene backbone by the click reaction (bpy = 2,2'-bipyridine). The resulting polystyrene-based assembly was characterized by NMR, IR and XPS spectroscopy, confirming the high efficiency of the click grafting. The photophysical and electrochemical properties of the polychromophore-CO₂ reduction catalyst assembly were investigated in both aqueous solution and DMF/TEOA mixed solution. Further photocatalytic reactions will be separately carried out in the aqueous solution and DMF/TEOA mixed solution with sacrificial electron donors. The possible photocatalytic products, CO and HCOOH, will be tested by GC and NMR.



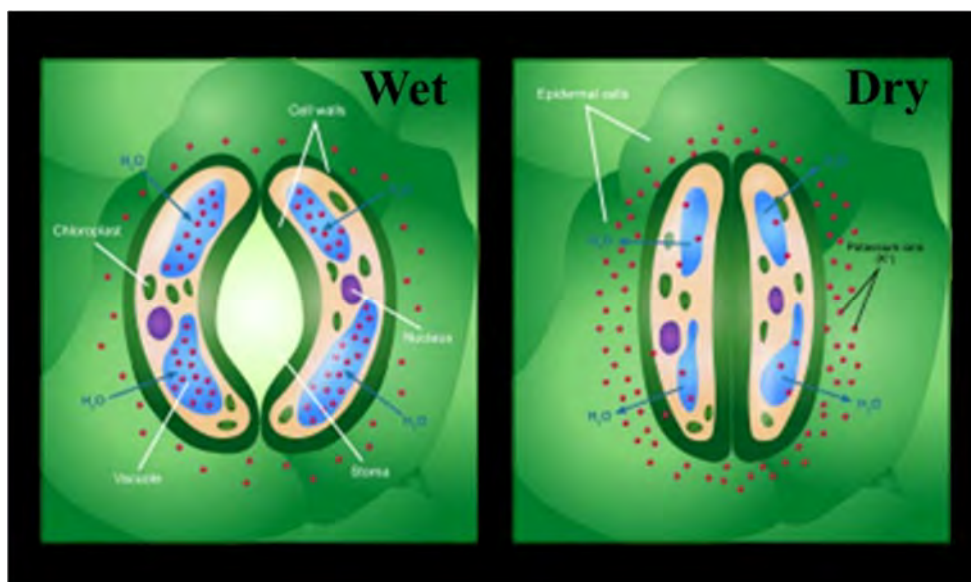
POLY 440: Breathable fabrics with smart pores to mimic leaf stomata

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A stoma (plural stomata) is a pore or opening in the epidermis of plant leaves, through which carbon dioxide is received for photosynthesis and water vapor is transpired. A stoma consists of two guard cells, having thicker and inextensible inner walls and outer walls that are thinner and more extensible. The stomata open and close through the swelling and shrinking of the two guard cells in response to environmental stimuli, e.g. high light intensity and high humidity.

In this project, we are fabricating the pores in a breathable fabric to mimic the structure and function of leaf stomata. In the artificial stomata, a special polymer is coated around a slit (“pore”) of the fabric to form “guard cells”. The polymer will bend asymmetrically toward one side under higher humidity (wet), leading the “pore” to open, while it stays still under normal humidity (dry) which keeps the “pore” close. In both conditions, the fabric maintains a flat surface without buckling, which means little effect on the overall dimension of the fabric.

The process is simple and easy to scale up. The polymer can be coated via digital liquid dispensers, or various industrial printing techniques, like screen printing or 3D printing. The slit can be cut by laser etching technology, and the dimensions can vary from micro- to millimeters. The dimension change of the pore under “open” and “close” states can be easily measured by the length and width change, or observed under optical microscope. The fine structure and morphology can be examined under scanning electron microscope (SEM). The air penetration or vapor transmission through the pores under different states can be measured by air permeability tester (e.g. KES-AP) or moisture vapor transmission rate (MVTR) tester.



POLY 441: Dandelion-like near infrared light photoinitiators: From synthesis to enhanced photopolymerization

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Although photopolymerization has been versatile in various applications, photopolymerization of thick materials still remains a great challenge due to the light-intensity gradient. Using upconversion nanoparticles (UCNPs) as internal lamps to convert near infrared light (NIR) into UV or visible light, we have realized more than 10 cm curing depth of both acrylate and thiol-ene systems. High-energy NIR laser is generally required for the excitation due to the limited upconversion luminescence (UCL) efficiency of UCNPs. NIR laser of high power can cause significant thermal effect and therefore restricts its wide applications in thermo sensitive materials and biomedical fields. In this contribution, we reported an efficient photopolymerization under low power NIR laser excitation using a novel dandelion-like photoinitiator. Herein, we use the scattered photoinitiators to graft onto the surface of UCNPs to prepare NIR light photoinitiators (Fig 1). The photoinitiators can be induced by NIR to produce the active free radical, like dandelion, to initiate photopolymerization. Compared to normal NIR light photoinitiators, electron spin resonance (ESR) revealed that the novel dandelion-like photoinitiator can produce more free radical. The photolysis and photopolymerization kinetics of the dandelion-like photoinitiators also have demonstrated that, the rate of photolysis and photopolymerization effectively increased based on confinement effect and *Förster resonance energy transfer (FRET)*. This method is expected to fabricate more extensive thick-bodied materials, further expanding photopolymerization applications.

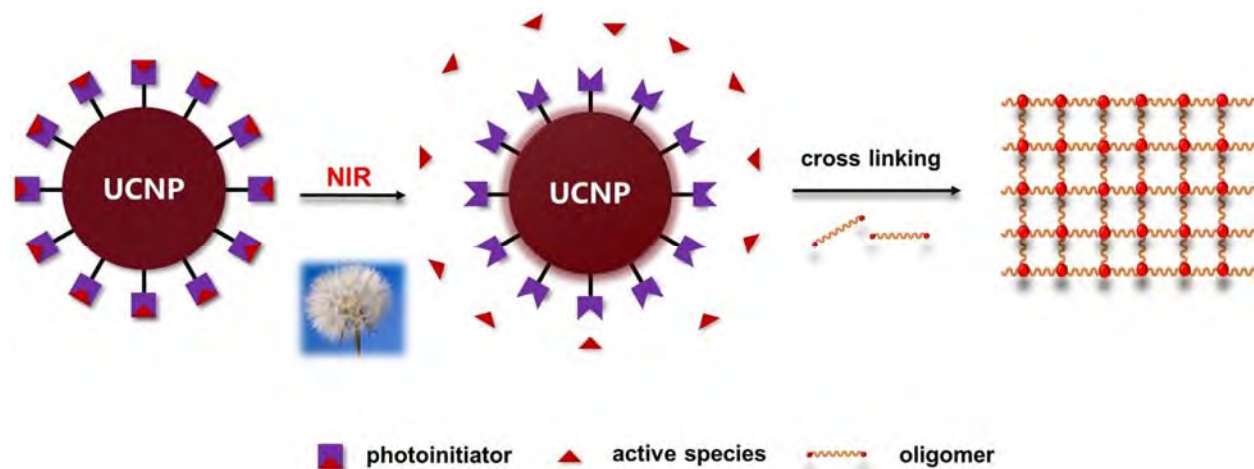
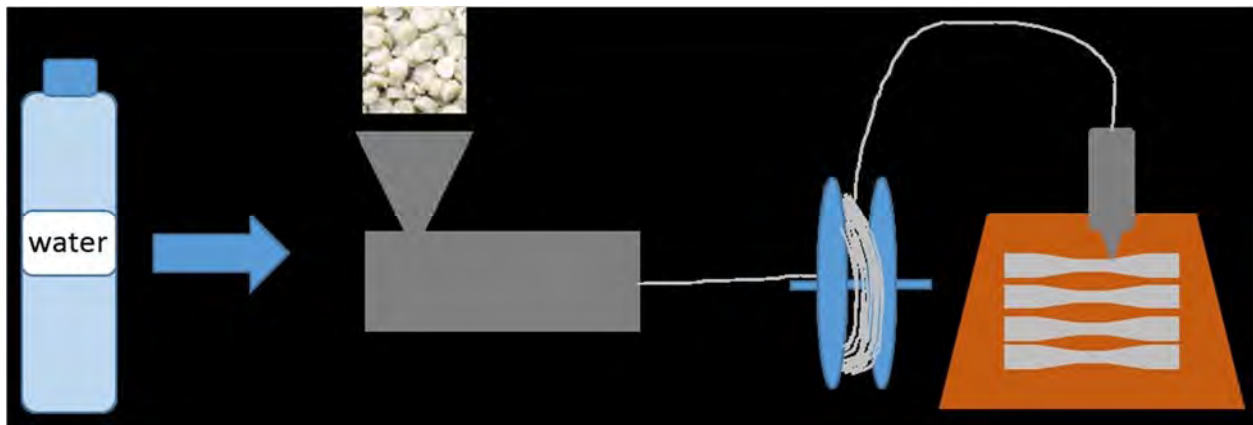


Fig 1. The photoinitiation mechanism of dandelion-like near infrared light photoinitiators

POLY 442: 3D printing feedstocks from recycled materials

Nicole E. Zander, *nicole.e.zander.civ@mail.mil*, Margaret Gillan. *Polymers*, US Army Research Laboratory, APG, Maryland, United States

United States Army warfighters in theater are often faced with the challenge of broken, damaged, or missing parts necessary to maintain the safety and productivity required. Waste plastics can be utilized to improve the self-reliance of warfighters on forward operating bases by cutting costs and decreasing the demand for the frequent resupplying of parts by the supply chain. In addition, the use of waste materials in additive manufacturing in the private sector would reduce cost and increase sustainability, providing a high-value output for used plastics. Experimentation is conducted to turn waste plastics filament that can be used in fused filament fabrication. The effect of extrusion temperature and number of extrusion cycles on polymer viscosity and crystallinity are explored. The effect of blends and fillers to impart additional functionality are also examined. Tensile specimens were tested and compared to die-cut and injection molded parts. Parts printed from recycled polyethylene terephthalate had the highest tensile strength of all recycled plastics evaluated (35.1 ± 8 MPa), and were comparable to parts printed from commercial polycarbonate-ABS filament. Elongation to failure of all recycled plastics was similar to their injection molded counterpart. In addition, select military parts were printed with recycled filament and compared to original parts. This research demonstrates some of the first work on the feasibility of using recycled plastic in additive manufacturing.

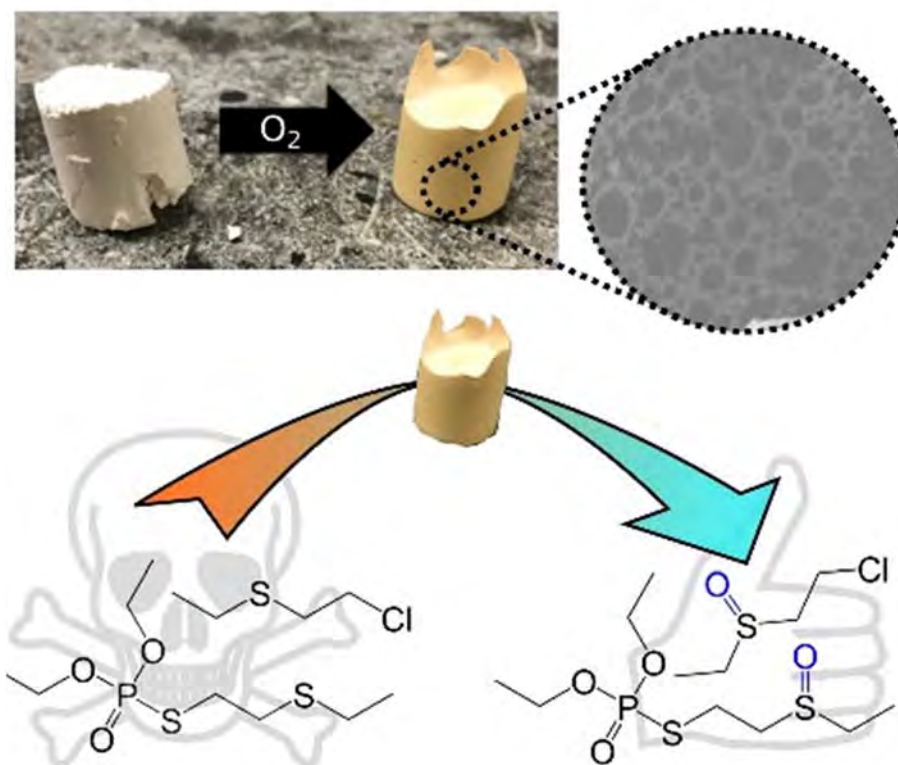


Recycled bottles are a viable and sustainable feedstock for 3D printing and can be used to generate parts on-demand in remote locations such as forward operating bases.

POLY 443: Room temperature activation of self-decontaminating polyHIPE foams for force protection applications

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Chemical warfare agents (CWA) remain a threat to the safety of first-responders, civilians and active service personnel. Self-decontaminating materials offer an advantage over traditional adsorptive materials in that they actively detoxify offending agents and prevent contaminated media from becoming secondary emitters. Here, porous polymer foams, fabricated via high internal phase emulsion (HIPE) templating, were found to rapidly detoxify chemical warfare agent simulants, Demeton-S and 2-chloroethyl ethyl sulfide, following oxidation at room temperature in air. The foams were synthesized via the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene and exhibited a hierarchical open-cellular structure characteristic of polyHIPEs. Upon exposure to oxygen the polydicyclopentadiene network formed stable hydroperoxide species that could be monitored over time via DSC. Challenge experiments and characterization via GC-MS indicated the formation of less toxic oxidation products. The relative simplicity of the detoxification chemistry and the highly porous form factor make these foams ideal candidates for application as self-decontaminating filter media

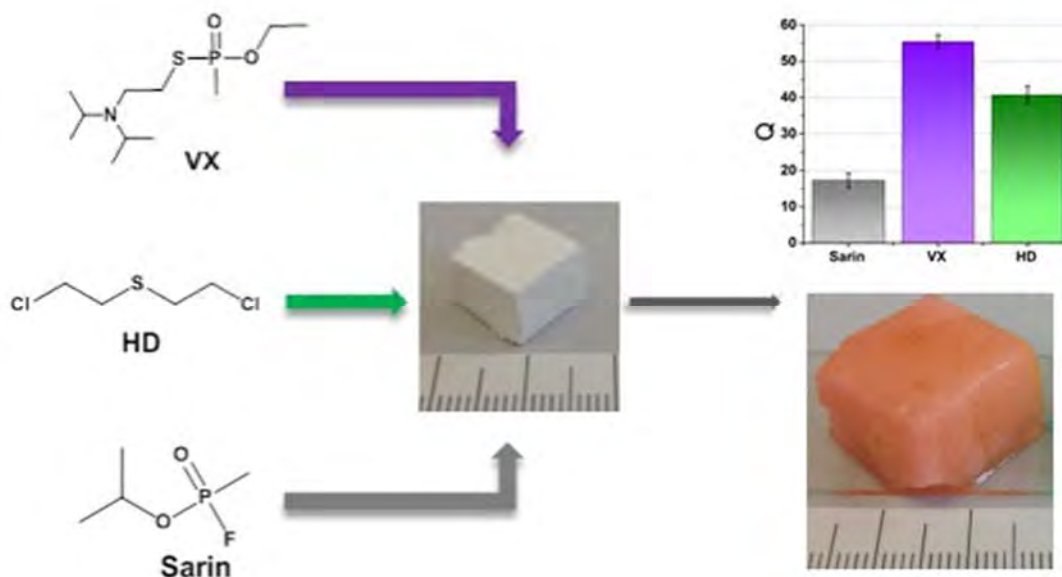


POLY 444: PolyHIPE composition modification: Towards a versatile chemical warfare agent absorbent

Alex Wright¹, alexjosephwright@gmail.com, **Simon J. Holder**², **Marcus Main**³, **Nicholas J. Cooper**³, **Barry Blight**^{4,2}. (1) Physical Sciences, University of Kent, Canterbury, United Kingdom (2) University of Kent, Canterbury, United Kingdom (3) Dstl Porton Down, Salisbury, United Kingdom (4) University of New Brunswick, Fredericton, New Brunswick, Canada

High internal phase emulsion polymers, formed through the polymerisation of an monomeric external phase, in an emulsion with an internal phase greater than 74% of the total volume, are growing in popularity in polymer research. The highly interconnected, porous and low density morphology allows them to be adapted to many different practical functions.

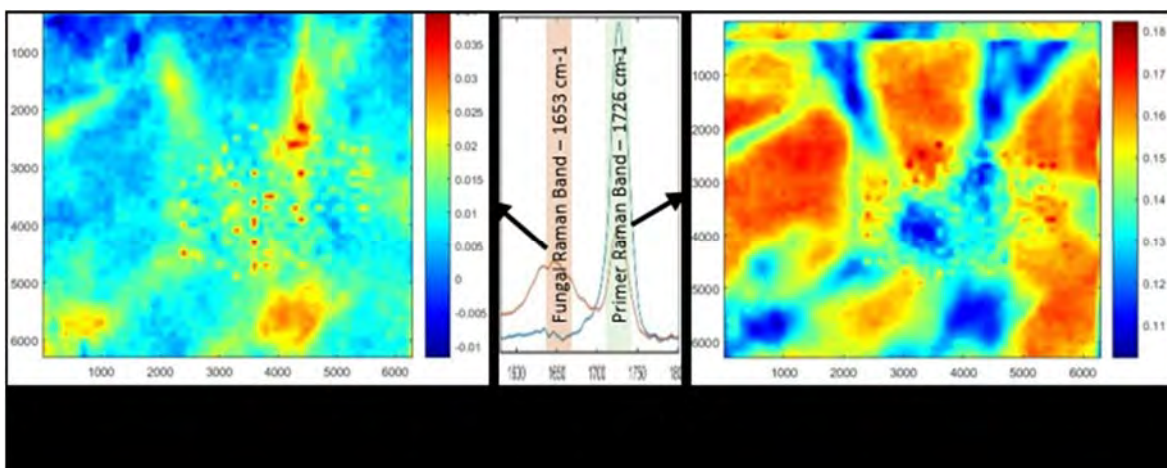
Our work focusses on the development of a novel polyHIPE, which has the ability to absorb a large number of chemical warfare agents (CWAs) to high swelling degrees. Our work begins with utilizing a poly(styrene-co-divinylbenzene) network with a low degree of crosslinking and a high internal phase fraction ($\geq 92\%$) of the emulsion to form a rapidly swelling absorbent polyHIPE. The composition of the polymer was then modified through the introduction of small amounts of vinylbenzyl chloride, along with an increase in internal phase fraction to vastly improve the swelling ability further in both sulfur mustard and the V-series of CWAs to record breaking values ($\geq 4200\text{wt}\%$). Further experimentation with different monomer compositions; including vinylic amines and the renewable terpene, myrcene, was carried out to determine if different properties and improved swelling performance could be achieved.



POLY 445: Characterization of fungal degradation mechanisms of organic coatings (polyurethane) using Fourier-transform infrared spectroscopy (FTIR)

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University of Illinois at Urbana Champaign, Urbana, Illinois, United States

Early detection of aircrafts coating system degradation is critical to prevent delamination and complete failure. Development of methods based on spectroscopic techniques are vital because of their potential to be used for *in-situ* assessment, and therefore early detection. Aircraft coating systems, usually containing polyurethane (PUR), are prone to degradation through microbes and harsh weathering conditions. This study used Attenuated Total Reflectance- Fourier Transform Infrared (ATR-FTIR) spectroscopy to assess fungal degradation of in-house prepared model coating systems. Growth conditions were optimized first for two fungal species, *Aureobasidium pullulans* and *Fusarium spp.* on Potato Dextrose Agar medium. Second, model coating systems were prepared on Al-coated glass slides with (A) white Universal bonding primer (Rust Oleum®) coating and (B) white Universal bonding primer + a clear top coat (Dupli-Color®). Third, fungi and the two coating systems were individually characterized using FTIR to obtain corresponding reference spectra. Finally, an accelerated fungal-biodegradation study was conducted by exposing the two coating systems with pre-grown fungi isolates at 28 °C and 80% humidity for ~10 weeks. The ATR-FTIR analysis of the fungal exposed samples showed decrease in the band intensities corresponding to various PUR bands (1726 cm⁻¹ Carbonyl (C=O) species; 1466 cm⁻¹ Aliphatic (CH₂) stretch PUR backbone; 1240 cm⁻¹ (C=O) + (O-CH₂) stretch; 1147 cm⁻¹ C-O-C stretch). Control coating systems were also incubated similarly, but were not exposed to fungi, did not show any decrease in PUR fungal degradation. Fungal exposed samples also showed increase in Amide-I band (1653 cm⁻¹) intensity indicating fungal growth. Data from other microscopy techniques such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Raman Spectroscopy will be also discussed. The results from this study will also have broad implications in an array of industries including aircraft and auto industry.

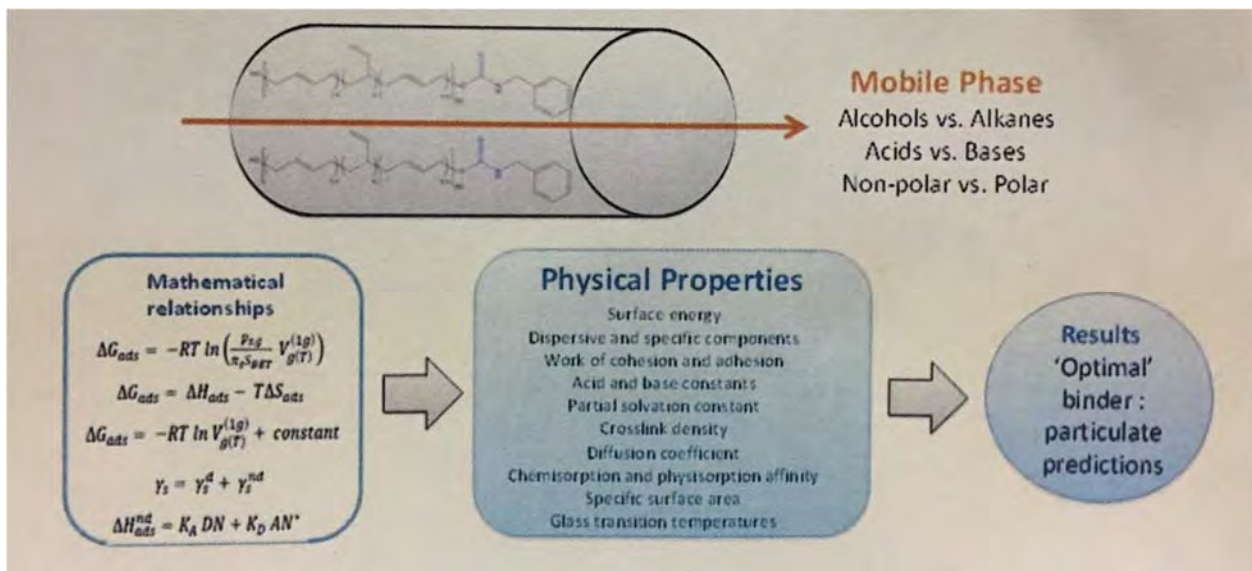


Spatial distribution of mold fungi (left) and primer coating (right) on a *A. pullulans* exposed coating system characterized by FTIR bands intensities at 1645 cm⁻¹ and 1726 cm⁻¹ wavenumbers.

POLY 446: Surface energy determinations in polymer systems by inverse gas chromatography

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An understanding of the bulk and surface properties of polyurethane based binder systems are critical to the manipulation of favorable interactions between a given binder system and particulates within a composite material. Inverse gas chromatography was utilized to provide surface characteristics (total surface energy, dispersive and specific or polar components, work of cohesion and/or adhesion) of solid binder samples in comparison to a series of well understood gas phase molecules. Contact angle measurements were utilized for comparison of the surface free energy of the solid binder sample and the interfacial tension (surface tension) between a liquid probe material and the solid binder surface. Primary outcomes include an increased understanding of the differences in the bulk and surface properties of the polyurethane based binder systems utilizing different measurement methods and the development of methods to characterize and evaluate new binders. Final success and progress was measured by the ability to reproducibly measure various surface energies, interactions and other properties of a series of binder systems by inverse gas chromatography and compare to contact angle measurements from both the laboratory and literature.



POLY 447: Cold weather protection via silver nanowire and hydrogel modified textiles

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The current protective ensemble for cold weather operations is the Extended Cold Weather Clothing System (ECWCS). It is a Soldier system that provides personal insulation in temperatures ranging from 4 °C to -51 °C, but this is only achieved through the use of seven layers totaling 12.8 lbs. The ECWCS is currently being reviewed for modifications that will reduce the overall burden to the Soldier. Fundamental research is underway that examines the potential incorporation of silver nanowires and hydrogels into textile based systems. The silver nanowires help retain body heat for the wearer. The incorporation of the silver nanowires can also help with resistance heating to help warm the textile with the assistance of an added power source. Inclusion of hydrogels into the textile will help with moisture management and the absorption of sweat away from the body during operations at freezing temperatures.

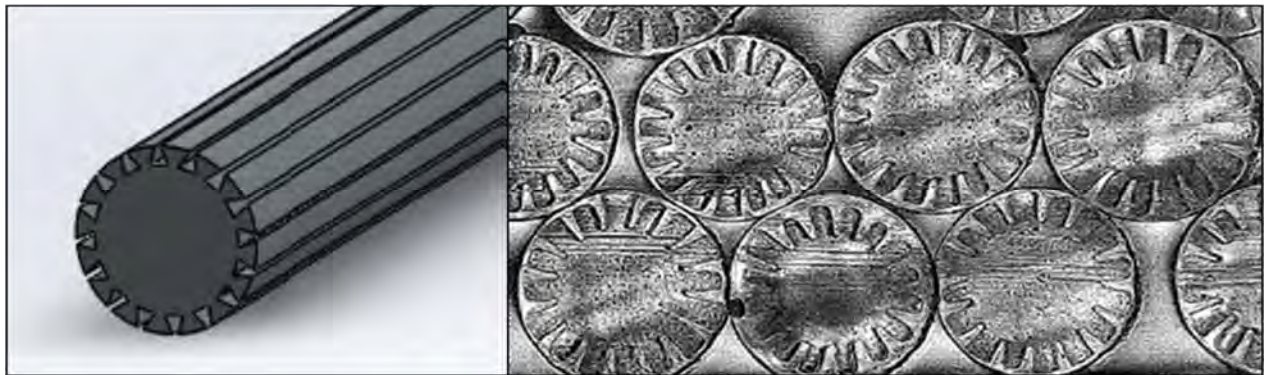
Three categories of hydrogels are being studied to determine feasibility: polyethyleneglycol (PEG), poly(N-isopropylacrylamide) (PNIPAAm), and polyacrylic acid (PAA). Different formulations of each hydrogel in bulk or microgel form will be examined to determine morphological effects due to freezing temperatures and rehydration studies after storage of the hydrogels at below freezing temperatures. Optical microscopy, SEM (ESEM), and DLS will be utilized to study hydrogel morphology and behavior at various cold temperatures.



POLY 448: Development of inherently omniphobic fibers and fabrics

Walter Zukas, wzukas@hotmail.com, *Nicole Hoffman, Quoc Truong. U.S. Army NSRDEC, Natick, Massachusetts, United States*

Liquid repellency is sought for military fabrics in order to keep the Warfighter dry and prevent chemical threats from penetrating. This repellency needs to be achieved for garments without significant interference to the evaporative process that keeps the Warfighter cool. Liquid repellency is currently achieved through the use of perfluorinated-based fabric treatments which provide a conformal coating on the fibers. However, many perfluorinated compounds are under regulatory scrutiny for their persistence in the environment and the health concerns they present. This presentation will address the development efforts, led by the Natick Soldier Research, Development and Engineering Center (NSRDEC), to produce inherently omniphobic surfaces on fibers and fabrics through a reentrant fiber geometry. The desired geometries are achieved through bicomponent fiber spinning with a water soluble polymer component and subsequent removal of this component. The figure below first illustrates a schematic of the reentrant concept then a micrograph of bicomponent fibers prior to the extraction of the outer soluble component. Material selection, bicomponent fiber processing conditions, fiber designs, fabric production, and test methods will be discussed. Results will be compared to conventional fabrics that were treated with the perfluorinated chemistries.

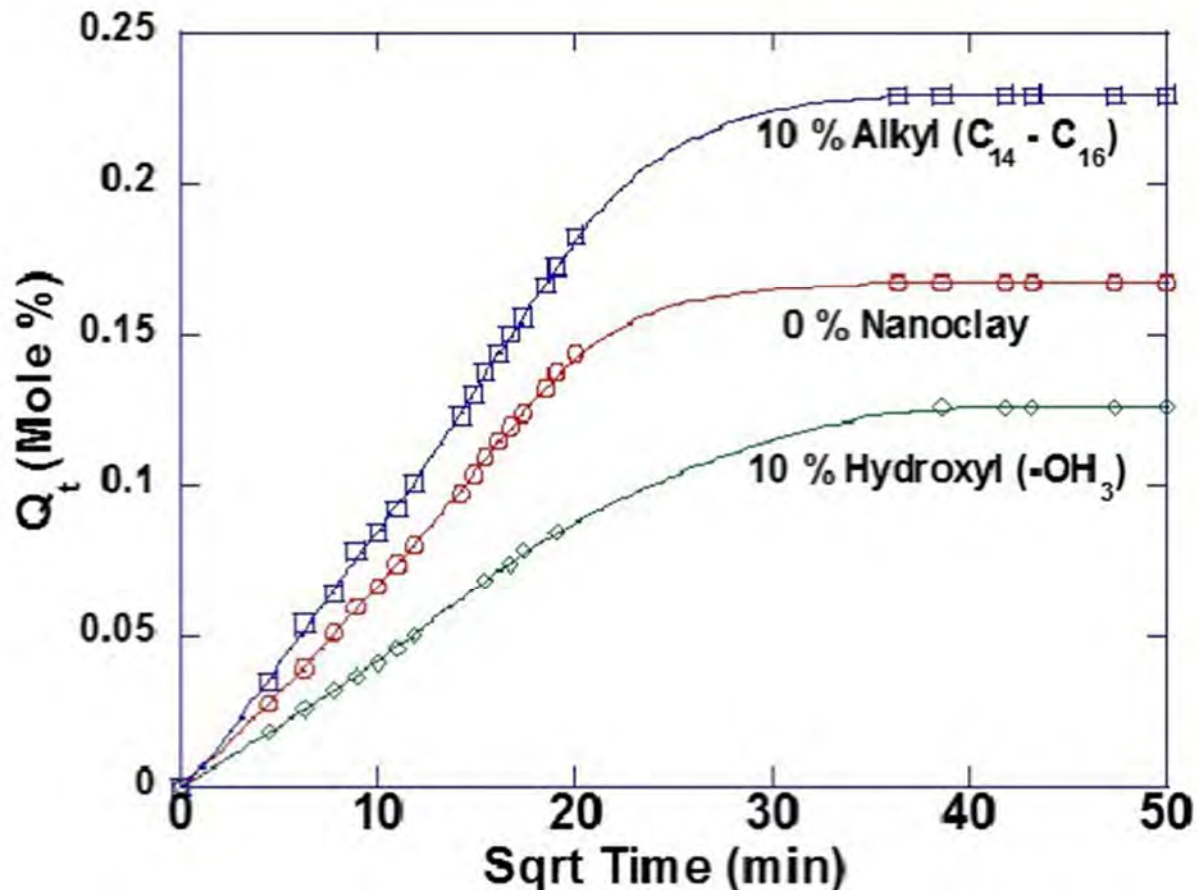


Schematic of reentrant fiber concept and photo of unextracted bicomponent fibers

POLY 449: Fuel transport properties of functionalized nanoclay/urethane composites

James M. Sloan, *james.m.sloan22.civ@mail.mil*, David P. Flanagan, Daniel C. DeSchepper, Henry O. Feuer. Materials Developmental & Transition Branch, US Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

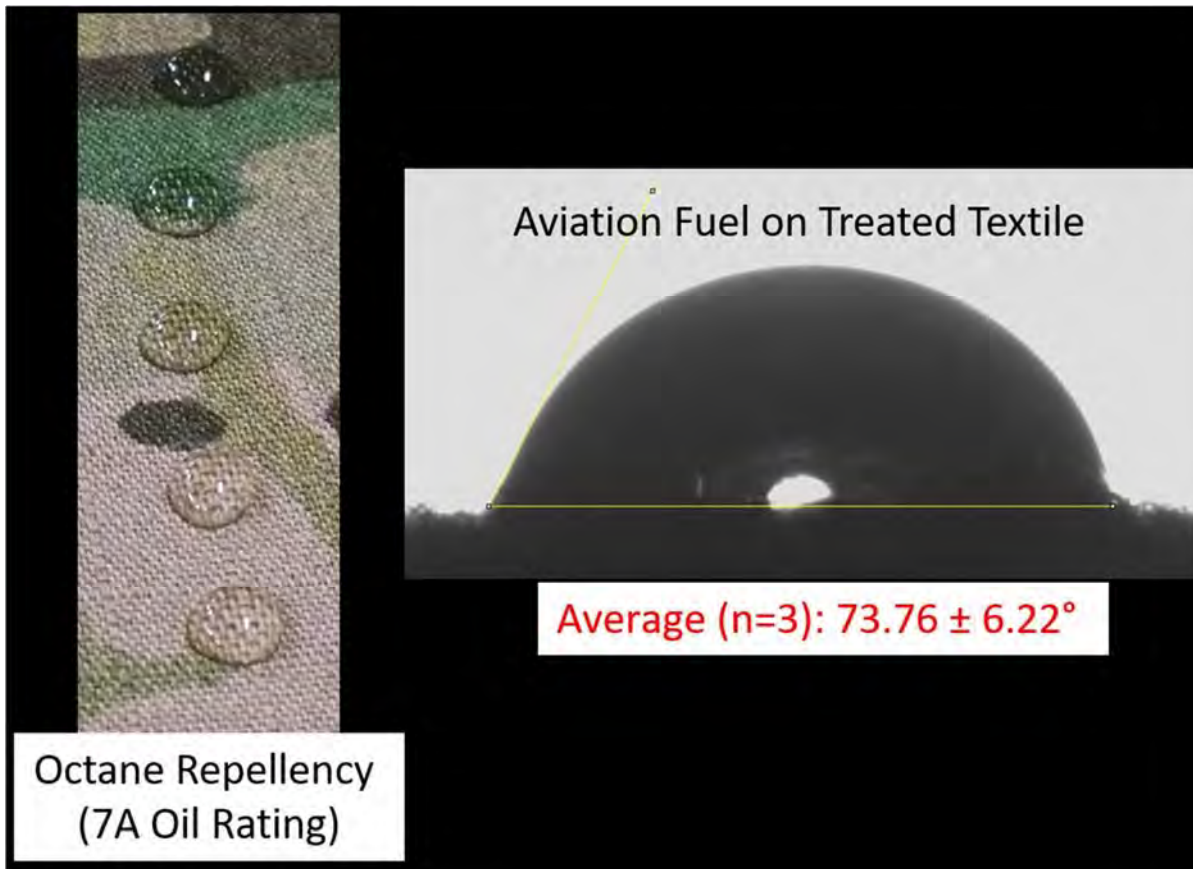
In this work, we consider the effect of the addition of functionalized clay particles to a polyether based polyurethane that is a candidate to be used as for flexible storage containment for a variety military fuels. We have synthesized urethanes and fully incorporated functionalized layered silicate inorganic nanoclay with concentrations varying from 0% to 15% by weight. The clays were functionalized with polar hydroxyl groups (-OH) and nonpolar long alkyl chains (-CH₃-(CH₂)₁₄-CH₃) and evaluated the diffusion of commercial and military grade fuels. The diffusion and permeation is found to be heavily dependent on the nature of the functionality of the functionalized particles. Nanoclays functionalized with nonpolar groups were found to increase the transport of fuel through the urethane membranes, while polar functionalization decreased transport.



POLY 450: Super repellent coatings for textiles for protection against aviation fuels

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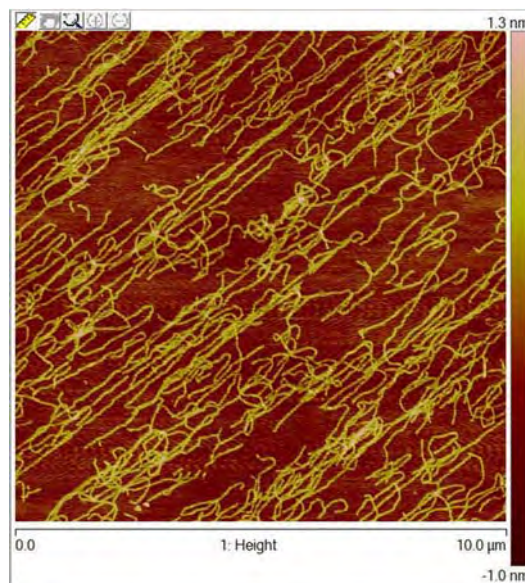
The current Fuel Handlers Coverall (FHC) is heavy and has a high thermal burden which leads Soldiers to remove the garment between fueling missions. The three main requirements of the FHC are fuel penetration protection, static dissipation and flame resistance. Super repellent coatings can provide a level of liquid protection against fuels and can help enhance the properties of the FHC without impacting the thermal burden to the Soldier. Several coatings, including perfluorinated chemistries such as C6, are investigated to show the tradespace between these properties and thermal burden. The liquid penetration properties are evaluated to understand the protection against fuels using tests such as Oil Rating (AATCC 118), Resistance of Materials Used in Protective Clothing to Penetration by Liquids (ASTM F903 - modified), and timed droplet wetting tests of F24 Jet Fuel on the textile. The effects the coating has on antistatic and flame resistance properties of textiles is also explored. Including how the flame resistance after F24 Jet Fuel contamination of the textile can be affected using a newly developed, in-house testing method. The thermal burden is evaluated by swatch level textile testing using guarded hot plate (thermal insulation – Clo) and moisture vapor transmission rates (MVTR) using dynamic moisture permeation cell (DMPC).



POLY 451: Self-assembling peptide nanofibers for rapid hemostasis

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Hemorrhagic shock continues to be one of the leading causes of fatality among warfighters. A great number of different hemostats have been used to promote hemostasis including the current standard of care QuickClot Combat Gauze (Z-Medica). However, none of these materials has all of the traits of the ideal hemostat. Previous work with self-assembling peptide nanofibers has shown their ability create a gel in solution that promotes rapid hemostasis. The peptide gel has been shown to promote immediate hemostasis when placed on top of a wound. These hemostatic peptides provide the possibility of an inexpensive and lightweight hemostat. By coating a degradable gelatin sponge with a Layer-by-Layer (LbL) film containing self-assembling peptides, this hemostatic material can be stored in a light weight and stable form. Previous work with the peptide RADA16-I has shown that these films are stable for at least 5 months at elevated temperatures. It has also been shown that cotton gauze coated with RADA16-I is able to promote hemostasis faster than control gauze in a porcine skin puncture injury. Recently, an additional self-assembling peptide, IEIK13, has been studied. Peptide structure analysis has shown that the self-assembling peptides exist in solution as nanofibers and also adsorb into LbL films as nanofibers. Release tests have shown the peptide's ability to be released from LbL films rapidly. Both peptides have shown the ability to gel in solution at dilute concentrations. The self-assembling peptides studied here offer a unique biological option for promoting hemostasis. Additionally, proof of concept in vivo studies have tested peptide coated gelatin sponges in a liver hemorrhage model in swine. These experiments have laid the groundwork for additional in vivo experiments and highlight the functionality and versatility of the self-assembling peptide hemostats.

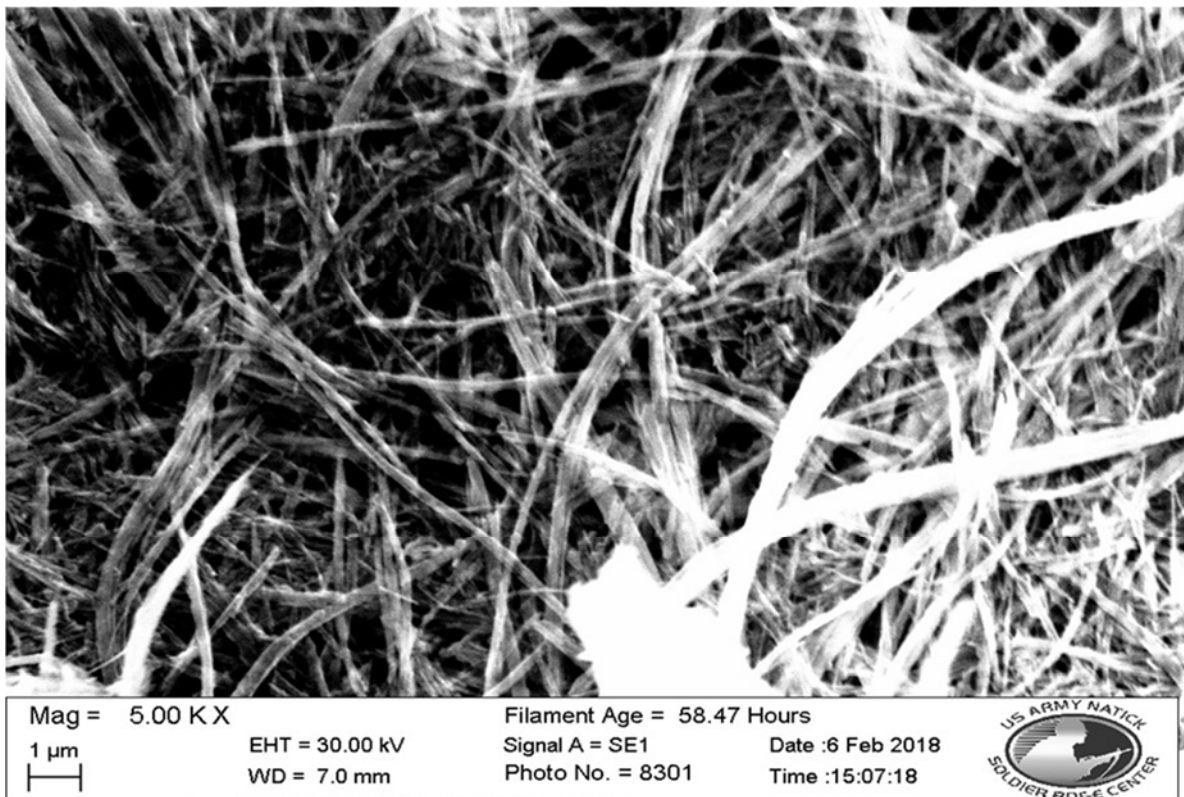


RADA16-I fibers adsorbed on a silicon substrate

POLY 452: Novel synthesis of ternary MgTiSi alloys from asbestos-chrysotile

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Asbestos is the cause of 104,000 deaths and 1,523,000 people have suffered permanent disability because of asbestos, and it is estimated that 125,000,000 are exposed to this compound worldwide. Yet it is also known to be one of the best fire retardants. It will be very advantageous to have a simple and facile way to transform such crystals in an inert additive that has yet the properties of fire retardant. In the past, compounds based on MgSi were treated with diammino exafluoro titanium. However, this treatment was never implemented to asbestos. Here we report the introduction of Ti in the chrysotile, one of the most important crystal forms of asbestos, to form a new fiber based on Mg_xTi_ySi_z. The reaction is fast and simple to execute. We will present optical, spectroscopy, and microscopy data suggesting a new facile way to create a novel compound. These new compounds can be employed as fire retardant and/or as promising hydrogen-storage materials for fuel cell batteries. Finally, this fast reaction can be implemented as a commercial analytical tool for detecting asbestos in air.

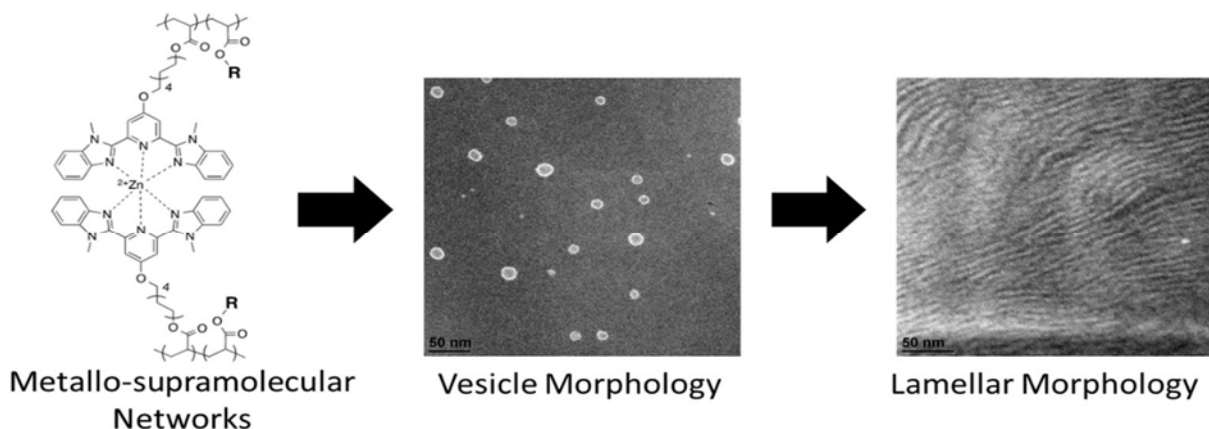


Chrysotile modified with Titanium

POLY 453: Tailoring acrylate-based metallo-supramolecular network morphologies with monomer feed ratio and excess metal-ligand complexes

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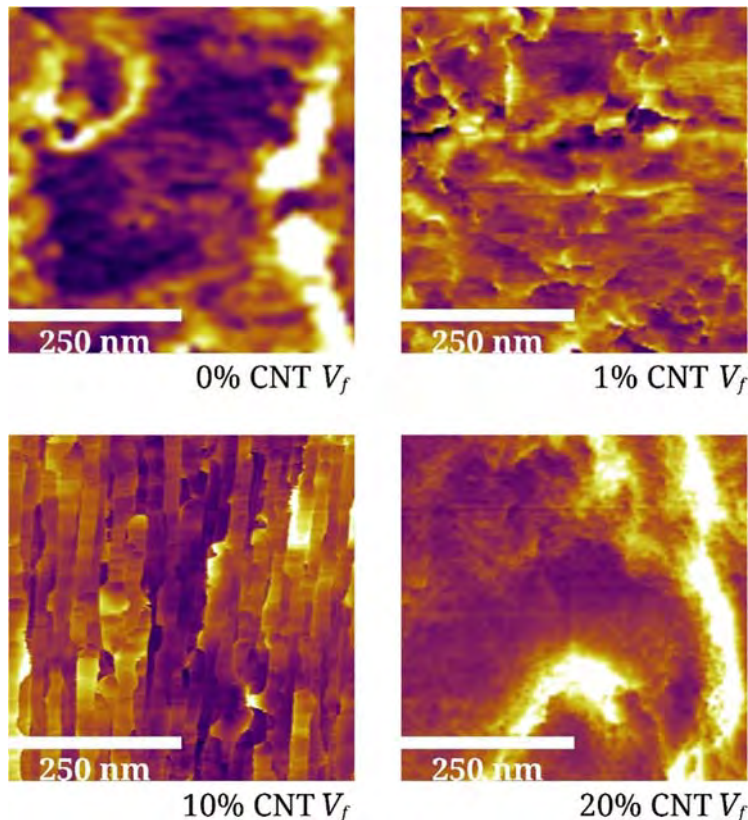
Finding new methods to alter polymer morphologies can often expand the application window of many polymers. A series of acrylate-based copolymers containing 2 to 10 percent 2,6-bis(1'-methylbenzimidazolyl)pyridine (MeBIP) pendent to the polymer backbone have been synthesized using reversible addition/fragmentation chain transfer polymerization (RAFT) techniques and converted to metallo-supramolecular copolymer networks with the addition of $\text{Zn}(\text{ClO}_4)_2$. The bulk morphologies of these metallo-supramolecular films were tuned from vesicle-type to lamellar morphology by adjusting the original MeBIP monomer feed ratio and with the addition of unbound metal-ligand complexes. The morphologies of these metallo-supramolecular networks were monitored using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). Due to the added Z-contrast arising from the zinc ions, energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) spectrum imaging were used to identify the different polymer phases.



POLY 454: Kinetic entrapment of poly(urethane-urea) hard domains via ultrahigh volume fraction aligned carbon nanotube arrays

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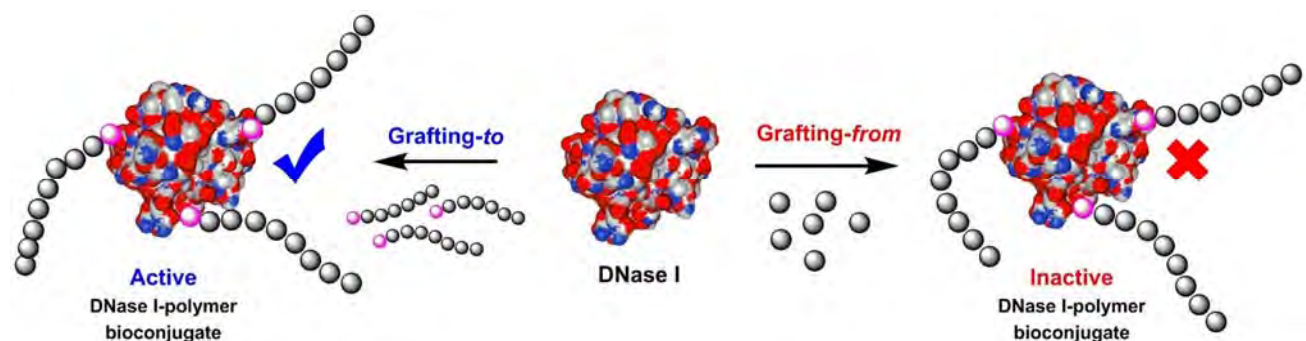
A poly(urethane-urea) has been developed and synthesized in situ in aligned carbon nanotube (A-CNTs) arrays with volume fractions (V_f) ranging from 1% to 30%. These samples were cured and imaged via atomic force microscopy to determine the effects of the A-CNTs on phase formation, size, orientation, etc. It has been found that the A-CNTs work to prevent the natural phase-separation which occurs during the 24-hour cure cycle. As A-CNT V_f increase, we see hard domain sizes drop significantly. At ultrahigh A-CNT V_f there appears to be homogeneous mixing of soft and hard domains due to the extreme packing of the A-CNTs, which prevents the free movement of chains and gives rise to thermodynamically unfavorable phase arrangement. At 10% A-CNT V_f there appears to be a unique optimization between chain mobility and A-CNT packing which results in highly-ordered and highly-oriented domains with diameter similar to the inter-CNT spacing in these samples. From this relationship between A-CNT packing density and PUU chain mobility, A-CNT V_f can be used as a method of microstructural control on the order of 10's of nanometers.



POLY 455: Importance of polymer grafting strategy for the retention of DNase I polymer hybrid activity

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Protein polymer hybrids represent an important and rapidly expanding class of biomaterials. Typically in these hybrids the linkage between the protein and the polymer is covalent. Methods for synthesis of these biohybrids can be generally sorted into the grafting-*from* or grafting-*to* strategy. These strategies are thought to be interchangeable with the only major decisions being a choice of synthetic accessibility and purification of the desired hybrid. In our study we found that the choice of the polymer ligation strategy played a major role in the stability and bioactivity of the final hybrid. We have chosen DNase I as a model RE for modification due to its potential clinical and pharmacological relevance. DNase I degrades DNA to lower molecular weight fragments through the catalysis of non-specific hydrolysis of double-stranded DNA predominantly. It is applied in preparation of RNA for a variety of purposes, including gene expression analysis and exome sequencing. In addition, DNase I is used to induce bacterial susceptibility to antibiotics and removal of biofilms from surfaces through the degradation of extracellular-DNA. Herein we found that the grafting-*from* strategy using either reversible addition-fragmentation chain transfer polymerization (RAFT) or atom transfer radical polymerization (ATRP) yielded biohybrids with no activity due to nonspecific reaction of initiator radical with amino acids on protein surface, whereas the grafting-*to* method gave active, thermally stable biohybrids.



POLY 456: Structure-property relationships through a novel FIB notch technique

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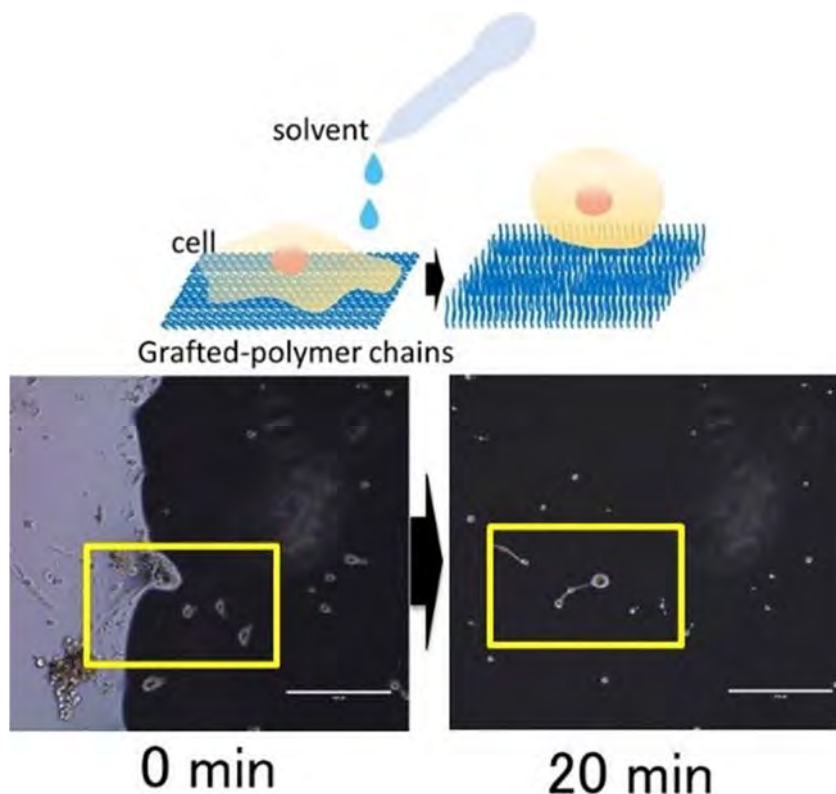
Advancements in processing techniques have facilitated the development of an expansive set of distinct high-performance DuPont™ Kevlar® fibers. Characterizing fibers' interior structures is vital for linking processing conditions with resulting structures and mechanical properties. However, the complex, multiscale structural motifs throughout Kevlar® fibers have introduced significant difficulties in developing direct, comprehensive understanding of these structures. Here we report detailed investigations of processing-internal structure-property relationships among four distinct classes of Kevlar® fibers (K119, K29, KM2+, and K49). We employ a novel focused ion beam (FIB) notch technique to obtain pristine interior fiber planes and measure morphology and transverse stiffness across these surfaces *via* multifrequency atomic force microscopy (AFM) maps. Combining multiscale AFM observations with tensile tests of single fibers drawn from the same tows, we uncover distinct interior structural phenomena that provided clear footprints of processing effects and corresponding impacts on mechanical behavior. Most notably, we uncover alternating stiffness bands that are especially apparent in low-modulus, non-heat-treated fibers, revealing a unique manifestation of internal structural variations that helps explain the observed trends in material responses.



POLY 457: Novel cell detaching system by polymer that is responsive to fluoruous solvent

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In this research, we proposed the novel solvent responsive systems for cell detachment. We designed the combination of polymer-grafted surfaces and the solvents. We could cultivate cells on the polymer-grafted surface and then detach them by just adding the solvent. We used fluoruous solvents to detach cultivated cells from the surface. Fluoruous solvents are known as their chemical stability, and immiscibility to water. Furthermore, some of them show low toxicity and are used for biomaterials like artificial blood. We quantified the polymer chain mobility by evaluating the stiffness change of the polymer-grafted layer by AFM. And we investigated the relation between stiffness change and cell detachment. From the results, the polymer layer had almost the same stiffness in the poor solvent as in the medium and the cells kept attached on the surface. In contrast, the stiffness of polymer layer in the good solvent decreased drastically to less than 1/100 compared with that in the medium, and the cells detached from the surface. This phenomenon indicates that increased mobility of the polymer chains induces the cell detachment. This system is expected to be applied for new biomaterials that enables efficient and low-damaging cell collecting in the future.

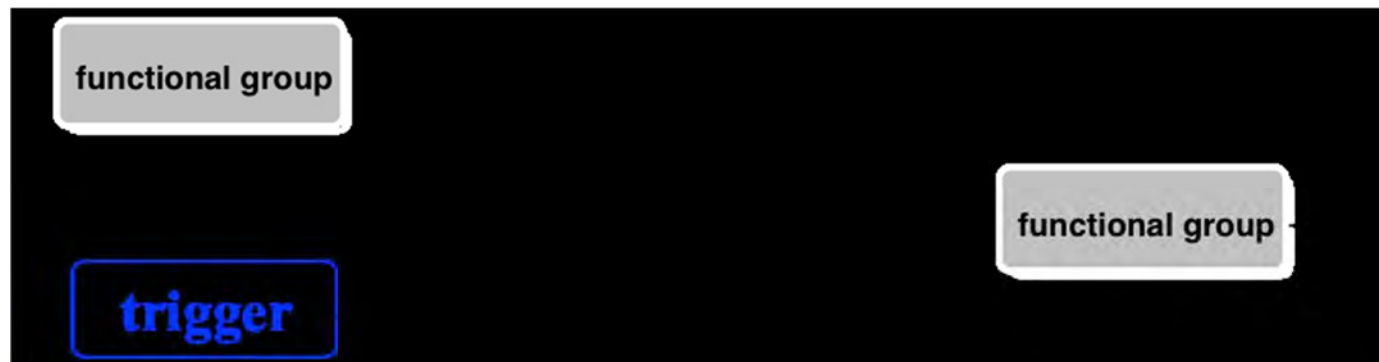


Cell detached from the surface after fluoruous solvent was added

POLY 458: New strategy for radical ring-opening polymerization of strainless macrocyclic monomers

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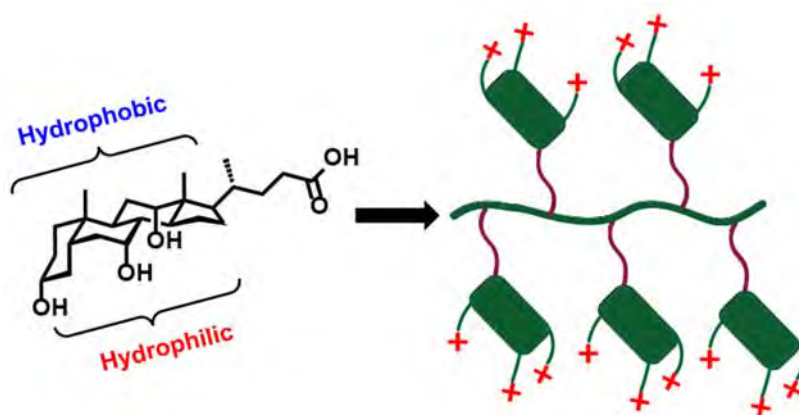
Radical ring-opening polymerization (ROP) provide a general platform for the synthesis of polymeric materials with complex main-chain functional groups that would otherwise be impossible to introduce through the polymerization of acyclic vinyl monomers. However, existing ROP strategies are still limited to polymerize strained low molecular weight cyclic monomers. Herein, we report a novel chain-growth, triggered ring-opening polymerization (TROP) approach for the rapid and controlled radical polymerization of strainless macrocyclic monomers. Our approach is general and polymerization is amendable for control using various controlled radical polymerization techniques. This polymerization has been used to synthesize block copolymers with other cyclic and acyclic functional monomers. The copolymers achieved high molecular weights, low dispersity, and controlled sequences.



POLY 459: Facial amphiphilic antimicrobial polymers using multicyclic bile acids

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Bacterial infections and antibiotic resistance, mainly by Gram-negative pathogens, have become a global healthcare crisis that is in urgent need of addressing. Numerous antimicrobial polymers had been developed over the past few decades. However, many of them suffer higher cytotoxicity against mammalian cells and are ineffective particularly against multidrug-resistant Gram-negative bacteria. As such, the development of new antimicrobial agents with enhanced activity and lower cytotoxicity are needed to prevent the inception of a post-antibiotic era. We used bile acid derivatives to prepare antimicrobial polymers. Bile acids are cholesterol-derived amphiphilic steroid acids produced in mammals and other vertebrates. We have synthesized multiple cationic charge-containing facial amphiphilic polymers via post-polymerization modification based on derivatives (lithocholic, deoxycholic, and cholic acid) of a multicyclic terpenoid, a bile acid. These derivatives bear single, double, and triple quaternary ammoniums head groups respectively. All these polymers surprisingly showed potent activity against Gram-negative bacteria. Cholic acid-based cationic polymers exhibited higher antimicrobial activity than that of other two derivatives. The enhanced activity of bile acid derivatives against Gram-negative bacteria is due to the presence of facially oriented hydrophilic cationic head groups and hydrophobicity of the multicyclic fused rings, which provide higher interactions with bacterial cells.



Bile acid-based facial amphiphilic polymer.

POLY 460: Studying the effect of mechanical properties of lipid-wrapped nanoparticles on cell-nanoparticle interactions

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Lipid-wrapped nanoparticles (NPs) exhibit a unique platform for a wide variety of applications, such as NP-based imaging, active and passive targeting, drug delivery, and probing specific mechanisms in molecular and cellular biology. The ganglioside GM3 is a host-derived glycosphingolipid which exists in the membrane of human immunodeficiency virus-1 (HIV-1). It has been identified as the corresponding receptor that mediates interactions between HIV-1 and Siglec1 (CD169), a protein expressed on dendritic cells (DCs) and macrophages, key cells of the immune system. Due to their ability to target CD169-expressing DCs and macrophages, GM3-incorporated Lipid-wrapped NPs create a unique platform to investigate cell-NP interactions. Endocytosis and intracellular fate of NPs depends on particle size, shape, surface properties, composition of the membrane, and core stiffness. We investigate the effect of the stiffness of these nano-materials on cell-NP interactions by making lipid-wrapped NPs out of different polymers. We use polylactic acid (PLA), and polylactic-co-glycolic acid (PLGA), due to expected different Young's modulus of these polymers. We monitor the cellular response, uptake pattern, intracellular fate, and spatiotemporal distribution of lipid-wrapped polymer NPs by fluorescence microscopy, using fluorescent markers for various endosomal compartments to help us understand these uptake mechanisms in better detail. This study, along with measurements of core stiffness for these NPs, helps us expand our knowledge about influences of core stiffness on cellular behaviors.

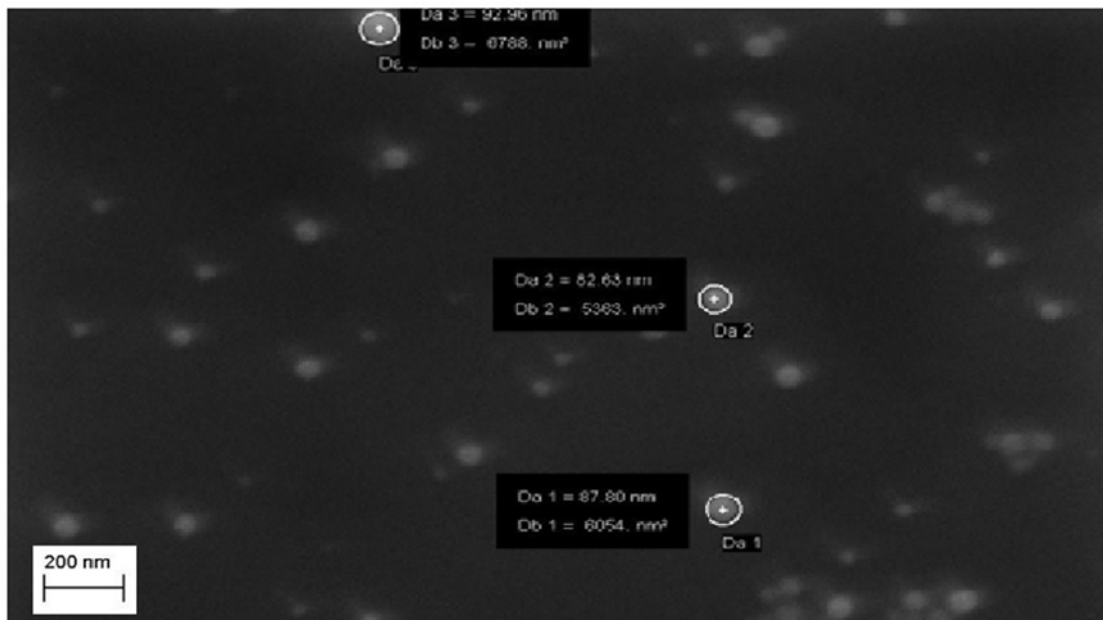
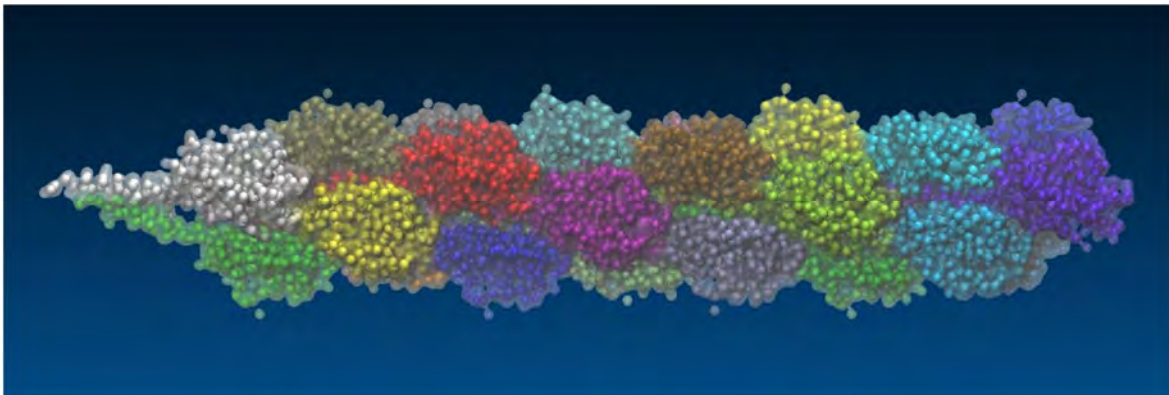


Figure 1. Scanning Electron Microscopy (SEM) of lipid-wrapped polymer NPs.

POLY 461: Comparing the dynamics of the *Neisseria meningitidis* and *Neisseria gonorrhoeae* type IV pilus filaments using all-atom molecular dynamics simulation

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Type IV pili (T4P) are long protein biopolymer filaments comprised of thousands of copies of a protein called pilin. T4P function as “grappling hooks” for bacteria and archaea, and are implicated in surface attachment, twitching motility, and bacterial infection. T4P can withstand very large forces, and have been found to undergo a force-induced structural transition to an elongated state in which amino acids buried in the native state become exposed to solvent. Recently, the highest resolution models ever reported of the T4P from *Neisseria meningitidis* (Nm T4P) and *Neisseria gonorrhoeae* (Ng T4P) were solved through a combination of cryo-electron microscopy and fitting of pilin x-ray crystal structures into the cryo-EM maps. However, these static structures do not offer insights into the dynamics of T4P filaments. Developing a dynamic understanding of these fascinating biomacromolecular systems can aid in understanding their great strength and plasticity, potentially leading to their use as novel adhesive biomaterials. Here both the Nm T4P and Ng T4P filament models are studied using all-atom molecular dynamics simulations. Simulations of the T4P systems are carried out in explicit solvent using Amber16 on GPUs implementing the hydrogen mass repartitioning method to accelerate the simulations. More than a microsecond of data for each system is obtained, revealing significant similarities in the dynamics of the two systems. Clustering and principal component analysis is performed in order to extract information about the major conformations that pilin subunits adopt in both T4P systems, and about the dominant modes of motion that pilin subunits exhibit in the filament environment. Filament helical symmetries, for example the rise and twist per pilin subunit, are also calculated and compared to those obtained from structural data. Secondary structure analysis of pilin subunits within the filament environment further demonstrates that for both Nm T4 and Ng T4P, while transient structure can form within a “melted” region of pilin alpha helix, this region remains significantly unstructured, which is consistent with the starting structural model.



Visual Molecular Dynamics rendering of a T4P filament. Pilin subunits are indicated in different colors.

POLY 462: Novel organic-inorganic and robust aerogel based on polyhedral oligomeric silsesquioxane (POSS)

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Silica aerogels are normally constructed of nanoparticles, aerogels have become a new kind of porous material. Aerogels are usually poor mechanical properties, which always limit their practical applications. Fortunately, many efforts have been made to reinforce aerogels. Traditionally, silica aerogels were prepared by tetraethylorthosilicate (TEOS). In this work, a novel precursor with polyhedral oligomeric silsesquioxane (POSS) with multi-alkoxy groups was used to prepare aerogels. OTS-POSS (Octa[2-((3-(trimethoxysilyl)propyl)thio)ethyl silsesquioxane) was synthesized via thiol-ene click chemistry. Benefiting from their robust inorganic cage skeleton and organic chains buffer zone, the OTS aerogels exhibit excellent mechanical properties. All hydrogel samples were prepared via traditional sol-gel process and used ambient pressure drying (APD) to produce aerogels. High compression modulus of 25.84MPa to aerogels could be obtained. Furthermore, it could be found that the particle size and pore distribution was another factor determined the mechanical property. This work guides a new way of producing porous materials and makes aerogels meet the requirements of practical applications.

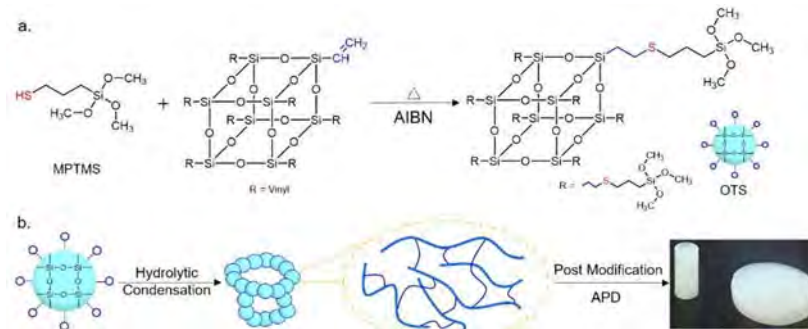


Figure 1. (a) Synthesis of the precursor. (b) Procedure for obtaining aerogels.

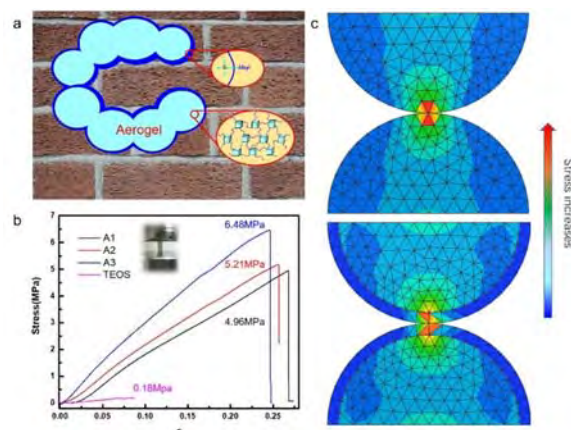
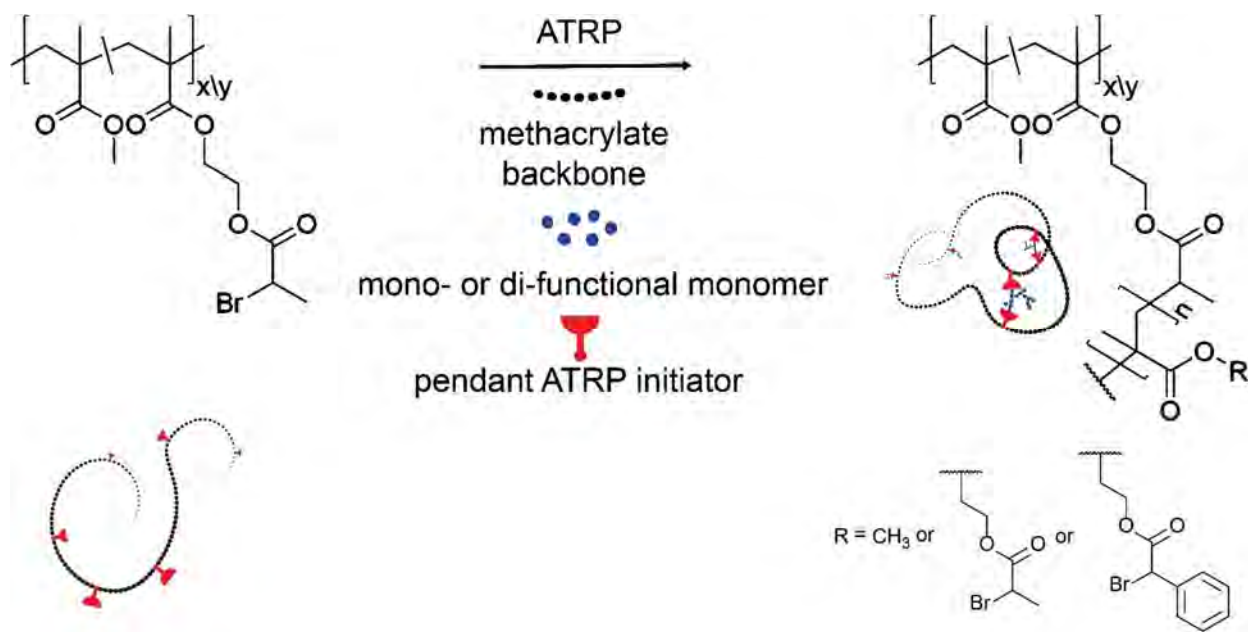


Figure 2. (a) Diagram of silica particle matrix and organic chains buffer zone. (b) Stress–strain curves of compression tests on aerogels. (c) Images of finite element analysis about aerogels.

POLY 463: Single-chain nanoparticles *via* intra-chain atom transfer radical coupling

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In nature, single amino-acid chains fold into precisely defined structures to perform a wide variety of amazing tasks such as information storage and catalysis. The keys to a given protein's performance are precise nanoenvironments (such as hydrophobic pockets) and specialized sites (such as active sites). In the endeavor to approach these designs synthetically, both to understand the fundamental principles behind the folding process and to engineer our own functional designs, we have synthesized polymer chains decorated with cross-linkers which combine to create so-called single-chain nanoparticles. In this work, methacrylates with pendant atom transfer radical polymerization initiators were prepared using RAFT. Subsequent intra-chain polymerization and coupling of a hyperbranching monomer was performed to prepare single-chain nanoparticles. The design is particularly versatile for two reasons. First, the chemistry of the intra-chain branches is highly tunable due to the broad scope of ATRP chemistry. Second, because unreacted branch ends remain available for further functionalization or polymerization steps, the examples presented here may act as a modular base for future application-specific designs.

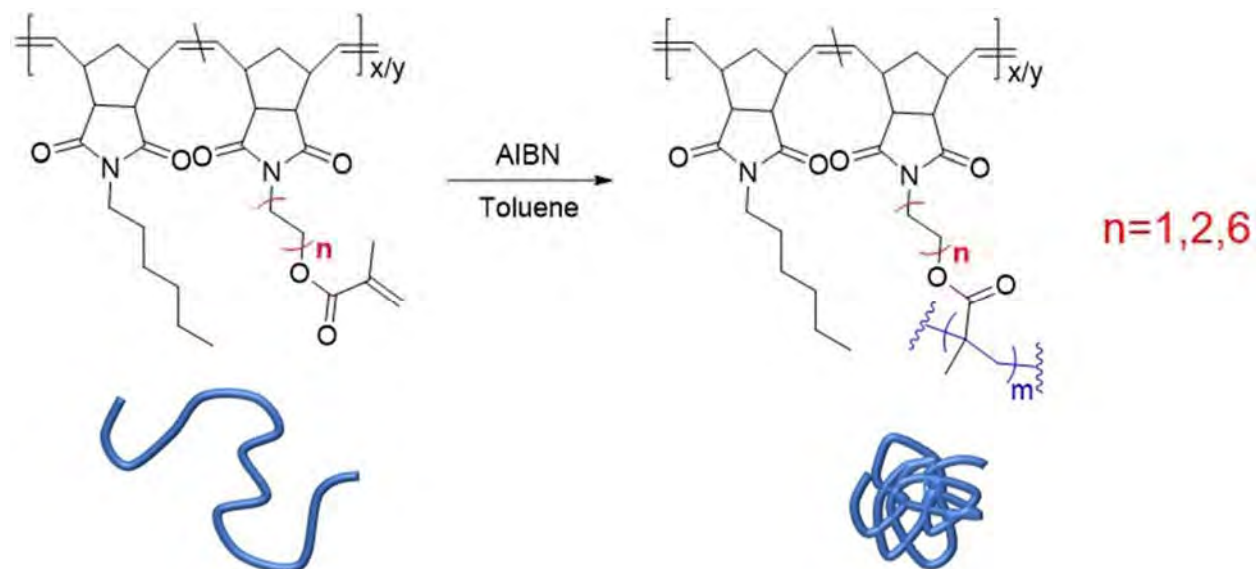


Single-chain nanoparticles were prepared by the intra-chain atom transfer radical polymerization and coupling of a hyperbranching monomers.

POLY 464: Effect of pendant groups on fabrication of poly(norbornene imide) single-chain nanoparticles

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Natural materials have been a source of inspiration to polymer chemists in the design of well-defined materials with advanced functionalities. The utility of biomacromolecules is a result of a specific three-dimensional shape with precise placement of functionality on the surface of the structure or its interior. Polymer chemists strive to create a bottom-up, controlled construction of materials with comparable precision demonstrated in natural materials. A technique that represents a significant step towards these ends is the collapse of single polymer chains in highly dilute solution. The resultant structures are termed single-chain nanoparticles (SCNP). A variety of crosslinking chemistries have been reported over the years. However, detailed research on the length and flexibility of pendant groups in relation to folding efficiency has not been thoroughly explored. Herein, a series of poly(norbornene imide) with pendant methacryloyl groups were synthesized through ring opening metathesis polymerization (ROMP). The designed polymers have various spacing between the polymerizable methacryloyl pendant groups and the polymer backbone. Upon radical initiation, intra-chain radical polymerization occurs, resulting in chain folding of the linear poly(norbornene imide) to form nanoparticles. The effect of length and flexibility of pendant groups on folding efficiency was monitored by GPC and NMR.

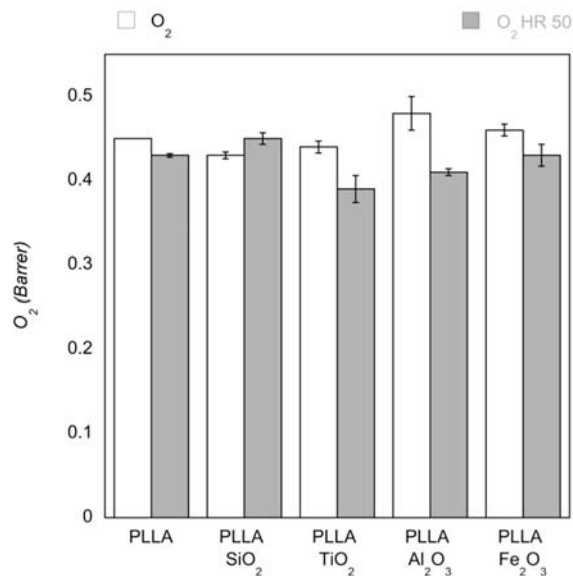


POLY 465: Polylactide nanocomposites: The influence of the interactions on the light and gas barrier properties

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In the search of novel materials that could replace commodity polymers, such as poly(ethylene terephthalate), poly(propylene), poly(ethylene) or poly(styrene), biodegradable polymers has been widely studied. However, their present a lower performance by means of mechanical properties and barrier character. In order to improve these properties different approaches have been carried out being one of them the addition of nanoparticles.

In this work polylactide is used as a model biopolymer to study the influence of the different metal oxide nanoparticles on the light and gas barrier properties. Four different nanoparticles: TiO₂, SiO₂, Fe₂O₃ and Al₂O₃ have been used and the permeability to water vapor and dry and humid oxygen is measured. The results obtained show that the interactions between the penetrants and the nanoparticles determine the permeability. These results are in accordance with water angle contact and zeta potential measurements. Furthermore, in some cases a great improvement in the barrier character is obtained taking into account that only 1 % of nanoparticles have been added. Overall, this works allows to gain a deeper insight on the effect of the nanoparticles on the transport properties which would lead to develop more efficient biodegradable packaging.

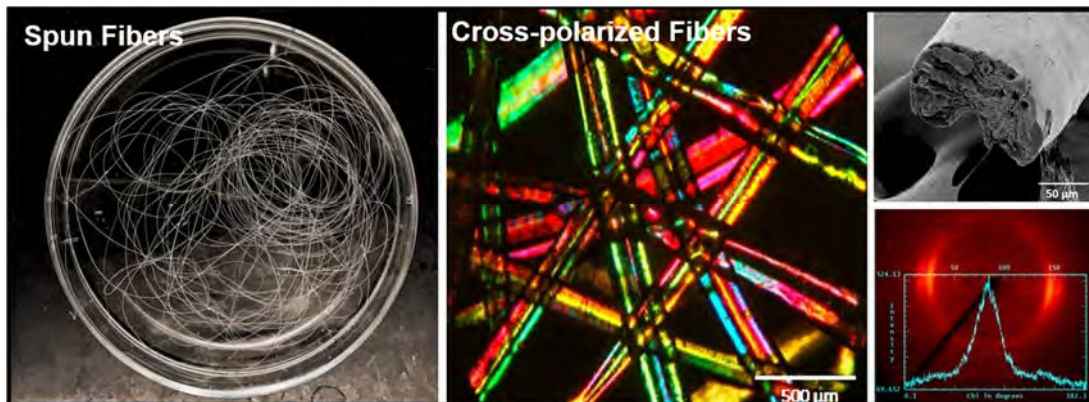


Oxygen permeability in dry and 50 % humidity conditions for PLLA and its nanocomposites

POLY 466: Effect of crystal orientation of cellulose nanocrystal (CNC) on properties of polyvinyl alcohol nanocomposite fibers

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Polyvinyl Alcohol (PVA) is water soluble, semi-crystalline, and biocompatible synthetic polymer having a wide range of potential applications in tissue scaffolding, filtration membranes, drug delivery, and optics. Commercially, they are used for cement and tear resistant fabric. However, PVA fibers have low strength and are subject to plasticization in humid environments. To overcome such shortcomings, cellulose nanocrystals (CNCs) are incorporated. This work focuses on using dry-jet-wet spinning as a technique to develop an industrially scalable process for PVA/CNC nanocomposite fibers with high strength and modulus. We hope that by preparing high modulus and low-cost polymer fibers we can develop sustainable and lower weight alternatives to glass fiber for structural composite applications. In this study, we used CNCs of different aspect ratios, which were extracted from wood pulp and cotton, to prepare PVA nanocomposite fibers and investigate their effect on the mechanical, thermal and morphological properties. The fibers were collected as-spun and with the first stage drawing up to draw ratio 2. Mechanical properties were tested using dynamic mechanical analysis (DMA). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the thermal stability of PVA/CNC fibers and understand the interactions between the dispersed and continuous phases. Furthermore, the degree of orientation along the spun fiber axis was quantified by 2D X-ray diffraction. As expected, the CNC orientation correlated to the mechanical properties of the composite fibers. Micromechanical models were used to predict the fiber performance and compare with experimental results. Finally, surface and cross-sectional morphologies of fibers were analyzed by scanning electron microscopy (SEM) and optical microscopy.

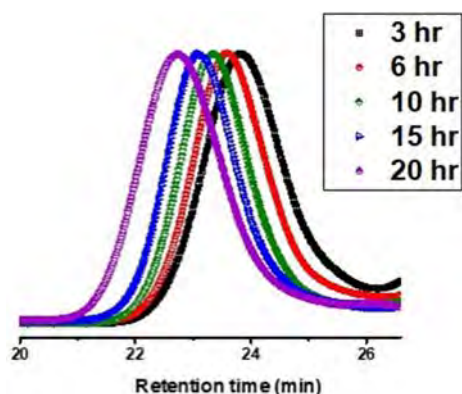


Images of as-spun, cross-polarized, SEM and 2D-XRD representation of PVA/CNC nanocomposite fibers.

POLY 467: SI-RAFT polymerization of dimethyl butadiene on silica nanoparticles for matrix-free “methyl rubber” nanocomposites

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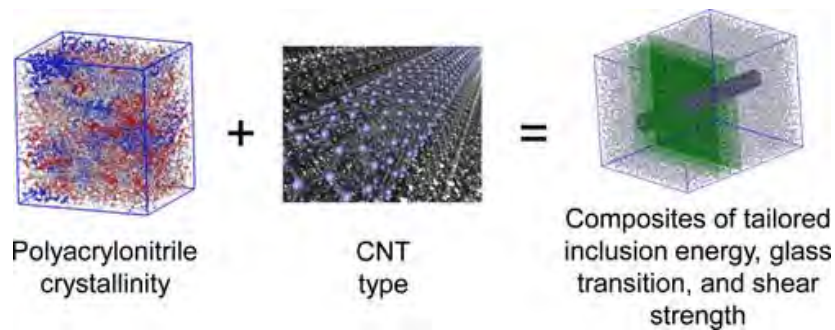
The properties of poly(dimethyl butadiene) (“methyl rubber”) have been an interesting topic in polymer science. The RAFT polymerization of dimethyl butadiene (DMB) and surface-initiated RAFT polymerization (SI-RAFT) on silica nanoparticles have been investigated. In this work, we studied the effects of chain graft density, RAFT agent selection, and polymerization solvent on molecular weight, polydispersity and polymerization kinetics. The free RAFT and SI-RAFT polymerization rates were studied and it was found that the free RAFT polymerization rate was slower than the SI-RAFT polymerization. The (PDMB-*g*-SiO₂) were cured to obtain matrix-free nanocomposites as rubbery films which exhibited good dispersion of silica nanoparticles and large improvements in mechanical properties compared with the unfilled cured rubber. Additionally, preliminary results were obtained on mixing the grafted nanoparticles in different matrices to investigate the mechanical properties and grafted particle dispersion. The inherent attractive properties of methyl rubber, e.g., low glass transition temperature (T_g), low degradability, and ability to be further modified through the double-bond-rich composition, combined with well dispersed nanoparticles provide a new platform for property enhancement in this rubbery polymer.



POLY 468: Nanoscale structure-property relationships of polyacrylonitrile/CNT composites as a function of polymer crystallinity and CNT diameter

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Polyacrylonitrile (PAN)/carbon nanotube (CNT) composites are used as precursors for ultrastrong and lightweight carbon fibers. This contribution presents insights into the structure at the atomic scale and the relationships to mechanical and thermal properties for different degrees of PAN preorientation and CNT diameter based on experimental data and molecular dynamics simulation. The inclusion of CNTs in the polymer matrix is favored for an intermediate degree of PAN orientation and small CNT diameter whereas high PAN crystallinity and larger CNT diameter disfavor CNT inclusion. We find that glass transition temperatures in composites are predictable with ± 5 K accuracy by simulations and correlate with the amount of CNT/polymer interfacial area per unit volume. I.e., an increase in T_g is observed in the presence of CNTs, for higher CNT volume fraction, and a decrease in T_g with larger CNT diameter at the same volume fraction. Changes in interfacial shear strength as a function of CNT characteristics and polymer crystallinity are explained and correlate with measurements for nanoscale/microscale domains.



Atomistic models of polyacrylonitrile of a given crystallinity and CNTs forming a composite model for the analysis of thermal and mechanical properties by computer simulations in comparison to experimental measurements.

POLY 469: All inorganic perovskite nanocrystals with precisely controlled optical properties and enhanced stability via non-linear amphiphilic block copolymers

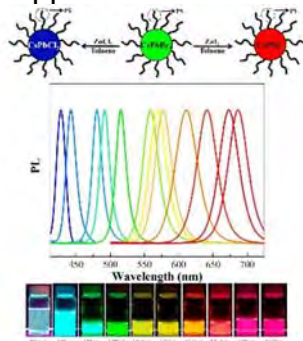
Young Jun Yoon¹, yoon67@gatech.edu, Yihuang Chen¹, Jaehan Jung¹, Yajing Chang¹, Chunhao Lin¹, Shengtao Yu¹, Shuguang Zhang¹, Cheng-hsin Lu¹, Shuang Pan¹, Zewei Wang¹, Zhitao Kang², Vladimir V. Tsukruk¹, Zhiqun Lin¹. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia, United States

Perovskite materials have garnered much attention over the past few years due to their excellent power conversion efficiency (PCE) in solar cells, outstanding quantum yield (QY) in LEDs, and overall low production cost. The major bottleneck for commercialization, however, is low stability, especially towards moisture and polar solvents.

Our strategy utilizes non-linear block copolymers with distinct polymer blocks as nanoreactors to simultaneously create nanostructured materials with precisely tuned dimensions as well as enhanced stability that cannot be achieved via conventional ligand assisted methods.

In our research, we have successfully synthesized Cs-based perovskite QDs with tailored dimensions that are intimately and permanently tethered with hydrophobic polystyrene by capitalizing on rationally designed star-like block copolymer poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS) as nanoreactors. By utilizing ATRP to synthesize low PDI PAA blocks (which can coordinate with perovskite precursors), we accurately control the size of the perovskite QDs, thus allowing strict control over light harvesting and emission at desired wavelengths in the visible region. Our results show that FWHM of PS-capped CsPbBr₃ QD photoluminescence (PL) was as low as 17.7 nm. Also by post anion exchange we were able to control the PL peak position from 400 nm to 700 nm.

Intriguingly, each PS-capped perovskite QD, for the first time, has a separate protective shell that can be precisely tailored to any desired length/thickness. The permanently tethered PS protective shell on the perovskite QD surface showed striking improvements in terms of stability. PS-capped CsPbBr₃ QD's QY, PL peak position, and FWHM in solution (toluene) was maintained for more than 2 months without any change. Also PS-capped CsPbBr₃ QDs showed up to 20x increase in water stability compared to conventional ligand-capped CsPbBr₃ QDs.

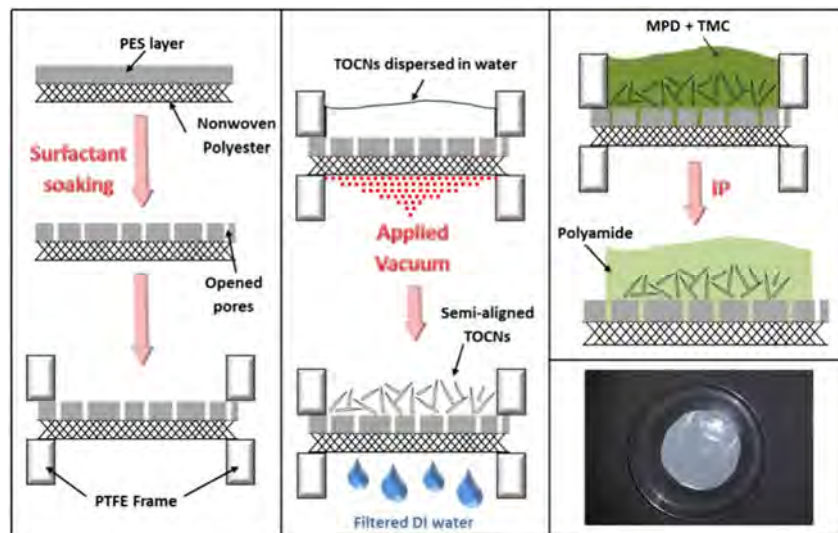


PS-capped Perovskite QDs

POLY 470: Interfacial transport in nanocellulose-based nanocomposite membranes for improved reverse osmosis performance

Stephen M. Martin^{1,2}, **Ethan Smith**^{1,2}, ethands@vt.edu, Johan Foster³. (1) Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States (2) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (3) Virginia Tech, Blacksburg, Virginia, United States

Improvement of current reverse osmosis membranes poses an intricate challenge that, if solved, could affect global access to clean water. Thin film composite (TFC) membranes are used commonly in industrial desalination processes, relying on a thin polyamide skin layer for selectivity. Recent studies in our research group involving the addition of nanoparticles to the selective polymer layer of existing TFC membranes have shown promising results, yielding higher water permeance (flux), improved chemical resistance, anti-biofouling properties, and mechanical property enhancement. It is desired to understand how the addition of nanoparticles to the polyamide skin layer influences polymer formation, thereby altering the transport properties of the overall membrane. In addition, these thin film nanocomposite (TFN) membranes are often cost-ineffective, prompting the search for an economically viable alternative. Nanocellulose has become a popular field of study given that it is produced on large scales globally in many different varieties. In this study, cellulose nanocrystals (CNCs) of varying lengths are explored as additives to TFN membranes. The high aspect ratios of the CNCs may assist the formation of transport pathways for water molecules, as well as improve the mechanical properties of the membranes. CNCs were deposited in situ during polyamide skin layer formation in various amounts and the resulting transport properties of the membranes were observed. Inclusion of CNCs has been shown to increase flux by 20% while maintaining acceptable levels of salt rejection, however, developing a consistent deposition method remains a challenge.

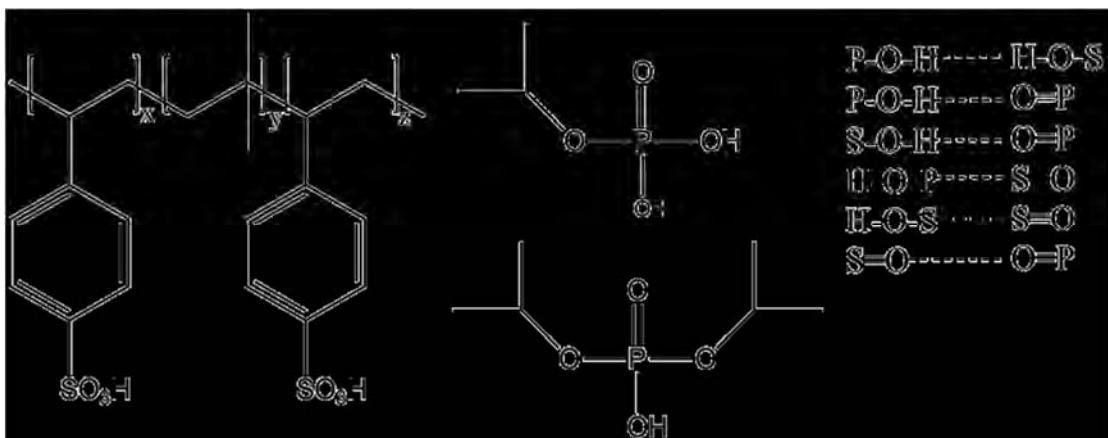


Schematic depicting the deposition of cellulose nanocrystals and subsequent interfacial polymerization of m-phenylene diamine and trimesoyl chloride to form a thin film nanocomposite membranes.

POLY 471: Effect of isopropyl phosphate incorporation on the morphology and transport properties of sulfonated poly(styrene-isobutylene-styrene) membranes

Eduardo Ruiz-Colon, eduardo.ruiz@upr.edu, Maritza Perez Perez, David Suleiman. Chemical Engineering, University of Puerto Rico at Mayagüez, Hatillo, Puerto Rico

This investigation focuses on the incorporation of phosphorus groups to improve the performance of sulfonated poly(styrene-isobutylene-styrene) (SIBS) in direct methanol fuel cell applications (DMFC). Membranes of a blend between sulfonated SIBS and isopropyl phosphate (IP) were prepared. The unique interactions between the phosphate and sulfonate groups influence the transport mechanism of protons and methanol. The resulting membranes with additional ionic domains were characterized to understand the resulting nanostructure and their effect on the transport properties for DMFC applications. Material characterization techniques employed include Fourier-Transform Infrared Spectroscopy (FT-IR), Thermal Gravimetric Analysis (TGA), Atomic Force Microscopy (AFM), and Small Angle X-ray Scattering (SAXS). In addition, transport properties such as methanol permeability; proton conductivity and others were measured to understand the connection between the resulting nanostructure and material applications. The intellectual merit of this investigation is the development of novel proton exchange membranes (PEMs) with unique ionic domains to enhance DMFC applications, while understanding how critical parameters (e.g., chemistry, water absorption and morphology) affect the proton transport mechanism within the membranes.



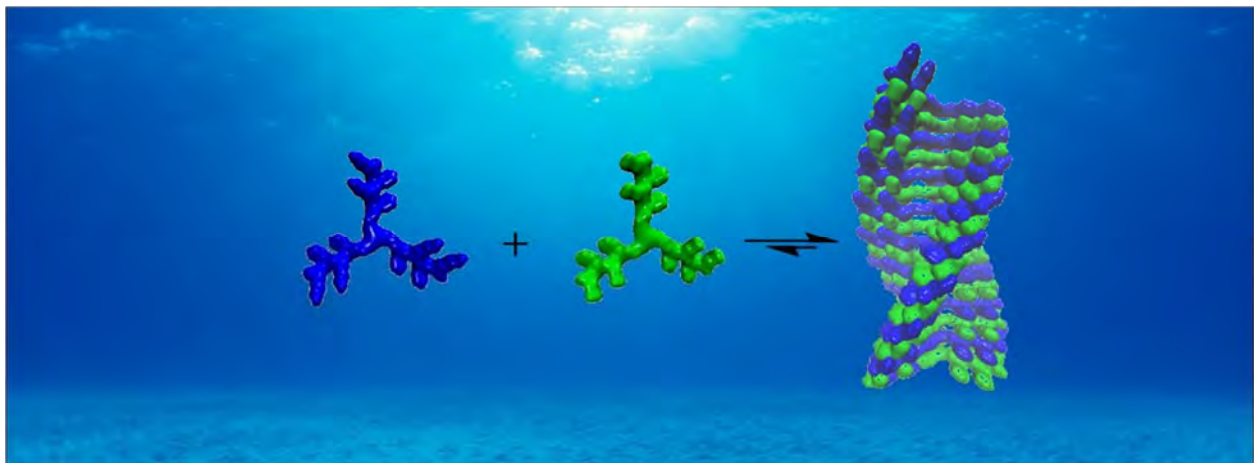
POLY 472: High fidelity supramolecular copolymers as tunable pH-responsive siRNA-carrier materials

Patrick Ahlers, paahlers@uni-mainz.de, Pol Besenius. Johannes Gutenberg-University, Mainz, Germany

Aqueous supramolecular polymers with stimuli responsive properties are promising candidates for biomedical applications. The challenge lies in installing functionality to a responsive and structurally well-defined material. Multicomponent supramolecular polymers are a particularly powerful tool to insert tunable and multiple functional groups into these dynamic materials.

In this contribution I will discuss two charge regulated supramolecular Copolymers. The first one is based on a cationic monomer with a GFKFKF encoded peptide sequence and an anionic component with a GFEFEF encoded peptide sequence. Using light scattering, circular dichroism spectroscopy and transmission electron microscopy we have investigated the influence of the comonomer feed ratio on the degree of polymerization and on the self-assembly kinetics. The fidelity in the copolymerization is remarkably high, and excess of either monomer of up to 50 mol % in the feed ratio does not lead to chain stoppering. After self-assembling into supramolecular alternating copolymers we can show the regulation of the pH-dependent switch from the copolymer to homopolymer state at acidic and basic pH values.

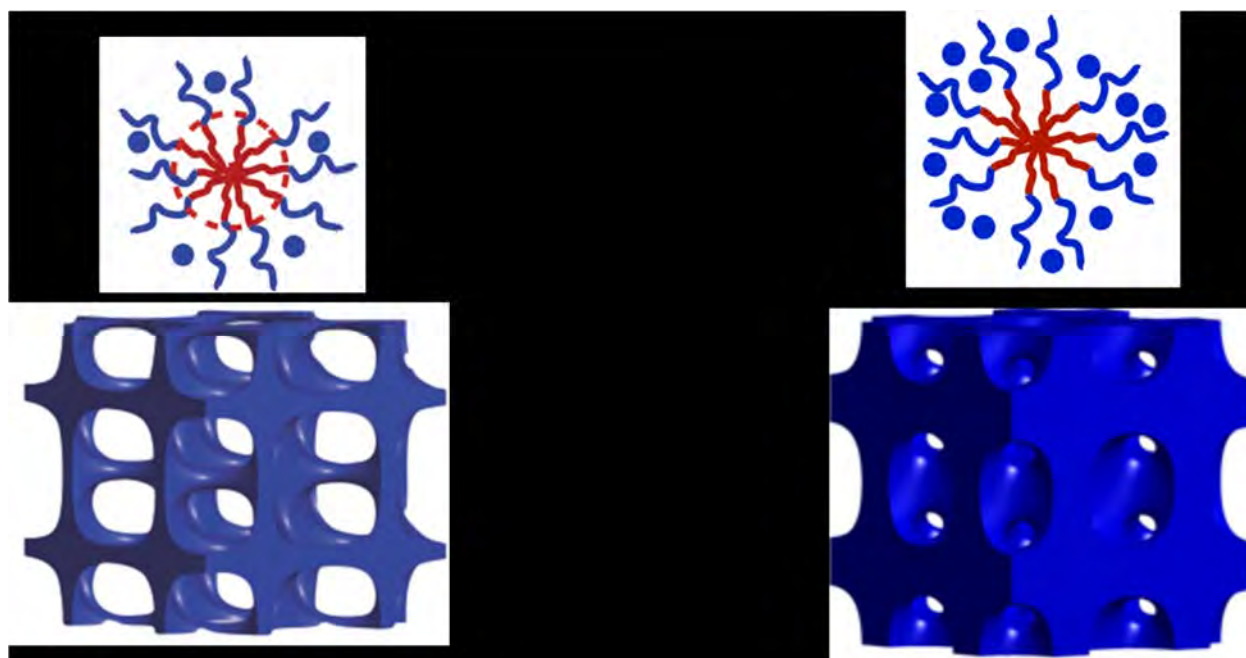
The second multicomponent system I discuss deals with reversible complexation of siRNA. Therefore we co-assemble an FHFHF encoded monomer equipped with tetraethylene glycol chains with a second monomer functionalized with an ethylene diamine dendritic building block to install positive charges at the periphery of the nanorod-like supramolecular polymers. In the polymeric state these are able to bind to siRNA. By lowering the pH below 6, the supramolecular nanorods disassemble because of the protonation of the histidine units and thus increased hydrophilicity which releases oligonucleotides via a pH-trigger as a promising strategy to release siRNA from intracellular compartments, like endosomes.



POLY 473: Kinetic-control on tunable nanomaterials

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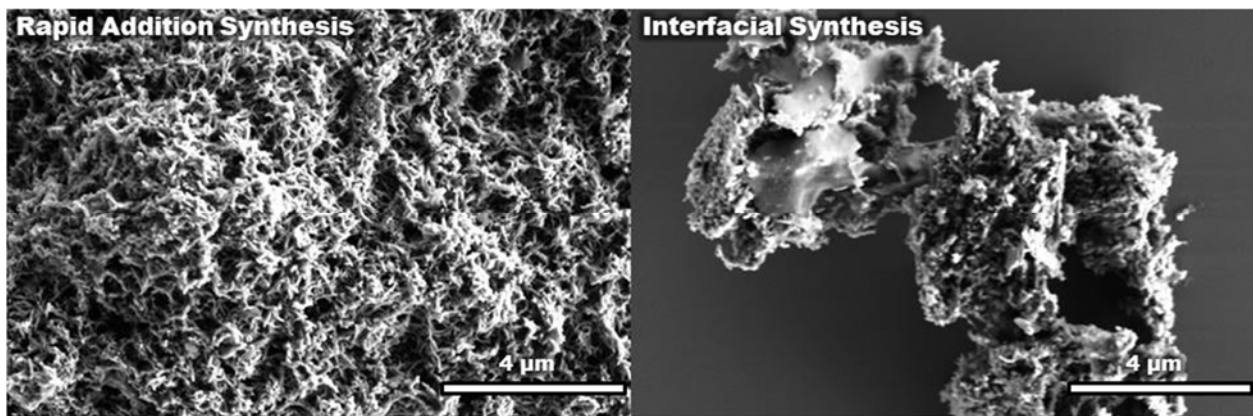
The controlled fabrications of porous materials are crucial for studying wide variety of structure-property and performance relationships in energy storage and conversion devices. Despite of great success in porous nanostructure development based upon block copolymer self-assembly, fully tunable nanostructures are remains elusive. However, fundamental studies of structure-performance relationship in energy devices require tunable materials with independent architecture control. A unique kinetic-controlled self-assembly based approach, persistent micelle templating (PMT), is recently reported introducing a block copolymer structure-directing agent, poly(ethyleneoxide-*block*-hexyl acrylate) and a solution processing guideline where the kinetic rates are adjusted by manipulating cosolvent amount. It leads to enable nanostructured materials with tunable 6-9 nm wall-thickness with constant pore diameters of 13 nm within single morphology. This opens a new era to regulate such a small architectural feature size controlling the micelle chain exchange. However, the excessive amount of cosolvent causes the formation of secondary pores into the material wall. This is addressed by improving the PMT approach via addition of major solvents of higher Hildebrand solubility parameters (δ) and minimizing the cosolvent amount. This new approach not only avoids the formation of secondary pores, it also expands the PMT window tunability. Moreover, a conceptual framework needed to realize PMT with ≤ 10 nm pores is in place by controlling polymer kinetics via solution thermodynamics.



POLY 474: Interfacial and rapid addition polyaniline nanofiber synthetic methods: A comparative study

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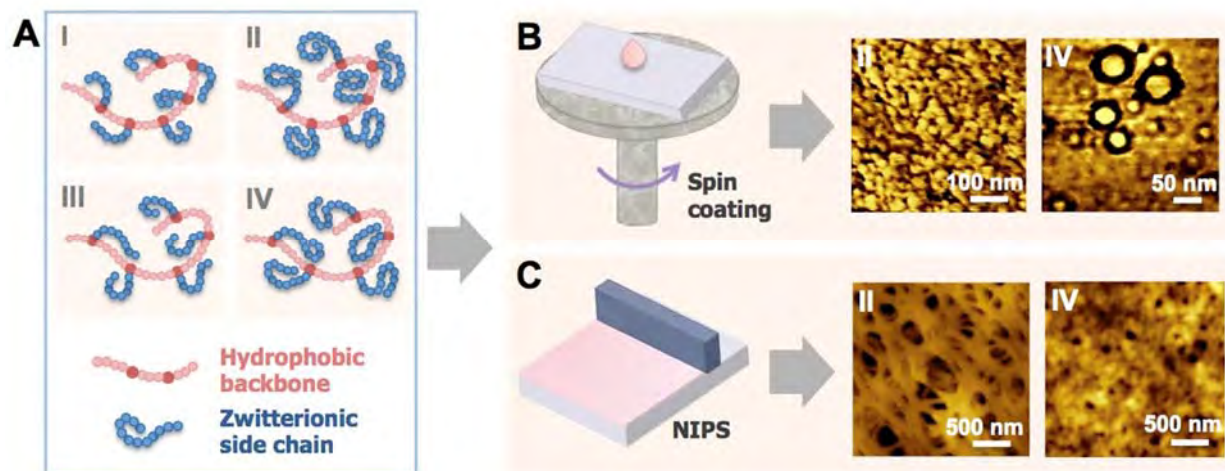
As one of the oldest known conductive polymers, polyaniline (PANI) is well known and studied. The synthesis with nanoscale morphology, namely nanofibers, has also been extensively studied with numerous synthetic methods known. However, these methods are rarely, if ever, compared. This leads to various claims of superiority for certain methods without direct evidence. In particular, this is true for the interfacial synthetic method for PANI nanofibers. This calls for a direct comparison between various methods and parameters. In this work, the two leading methods for the production of PANI nanofibers are investigated: the interfacial synthesis and the simpler rapid addition synthesis (RAS). It is shown that the interfacial synthesis method does not produce more pristine nanofibers than the RAS method, and in fact shows worse growth and suspension. Furthermore, the underlying principles of the interfacial synthesis are flawed as the phase separation does not prevent the monomer and initiator from interacting in regions other than the interface, as the monomer is free to diffuse into either layer.



POLY 475: Porous thin films with hierarchical structures formed by self-assembly of zwitterionic comb copolymers

Papatya Kaner, *papatya.kaner@tufts.edu*, Ilin Sadeghi, Ayse Asatekin. *Chemical and Biological Engineering, Tufts University, Medford, Massachusetts, United States*

Amphiphilic copolymers comprising a hydrophobic backbone with polar zwitterionic side groups are inclined to microphase separation due to molecular dissimilarity between the constituents, which stimulates interesting self-assembly in bulk. The drive for microphase separation is further enhanced in comb-shaped copolymers with this combination of constituents because of the architectural distinction between the backbone and zwitterionic side chains. We developed selective thin films whose morphology and function arise from the self-assembled nanostructure of the zwitterionic comb copolymer. First, we established a correlation between polymer chemistry, film preparation method, self-assembled domain size, and thin film morphology. To achieve that, we synthesized a series of zwitterionic comb copolymers with varying zwitterionic side chain frequency and length, and applied each of these copolymers as a thin film on glass substrate using different deposition methods. Upon examining the resulting self-assembled nanostructures, we employed for thin film composite development the zwitterionic comb copolymer that led to a continuous nanoporous network, which is intriguing for water transport applications. We applied this copolymer by non-solvent induced phase separation as a thin selective layer on a porous support to attain a mechanically strong thin film composite. Hierarchical features including 17 ± 5 nm spherical micelles along with larger nanopores of 85 ± 45 nm arose from the self-assembly of the copolymer in this bilayer system. In addition, we could govern the domain size simply by using zwitterionic homopolymer additive. The films proved ionic strength responsive permeation in ultrafiltration range with a pore density as high as 10^{13} pores/m².



(a) A family of zwitterionic comb copolymers featuring a hydrophobic backbone and zwitterionic side chains were prepared with varying side chain frequency and length. Each copolymer was applied as a thin film both by (b) spin coating and (c) non-solvent induced phase separation (NIPS), and then the surface nanostructure was imaged by Atomic Force Microscopy (AFM).

POLY 476: Facile fabrication of functional hydrogel from enzymatically synthesized polymeric DNAs

Leilei Tian, tianll@sustc.edu.cn. South University of Science & Technology of China, Shenzhen, Guangdong, China

Recently, due to the unique features of DNA, such as sequence programmability, distinct molecular recognition, and precise self-assembly, the smart DNA hydrogel has attracted tremendous research interests. DNA hydrogels are generally either fully self-assembled from oligonucleotides or cross-linked from oligonucleotide-polymer hybrids. The fabrication methods are generally costly and complicated, which limits their practical applications. Here we report a method to automatically produce hydrogels by rolling circle amplifications (RCAs). In this method, the functional cross-linking sites are introduced to the polymeric DNA chains on the meantime of RCA amplifications; and the properties of the hydrogel can be tuned in a very facile way through template design. First we developed a RCA hydrogel with horseradish-peroxidase-like catalytic capability. The catalytic hydrogel exhibits highly improved stability at elevated temperatures or during a long-term storage. Integrated with glucose oxidase, the complex hydrogel can be applied to the sensitive and reliable detection of glucose. We also attempted to realize stimuli-responsive hydrogels on the basis of the i-motif structures. Through carefully studies, the keys to fabricate a stable and stimuli-responsive hydrogel are carefully identified, i.e. the choice of a moderate intermolecular interaction and the formation of hierarchical self-assemblies between DNAs and magnesium pyrophosphate (a byproduct of RCA).

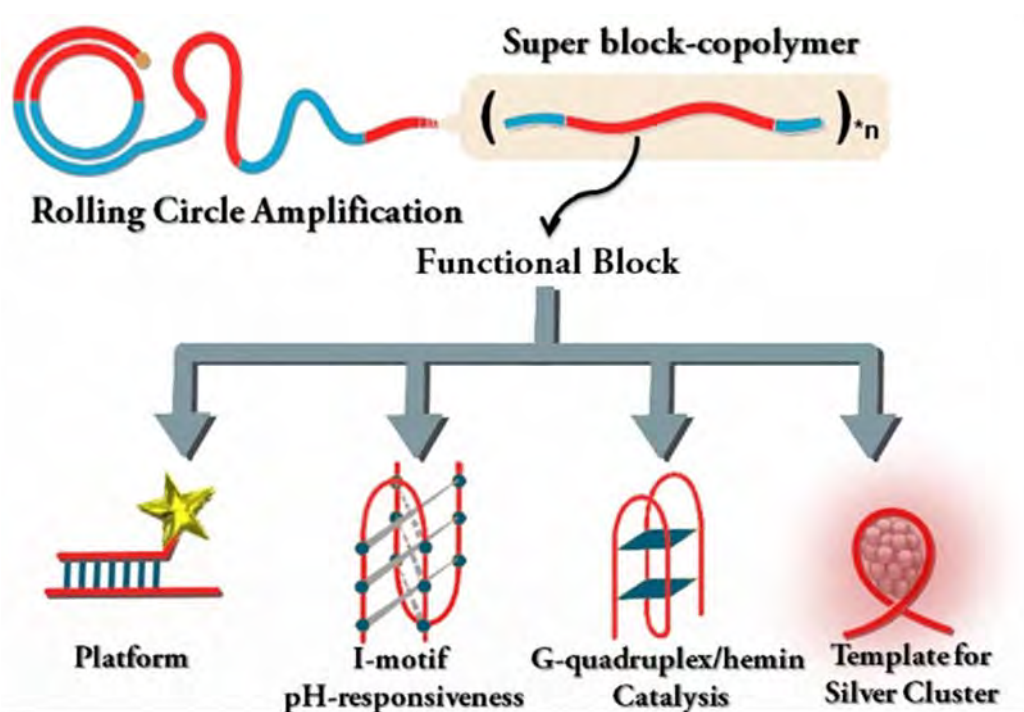
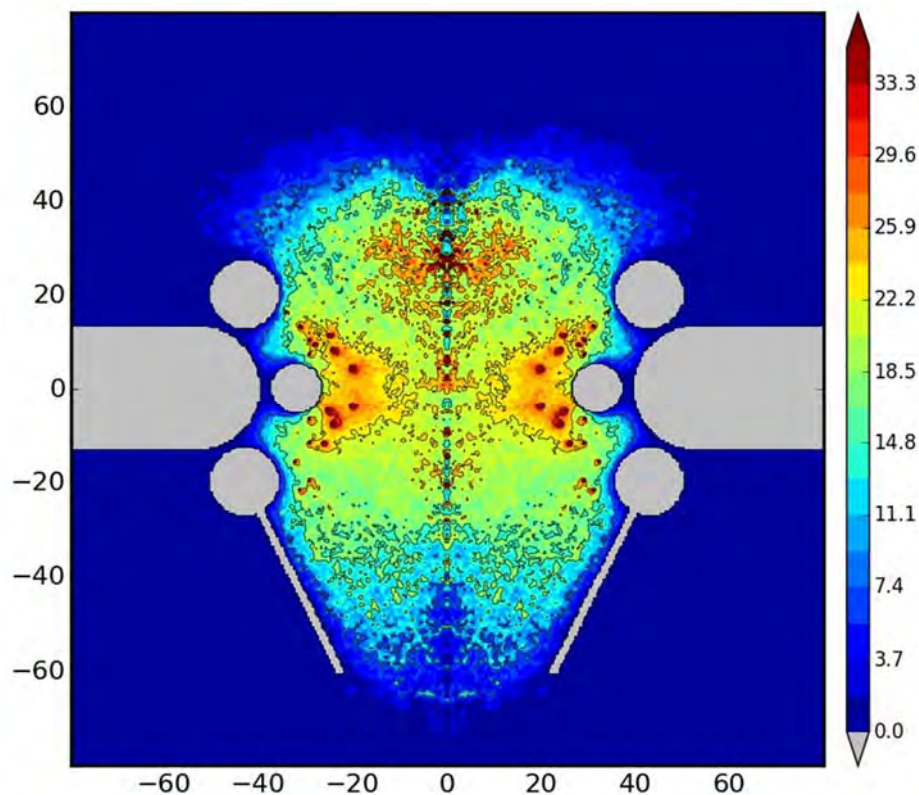


Illustration of the design strategy for the fabrication of functional DNA hydrogels from enzymatically amplified polymeric DNAs.

POLY 477: Theoretical anatomy of the Nuclear Pore Complex

Kai Huang, huangk05@gmail.com, Igal Szleifer. Northwestern University, Evanston, Illinois, United States

As the most immense and complicated biological nanopore that exists in nature, the Nuclear Pore Complex (NPC) employs intrinsically disordered proteins called phenylalanine-glycine nucleoporins (FG-Nups) to mediate the mass exchange between cytoplasm and nucleus in a highly selective and efficient way. Despite extensive study, the functional structure and transport mechanism of the NPC is still elusive and heatedly debated. We have used a molecular theory to investigate the structure of the FG-Nups. The theory explicitly considers the sequences of Nups and the interplay between electrostatics, hydrophobicity, steric interaction and the entropy of various species in the system. Our theory discovers a sophisticated structure that is asymmetric and heterogeneous, which could not be simply described as either polymer brush or gel. Our results revealed unprecedented structural details of the NPC, including the density and pairing rate of the FG-repeats, the distribution of various individual FG-Nups, and the self-built electrostatic potential inside the NPC. Based on our structural analysis we proposed a hypothesis of the NPC functional structure that allows an intuitive understanding of the path-selective transport for different cargoes and supports many recent experimental findings within a unified picture. Our insights can be used to guide the rational design of artificial smart nanopores based on polymers.

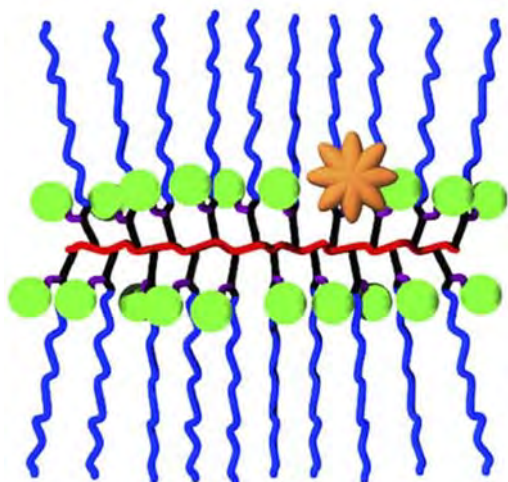


Volume fraction ($\times 10^{-3}$) of the FG-Nups inside the NPC predicted by the molecular theory. The grey region shows the coarse-grained nuclear envelop, scaffolds and basket.

POLY 478: Backbone-degradable brush polymers: Synthesis and biological applications

Peyton Shieh, *pshieh@berkeley.edu*, Jeremiah A. Johnson. MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

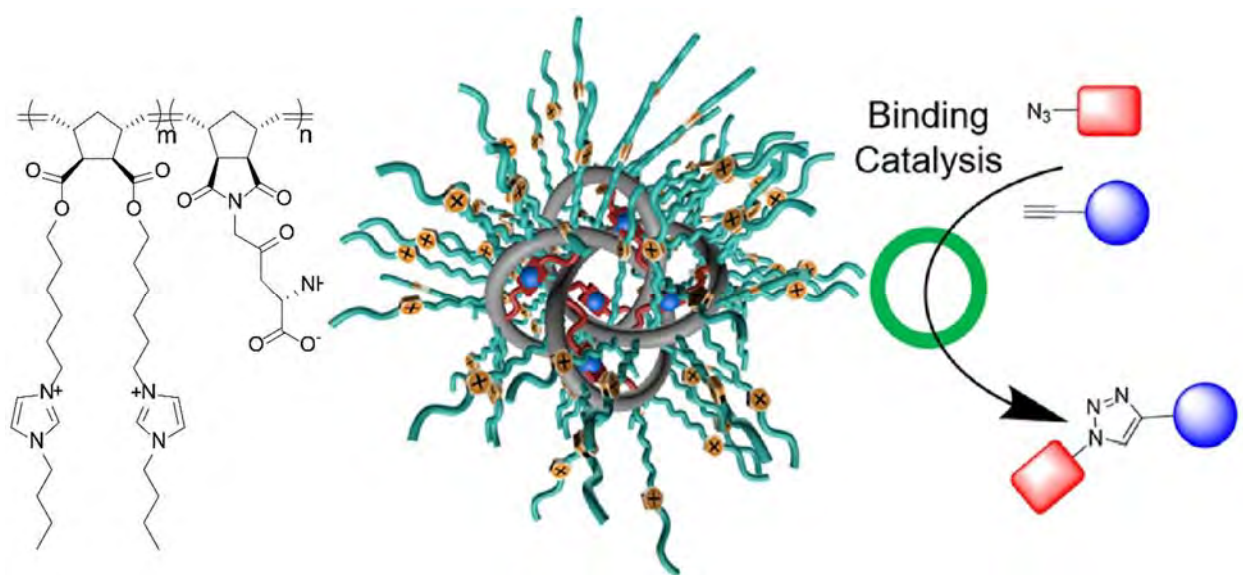
Ring opening metathesis polymerization (ROMP) of strained alkenes is a powerful method to prepare polymeric scaffolds for applications in biology. A common limitation of these materials, however, has been their all-carbon backbone, which significantly limits their biodegradability. To address this issue, laboratories have developed a variety of strained-alkene monomers bearing heteroatoms that can degrade under acidic conditions. These monomers, however, typically require complex synthetic sequences and degrade only under forcing conditions. Here, we present an alternative solution to develop backbone degradable brush polymers prepared via graft-through ROMP, enabling precise control over degradation kinetics under mild aqueous conditions. With these polymers in hand, we describe our efforts to use these backbone degradable polymers for applications in biology and biomedicine.



POLY 479: Highly efficient single-chain organic nanoparticle catalyst for click chemistry

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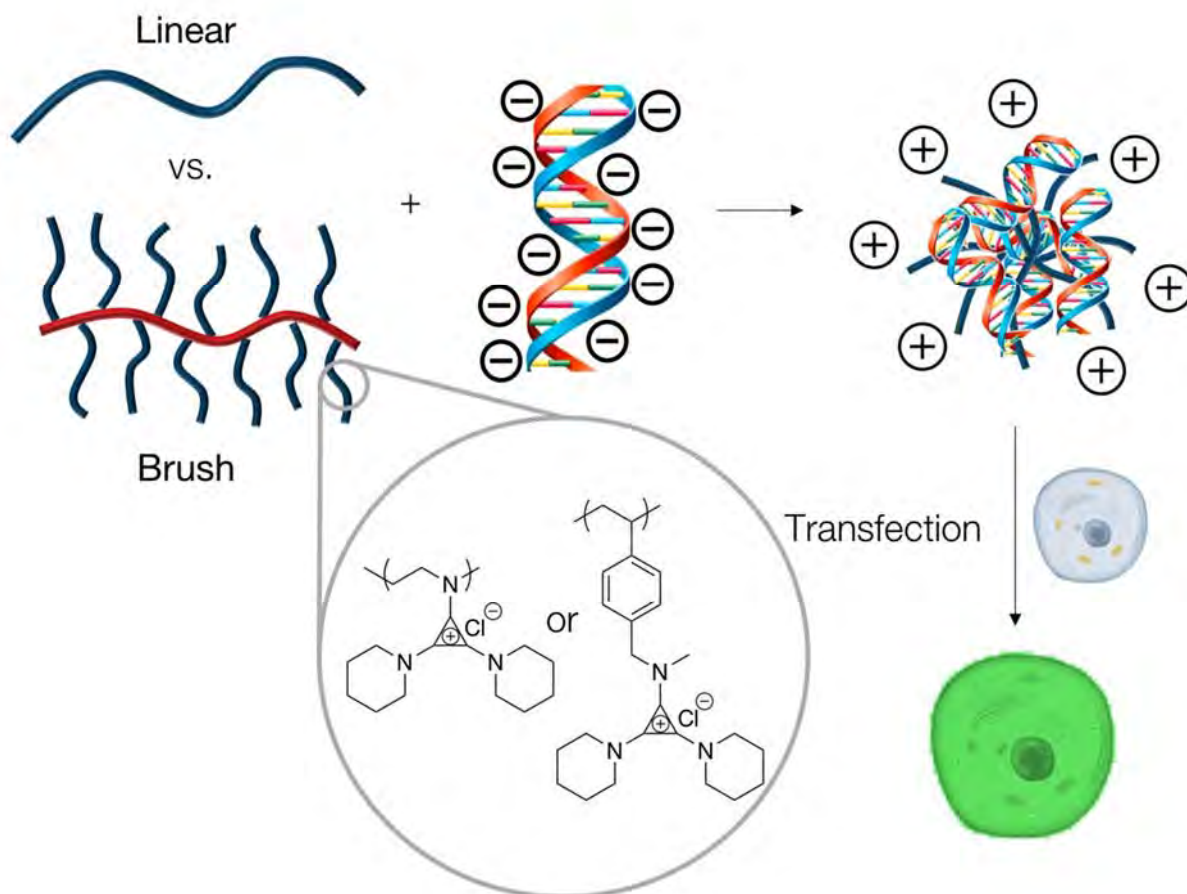
Single-chain polymeric nanoparticles (SCPNS), formed by the controlled intramolecular crosslinking of linear polymers, have received intense interest because of their finely tuned properties. Applications of SCPNs have been reported in bioimaging, nano-assembly, and catalysis. Catalysis by SCPNs is particularly interesting because their enzyme-like structure can afford significant increases in efficiency, selectivity, and stability. This talk will focus on a copper crosslinked single-chain polymeric nanoparticle (CuSCPNS) that folds by both hydrophobic interactions and coordination between amino acid side-chains and copper ions. The CuSCPNS significantly improve the efficiency of CuAAC click reactions in aqueous media with ppm catalyst loadings. A structure-activity relationship was carried out using a fluorogenic click reaction, demonstrating the enzyme-like binding process between the polymer scaffold and substrates. Understanding the detailed mechanism of SCPNS based catalyst as well as their structure-activity relationship may facilitate future designing of highly efficient polymeric catalysts with different functionalities, and expanding their potentials applications.



POLY 480: Cyclopropenium polymers: A platform for nonviral gene delivery materials

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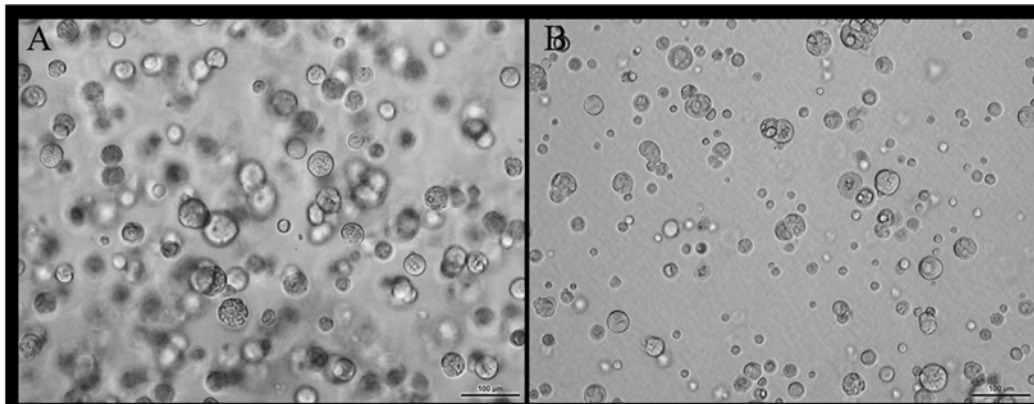
Gene therapy holds potential as a treatment for many diseases, but is limited by the inefficiency, toxicity, and lack of generality of the delivery vector. Cationic polymers are a promising nonviral vector because of their biocompatibility, their modular chemistry, and the ability to finely tune their size, shape, and properties. This presentation will focus on a novel class of cationic polymers that incorporates cyclopropenium (CP), a highly modular, stable, and electron-rich Hückel aromatic ion. Polymers containing either main-chain or pendent secondary amines can be rapidly functionalized with CP providing access to a wide variety of polymer architectures. Linear polymers can be readily synthesized via controllable radical polymerizations and brush polymers are prepared from sequential orthogonal living polymerization techniques. This presentation will compare CP polymers of varying shape and backbone for their biocompatibility and DNA transfection efficiency.



POLY 481 Assembly and differentiation of salivary stem/progenitor cells in bioactive synthetic matrices

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Salivary glands produce saliva in response to a wide range of biochemical input and environmental cues to maintain oral homeostasis. Xerostomia is the inevitable consequence of the standard radiation treatment for head and neck cancers, and leads to severe dental issues, difficulties in swallowing, speaking, and eating, gradual weight loss, and overall discomfort. Current therapies have not proven effective in long-term application and tissue engineering represents a promising alternative towards the treatment of hyposalivation. We have successfully isolated human salivary gland stem/progenitor cells (hS/PCs) from patients prior to the radiation treatment and characterized these cells on 2D and in 3D in a physiologically relevant multicellular format. We have synthesized hyaluronic acid (HA)-derived synthetic matrices with time-dependent, dynamic features that promotes the organized growth and 3D assembly of hS/PCs. Multicellular structures formed in these hydrogels had an average diameter of 50-80 μm and individual cells expressing key stem/progenitor markers were held together through tight junctions. Further modification of the synthetic environment with covalently conjugated peptide signals derived from the basement membrane and the surrounding mesenchyme, RGDSP (from fibronectin), TWSKV (from perlecan domain IV), YIGSR and IKVAV (from laminin 111), led to the formation of more organized structures with improved cell viability, enhanced cell proliferation and a general decrease in cellular expression of progenitor markers. Cells cultured in gels displaying YIGSR or TWSKV signals expressed a higher level of the acinar marker as compared to those maintained in peptide-free control gels. In hydrogels presenting both RGDSP and TWSKV signals, cellular response was dominated by RGDSP, and cells tend to be more ductal. Collectively, the synthetic hydrogel with dangling peptide and time-dependent features creates a biomimetic environment that stimulates cellular organization, differentiation, and salivary gland function.

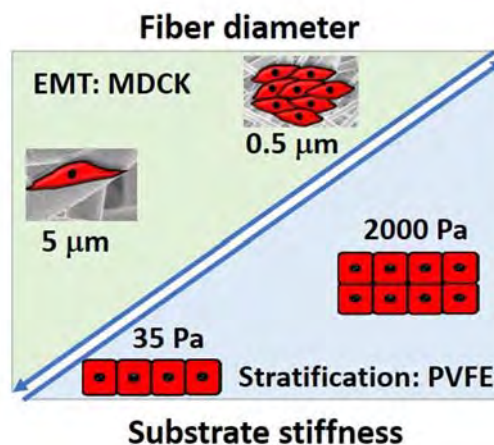


Brightfield images of hS/PC spheroid assembly after 14 days of culture in RGDSP peptide modified hydrogel network (A) and no peptide control gels (B).

POLY 482: Tuning matrix properties to regulate the phenotype and functions of epithelial cells

Anitha Ravikrishnan¹, anitha@udel.edu, Eric W. Fowler¹, Xinqiao Jia^{1,2}. (1) Material Science and Engineering, University of Delaware, Newark, Delaware, United States (2) Department of Biomedical Engineering, University of Delaware, Newark, Delaware, United States

There is a critical need for fundamental understandings on how biochemical and biophysical cues from the cellular microenvironment regulate epithelial cell fate. Using electrospun fibrous scaffolds with surface conjugated cell-adhesive motifs, we investigated the effects of fiber diameter on epithelial-to-mesenchymal transition (EMT), a process in which epithelial cells undergo drastic cytoskeletal changes and adopt a more mesenchymal-like morphology. Madin-Darby canine kidney (MDCK) epithelial cells cultured on 0.5 μm scaffolds formed closely packed cell clusters held together by tight junctions. Contrarily, on the 5 μm scaffolds they adopt a more spindle-shaped morphology, indicating EMT. Upon stimulation with hepatocyte growth factor (HGF), an EMT inducer, cells on sub-micron scaffolds acquired mesenchymal-like morphology and started to scatter, whereas those on 5 μm fibers remained anchored on individual fibers without a significant morphological change. In a separate project, we evaluated the effects of substrate stiffness and ligand presentation on the differentiation of primary porcine vocal fold epithelial cells (PVFE). Synthetic matrices presenting key peptide signals derived from laminin (AG73) and fibronectin (RGD) were prepared using hyaluronic acid derivatives carrying thiol or acrylate groups and maleimide-functionalized peptides. Two types of hydrogels with varying stiffness (G' : 35 and 2000 Pa) were examined. Our results show that PVFEs readily attached to both substrates, but only formed stratified epithelium on stiffer hydrogels in presence of both AG73 and RGD peptide signals, indicating both matrix stiffness and cell-adhesive cues serve as an important regulator of epithelial cell fate. This work highlights the importance of topographical cues and biomechanical signals in regulating cellular interaction and differentiation.



Biophysical cues of synthetic matrices mediate the phenotypes and functions of epithelial cells.

POLY 483: Interactions between biosystems and 3D-microstructured surfaces

Sebastian Anders¹, *sebastian.anders@imtek.uni-freiburg.de*, *Nayana Tusamda Wakhloo*², *Oswald Prucker*¹, *Karine Anselme*², *Juergen Ruehe*¹. (1) *Department of Microsystems Engineering - Chemistry and Physics of Interfaces, University of Freiburg, Freiburg, Germany, Germany* (2) *Institut de Science des Materiaux de Mulhouse (IS2M), Université de Haute-Alsace, Mulhouse, France*

Previous studies have shown that the nucleus of cancer cells can deform and wrap themselves around microstructures (post arrays) under certain conditions (Figure 1 a). One key parameter in such systems is the chemical property of the surfaces which controls the affinity of the cells to the substrate. The mechanical parameters of the used materials especially on microstructured surfaces might be of equal importance for the cell adhesion and deformation. In this project we study post arrays that are made from hydrogels, which are very soft materials when swollen in water. The Young's modulus is in the area of cancer cells so that the cells are even able to deform them. The polymer is crosslinked in the swollen state and the microstructures can be generated by lithographic method. The hydrogel currently employed is based on the cell-repellent polydimethylacrylamide, PDMAA. Because of entropic reasons the surface is however cell attractive. The surface can be modified so that the surface chemistries on top of the pillars and in the valleys between are different. Its surface can be coated with a cell-attractive polymer like poly(dimethylacrylamide - sodium 4-vinylbenzenesulfonate - methylacryloyloxybenzophenone), P(DMAA-SSNa-MABP) or the cell-repellent polymer poly(dimethylacrylamide - methylacryloyloxybenzophenone), P(PDMAA-MABP). By microcontact printing the top of the pillars can be coated with cell-repellent polymer like PDMAA. This finally leads to arrays with cell-attractive valleys and cell-repellent top faces (Figure 1 b). First cell investigations with SaOS-2 cells have shown that the nuclei are deformed on both coated and uncoated microstructures.

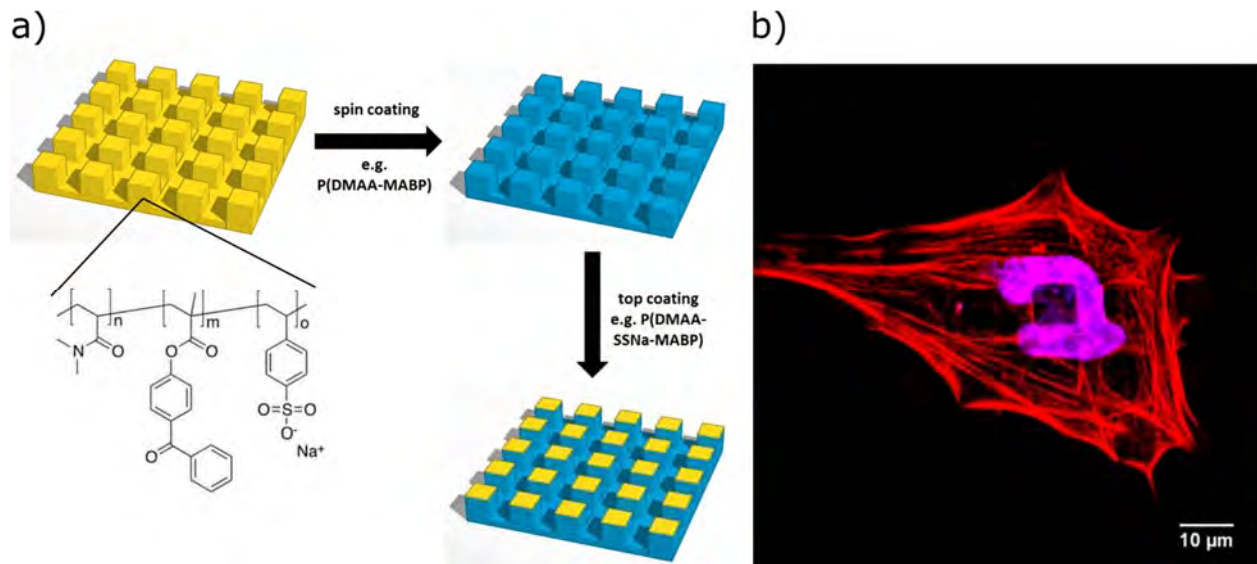


Figure 1: a) Surface modification of hydrogels ; b) deformed cell

POLY 484: Polyproline as a minimal mimic of antifreeze glycoproteins and its use in cellular cryopreservation

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Antifreeze (glyco)proteins, AF(G)Ps, are a class of unique biomacromolecules found in the tissues and blood serum of extremophile species, allowing them to survive in sub-zero temperatures. One of the key properties of AF(G)Ps is to inhibit extracellular ice crystal growth, which is often associated with cell death during cryopreservation. This ice recrystallization inhibitory (IRI) effect has many potential applications in cell/tissue storage and biobanking, enabling future regenerative medicine treatments. However, AF(G)Ps are potentially immunogenic, and are difficult to synthesise or extract from natural sources. We are therefore developing new IRI active biomimetics of AF(G)Ps based on synthetic macromolecular scaffolds, to both understand how they function and to translate into biomedical applications; by replacing or enhancing solvent-based cryoprotective techniques.

Whilst no X-Ray crystal structure of AF(G)P exists, one of its key structural components which has been identified is its adoption of an amphipathic polyproline II (PPII) helix. We hypothesised that polyproline could be a minimal AF(G)P mimetic owing to its intrinsic amphiphilicity and its similar adoption of the synonymous PPII helix.

Here we report on the IRI activity of polyproline, which is capable of acting as a minimum (and easily accessible) biosynthetic mimic of antifreeze proteins, whilst significantly enhancing adherent cell line recovery in cryopreservation to over 50% (from ~ 25% in DMSO alone). We will demonstrate polyproline's potential as a versatile additive in the emerging field of macromolecular cryoprotectants.

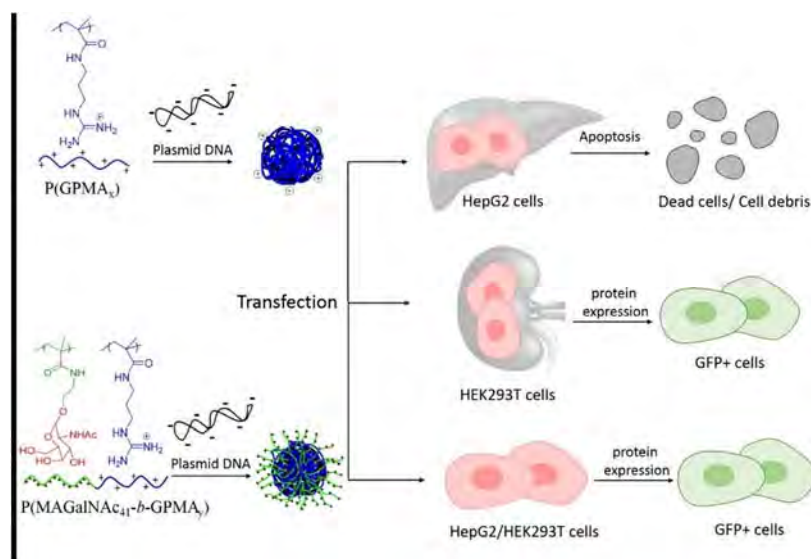


A) Amphipathic solution structure of AFGP. B) Amphipathic surface model of our synthetic AFGP biomimetic. C) 'Splat' microscopy of uncontrolled ice crystal growth (left) and inhibited growth in the presence of our synthetic biomimetic (right)

POLY 485: Guanidium-based cell penetrating polymers as delivery agents trigger apoptosis in HepG2 cells but can be alleviated by conjugating to hydrophilic block

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Gene and cell therapy hold great promise to treat a wide variety of acquired and inherited diseases. Guanidinium-containing polycations have attracted recent interest to be incorporated into delivery vehicles due to their membrane penetration properties and potential to increase delivery efficiency. Herein, a series of 3-guanidinopropyl methacrylamide (GPMA)-derived homopolymers and block copolymers were synthesized as gene delivery vectors via aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization. In the block copolymers, methacrylamidoethyl *N*-acetyl-D-galactosamine (MAGalNAc) derived from *N*-acetyl-D-galactosamine (GalNAc) was conjugated to GPMA as a hydrophilic block to specifically target hepatocytes via asialoglycoprotein receptors (ASGPRs), and provide steric protection to polymer-DNA complexes (polyplexes) from colloidal aggregation. Cellular internalization, transfection efficiency, and cytotoxicity of the polyplexes were studied *in vitro* using human hepatocellular carcinoma (HepG2) cells and human embryonic kidney (HEK 293T) cells. Results showed that polyplexes formed with P(GPMA) homopolymers were internalized into cells very effectively through both endocytosis and membrane penetration. However, in HepG2 cells, P(GPMA) polyplexes were highly toxic and triggered apoptosis. In general, the formation of polyplexes with block copolymers resulted in higher cell viability in HepG2 cells. Interestingly, the toxicity of P(GPMA)-bonded polyplexes were much lower in HEK 293T cells. In conclusion, guanidinium-based P(GPMA) polymers as gene delivery vehicles should be carefully tailored towards specific cell/tissue types to avoid unwanted toxicity.



POLY 486: Encapsulation of conjugated polymers for use as biological imaging agents

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Conjugated polymers (CPs) are organic semiconductors with a backbone of alternating multiple and single bonds which exhibit efficient coupling between optoelectronic segments. They have been used in a number of applications due to their optical properties such as bright photoluminescence and photo-stability. However, they are inherently hydrophobic which means, and in order to generate nanoparticles, either the micro-emulsion or nanoprecipitation method is used.

Conjugated polymer nanoparticles (CPNs) have a number of advantages over quantum dots (QDs) such as ease of processing, large absorption coefficients, tuneable optical properties, controllable dimensions and biologically inert components circumventing the issue of heavy metal toxicity of QDs. By using the nanoprecipitation method, we are able to encapsulate the CPs inside different chemical compositions and have done so with hydrophobins, as well as phospholipids, silica shells and a biodegradable polymer. We present work with conjugated polymer encapsulated in the self-assembling polymer *poly(styrene-co-maleic acid)* (PSMA) containing iron oxide with an emission peak of 657 nm and a quantum yield of 21%. We also show comparison of the conjugated polymer relating to size and optical properties dependent on the micelles used, These nanoparticles have an average size of 65 nm and a zeta potential of -30 mV. We show that the nanoparticles are uptaken by HeLa, HCE and T-cells through subsequent imaging with a confocal scanning laser microscope, as well as being inherently non-toxic to cell viability and proliferation.

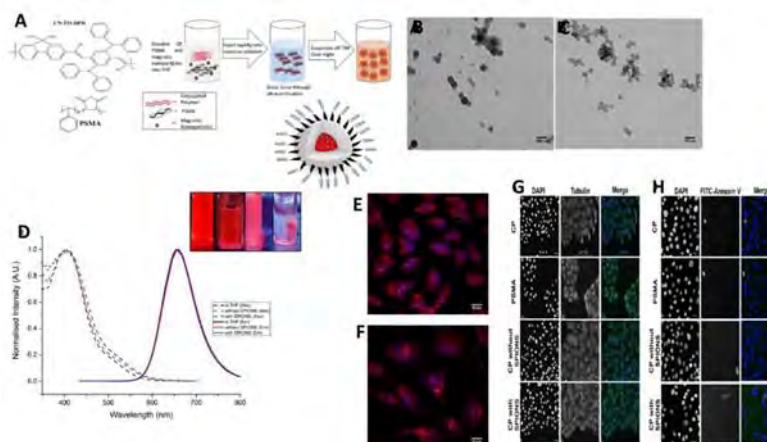
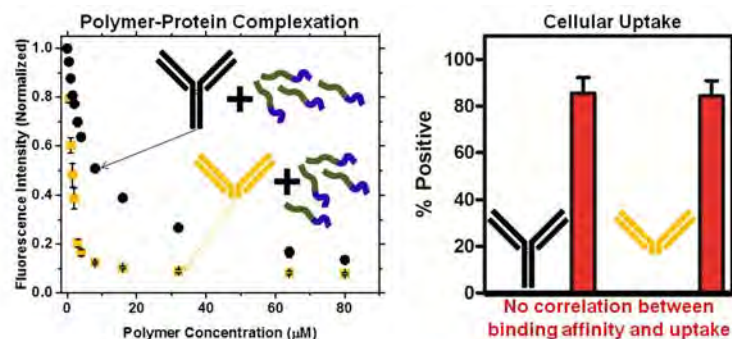


Figure A) schematic overview of the process of making the CPN containing iron oxide. TEM images showing B) CPNs not containing iron oxide vs C) CPNs containing iron oxide (small dark dots within the NP) Scale bar = 100 nm. D) Spectra of absorption and emission of the CP, insert image of CPNs in water against magnet after 24 hrs. E)F) Uptake study of CPN in HeLa cells, E) without iron oxide, F) with iron oxide. G)H) Cytotoxicity study of HeLa and HCE cells utilising annexin V stain kit.

POLY 487: Role of transporter-cargo binding in polymer-mediated intracellular protein delivery

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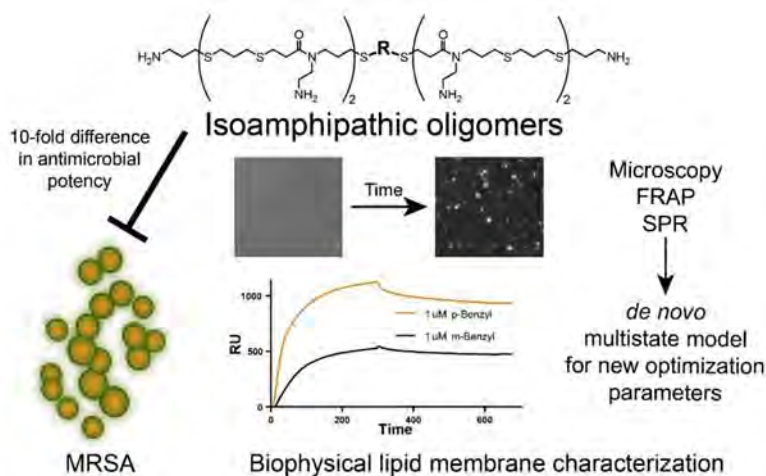
Delivering biologically active macromolecules into the cellular environment is a promising approach for both the development of novel therapeutics and the discovery of new cellular processes. However, progress towards these goals is hindered because the cellular membrane generally acts as a restrictive barrier to exogenous biomacromolecules. Finding ways to surmount the barrier is crucial because it has far reaching implications in the fields of nanomedicine and fundamental cell biology. Historically, cell penetrating peptides (CPPs) have provided one way to cross the cellular membrane and deliver other biomacromolecules. More recently, CPPs have been mimicked with synthetic block copolymer scaffolds to create CPPMs resulting in more effective membrane penetrators. Both CPPs and their mimics can be used to non-covalently complex with or bind to protein cargo for delivery applications eliminating the need to employ covalent conjugation chemistry methods. This work sought to explore the non-covalent nature of polymer-cargo association, namely binding strength, and to correlate it to intracellular delivery using a model protein delivery system featuring CPPMs. Specifically, ring-opening metathesis polymerization (ROMP)-based CPPMs were examined for their ability to bind to a variety of protein cargoes, including an antibody, with various isoelectric points and sizes. Binding curves were obtained using fluorescence quenching experiments and fit using a multiple, independent sites binding model. The calculated dissociation constants varied by orders of magnitude, from strong to weak binding, depending on the charge and size of the protein cargo. This demonstrated that ROMP-based CPPMs have binding preferences for some protein cargoes over others. Since higher polymer-protein affinity should shift the binding equilibrium to favor complex formation, it was anticipated that increased binding ability would correlate with increased cellular uptake of protein. Surprisingly, intracellular uptake studies revealed that despite the large range of dissociation constants among complexes, protein internalization levels were uncorrelated with CPPM binding ability.



POLY 488: Multistate characterization of interactions of isoamphipathic oligomers with bacterial mimetic membranes

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The amphipathic nature of many antimicrobial peptides is critical to their action against bacteria and has been well studied. It is generally understood that their cationic charge initiates binding and hydrophobicity directs insertion steps toward membrane disruption. These simple parameters have long rationalized interactions within this molecular class even for more complex alpha-helix forming peptides, where interfacial hydrophobicity affects function. Aside from a few examples (e.g. daptomycin), this class of membrane-disrupting antimicrobials are typically not selective enough for systemic delivery, but many are sufficient for topical use. This clinical difficulty likely stems from a lack of additional fundamental parameters to optimize within this antimicrobial class. Using sequence-defined oligothioetheramides (oligoTEAs), we have created isomers of the same size, shape, and amphipathicity to explore new parameters for sequence-structure-function optimization. Despite their extensive physical and solution-phase similarities, our oligoTEA isomers show approximately a 10-fold difference in potency against bacterial strains including methicillin-resistant *Staphylococcus aureus* (MRSA). Biophysical characterization of our oligoTEAs on supported lipid bilayers reveal distinct interactions observable by fluorescence microscopy, fluorescence recovery after photobleaching (FRAP), and surface plasmon resonance (SPR). These techniques support and describe multiple kinetic states of binding, insertion, aggregation, and aggregate extraction from the lipid membrane surface. We have characterized the flux of membrane extraction, focusing on concentration dependence and kinetics of lipid removal. Also, changes to membrane fluidity of the supported lipid bilayer contribute to specific kinetic parameters in the membrane disruption. In all, these observations and parameters have converged to create a comprehensive model that describes the multi-state process of oligoTEA-membrane disruption, outside of typically understood cationic or hydrophobic composition.

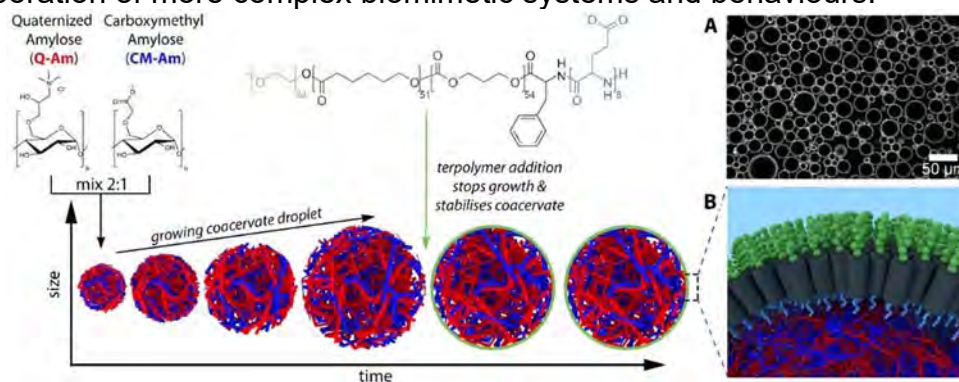


POLY 489: Copolymer-stabilized coacervate microdroplets as multicompartmentalized artificial cells

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Complex coacervates are a membrane-free, solution-phase material that are formed by the electrostatic interactions between oppositely-charged macromolecules. They are interesting from an artificial cell perspective because they resemble the cell cytosol, particularly as a crowded and charged environment. However, due to their inherently membrane-free nature, they are unstable, with coacervate droplets prone to coalescence on relatively short time scales, which inhibits their use in longer experiments. This work describes the development of a triblock copolymer that self-assembles on the surface of an amylose-based complex coacervate, forming a robust, passivating layer that prevents droplet coalescence and content mixing. These discrete, cell-sized, polymer-stabilized coacervate droplets are capable of encapsulating macromolecular cargo, which remain in an active conformation. In addition, the polymer membrane is semi-permeable, enabling the incorporation of a simple enzymatic cascade in different protocell populations, a rudimentary demonstration of protocellular communication.

This robust scaffold has now been utilized to demonstrate the formation of a multicompartment system. Through the encapsulation within the coacervate protocell of nanometre-sized polymer vesicles containing functional enzymes, it is possible to generate assemblies reminiscent of organelles within a eukaryotic cell. This structural motif was used to incorporate detrimental enzymes such as amylase (degrades the amylose network) into the polymersomes, creating hostile yet chemically isolated nanoenvironments akin to the lysozyme. These polymer-stabilized coacervate droplets already offer many characteristics that are interesting to the artificial cell community, while also being modular and open to further polymer engineering, paving the way for the incorporation of more complex biomimetic systems and behaviours.



Hierarchical self-assembly of a triblock copolymer on the surface of a coacervate droplet to induce stabilization. **A** Confocal image of copolymer-stabilized coacervate droplets. **B** Proposed model of self-assembly, directed by complementary charge interactions between the polymer (-ve) and coacervate (+ve).

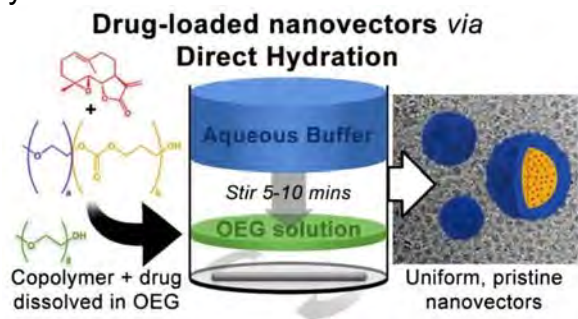
POLY 490: Drug-loaded (copolymeric) nanovectors *via* direct hydration as a new nanomedical platform for leukemia therapy

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Although there has been much research activity on the topic of nanoscopic drug delivery, there is currently a lack of translated research that is receiving attention in the medical community. Adopting an integrated approach to the development of nanomedical therapeutics offers a solution to the bottleneck that exists at the present time. Working at the interface between functional polymeric nanomaterials and cancer biology, however challenging, opens that way to develop functional nanomaterials that can be effective in a biomedical context. With this in mind, we have developed a biodegradable nanovector technology comprising poly(ethylene glycol)-*block*-poly(trimethylene carbonate) (PEG-PTMC) block copolymers that can be loaded with hydrophobic drugs and assembled without the use of any harmful solvents *via* direct hydration (**Figure 1**).

To demonstrate utility of this nanomedical platform we have studied the potential delivery of a leukemia-specific drug, parthenolide (PTL), which has shown promise but is yet to be translated in a medically viable system. Acute lymphoblastic leukaemia (ALL) accounts for more deaths in childhood than any other cancer and survival in relapsed disease has plateaued at around 56%. Because current treatment-related toxicity is so high there are life-threatening complications in over 60% of survivors and, therefore, there is an urgent need for less toxic, more efficacious therapies. Although PTL has shown promising results up to this point, it cannot be effectively utilized *in vivo* due to its hydrophobicity.

PTL-loaded PEG-PTMC nanovectors have well-defined size characteristics, highly efficient drug loading, controlled release, are inherently non-toxic and demonstrate therapeutic efficacy and specificity towards ALL *in vitro*. Physicochemical characterization of the resulting nanovectors was conducted using asymmetric flow field-flow fractionation (AF4) coupled with MALS/QELS, supported by ¹H (NOESY) NMR to confirm high levels of drug encapsulation. The producibility of PEG-PTMC nanovectors makes this an exciting platform technology for further exploitation in anticancer (nano)therapy.



POLY 491: Targeted delivery of tumor-responsive polymer anticancer prodrugs

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The main challenge for chemotherapy is lack of selectivity which leading to severe side effect and low therapeutic efficacy. Targeted delivery and tumor-specific activation/release are the main strategies to improve selectivity. Their combination can substantially enhanced the chemotherapy through greatly improving the selectivity. Tumor-targeting polymer prodrugs comprising of Cu^{2+} and glutathione responsive linkers were designed and synthesized in this paper (Figure 1). They could release toxic Cu^{2+} complex and other anticancer drugs in cancer cells. Both in vitro and in vivo experiments indicated they had great anticancer efficacy, even against multidrug resistance cancers.

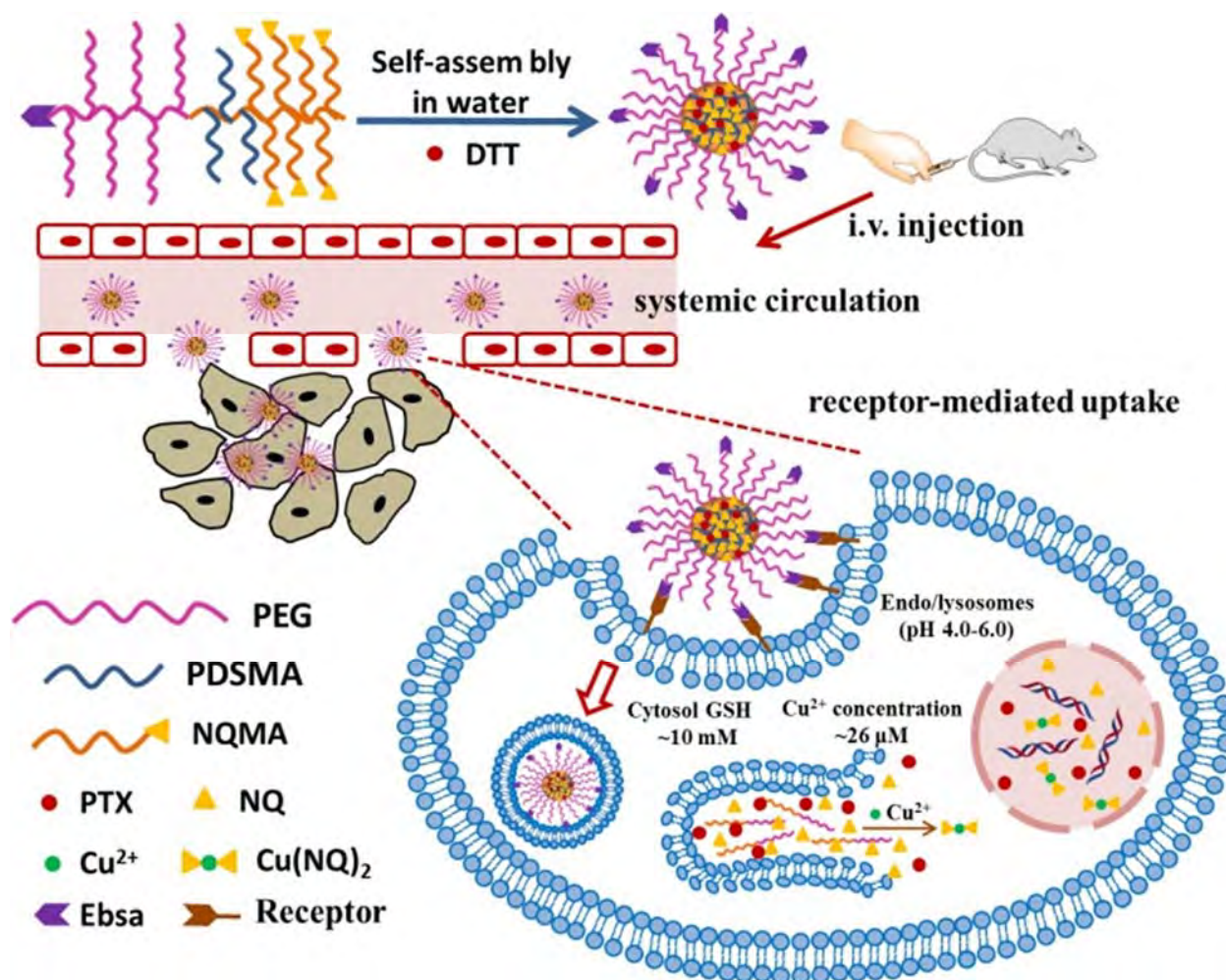


Figure 1. The design of the targeted polymer anticancer prodrugs with tumor-responsive release.

POLY 492: Programmable liquid crystalline elastomers using light activated covalent adaptable networks

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Covalent adaptable networks (CANs) allow otherwise static networks to become dynamic under specific and controllable stimuli. By implementing CANs into a liquid crystal elastomer (LCE), the ability to harness the thermoreversibility of LC phase transitions with dynamic network behavior, enables the programming of reversible two-way shape changes by covalently stabilizing directed order. Through the use of radical generating photoinitiators to activate a cascading bond exchange reaction, the covalent adaptability is selectively confined to irradiated areas with light, without impinging on the thermal LC phase transitions, thus creating a highly spatiotemporally controlled, programmable system. LCEs were programmed using heat and mechanical deformation, initiated by the exchange reaction. The exchange enables the covalent network to reorganize towards equilibrium under the applied conditions. It relieves stress incurred on the system from the mechanical deformation and reorganizes the permanent network. We have implemented this into two applications which take advantage of the unique combination of CANs and LCs. This includes programming a physical two-way shape change and a reversible color change, which is added into the system through incorporation of a chiral dopant. The chiral dopant induces a helical twist in the alignment of the mesogens giving rise to a predictable reflection band that can be mechanically strained to change the periodicity of the helix and yield a shifted reflection band. The system is only limited by the magnitude and direction of implementable strain. Understanding the phase transition of the LC component of the elastomer system allows for control over the optical properties along with the amount of reversible actuation that can be obtained by the system. This research is important for understanding how LCEs can be transitioned into applications such as soft robotics and optics.

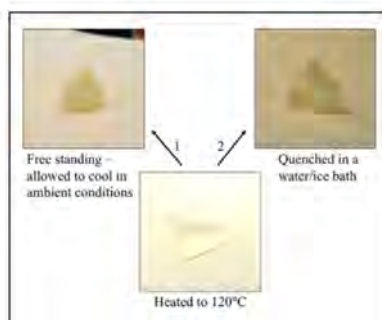
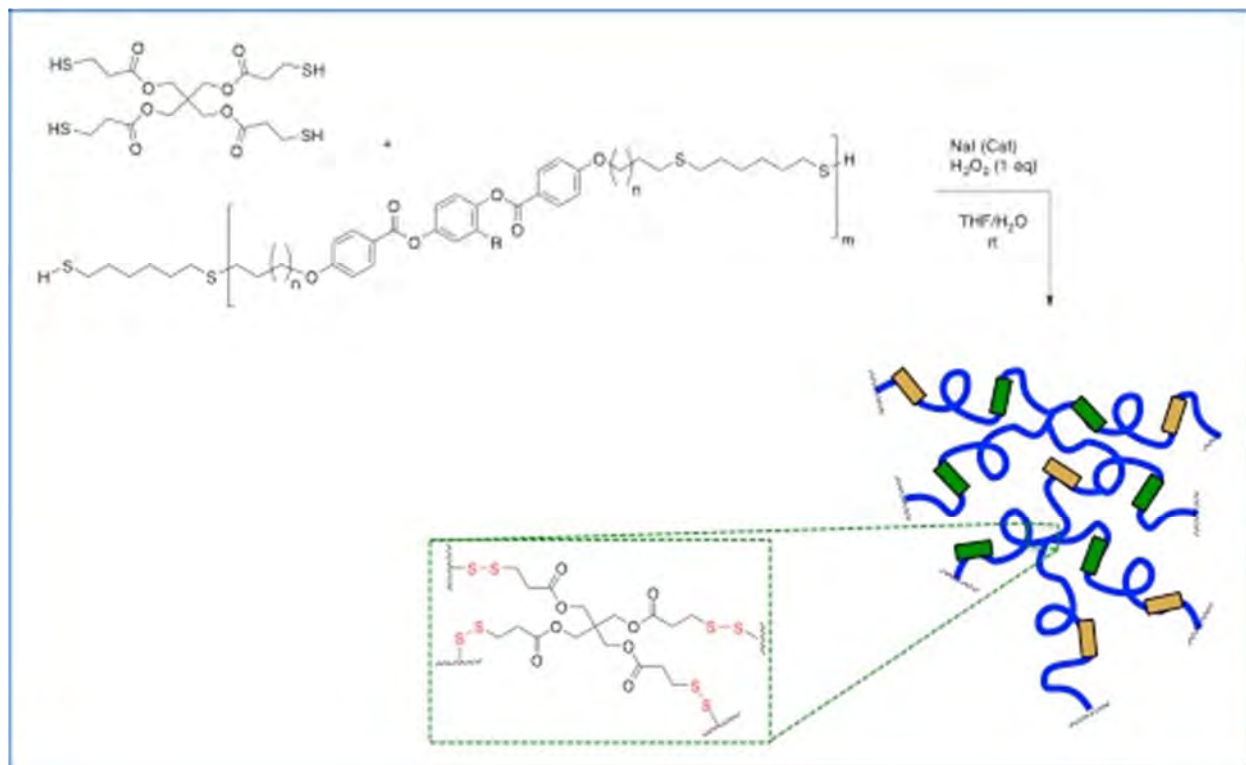


Figure 1: A programmed LCE is heated to its isotropic phase and follows one of two paths. 1 – Cooled in ambient conditions. LCs were allowed to fully orient. 2 – Quench cooled in a water/ice bath where the thermomechanical properties of the network prevent the programmed shape to fully recover.

POLY 493: Tuning dynamic liquid crystal networks via mesogen copolymerization

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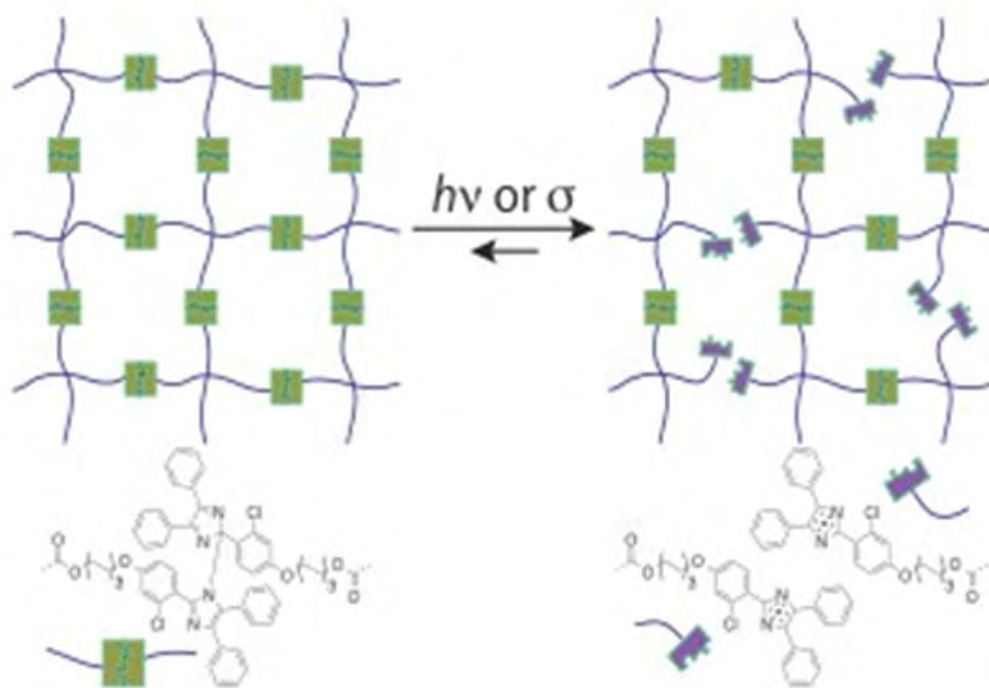
Previously, disulfide networks have been investigated as shape memory materials and adhesives. These covalently crosslinked polymers are dynamic under high intensity UV light or high temperatures, making them both self-healing and reprocessable. We have shown that inclusion of liquid crystal (LC) mesogens in disulfide networks can be used to prepare dynamic metallo-, photo-, and thermo- responsive elastomers. Notably, dynamic disulfide networks containing BIP (a metal-binding mesogen) exhibit extensive creep, possibly due to a lowered S-S exchange temperature. Here, in order to combat this effect, we explore a new family of dynamic disulfide networks created by the copolymerization and crosslinking of non-nucleophilic mesogens. We show that a high degree of control over the resultant thermal transitions (e.g. melting temperature, glass transition temperature, and clearing temperature), mechanical performance, and rheological properties can be achieved using this relatively simple strategy. Moreover, we demonstrate that the inclusion of small quantities of BIP can be used to tune the extent of creep and impart metallotropic phase transitions in the material.



POLY 494: Intrinsically-healable, self-reporting thermosets by activation of latent, long-lived reactive species

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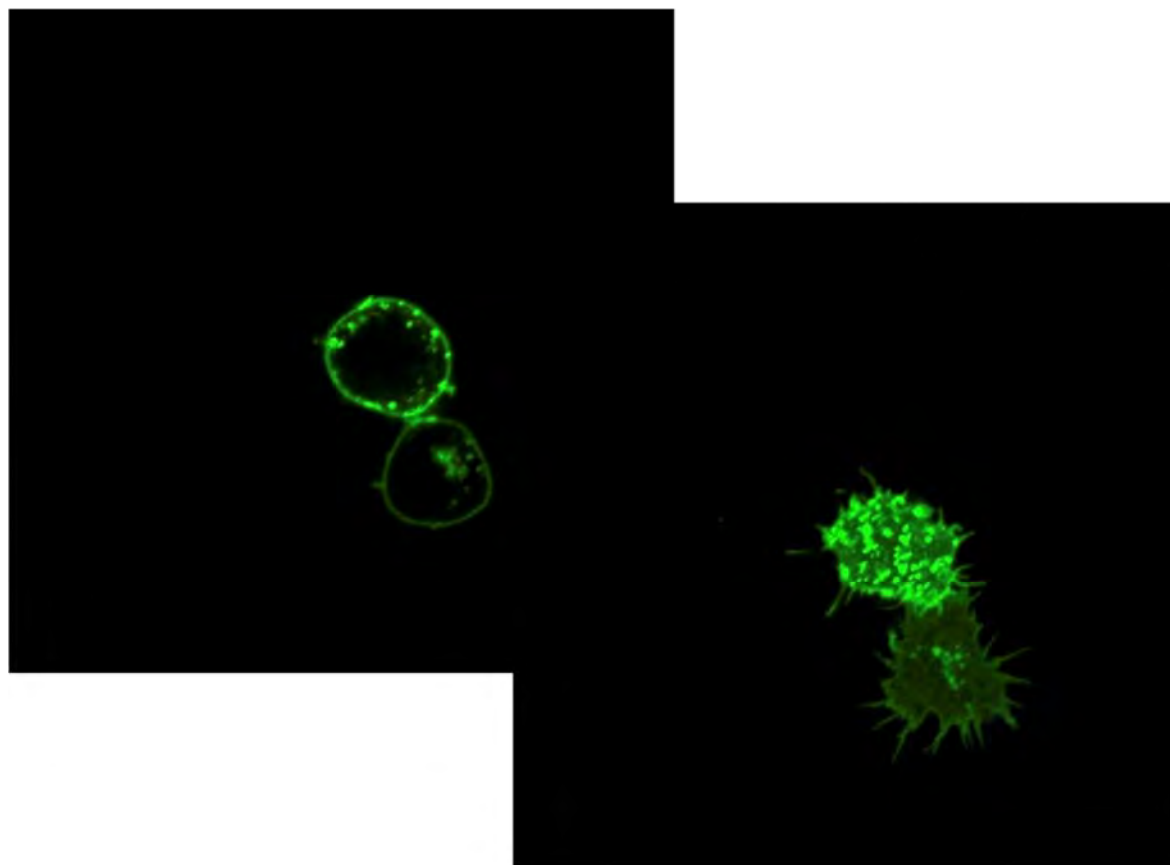
Both di- and tetra-hydroxy, hexaarylbiimidazole (HABI)-based monomers were synthesized in an effort to incorporate into a reversibly photo- and mechano-cleavable moiety within the backbone of covalently cross-linked polyurethane networks. These polymeric materials were hypothesized to be capable of sub-glass transition temperature (T_g) cold welding, attributable to the transient cross-link density reduction, and concomitant reduction in T_g and increase in molecular mobility, afforded by the reversible, athermal cleavage of backbone-borne HABI moieties. Exhibiting moduli of ~ 2 GPa at room temperature and T_g of $\sim 77^\circ\text{C}$, as determined by dynamic mechanical analysis (DMA), the glassy polyurethane thermosets examined here were fabricated by co-reacting hydroxy-bearing HABIs with isophorone diisocyanate. These networks were irradiated at 405 nm while mounted in the DMA during a constant frequency temperature sweep, revealing a significant T_g decrease with raised irradiation intensity (T_g of $\sim 60^\circ\text{C}$ at $6\text{ mW}/\text{cm}^2$ and $\sim 49^\circ\text{C}$ at $60\text{ mW}/\text{cm}^2$). Photo-cleavage of the HABI moiety was successfully demonstrated to achieve self-healing by subjecting thin films to $60\text{ mW}/\text{cm}^2$ irradiation for three hours, and subsequent healing (recombination of cross-links) for 48 hrs. Additionally, samples of these HABI-incorporating polyurethane networks were successfully subjected to ultrasonic welding, indicating the capacity for mechano-induced cleavage and subsequent healing. Finally, HABI-bearing polyurethane samples were examined for their ability to undergo cold welding with mechanical force using an anvil.



POLY 495: Glycopolymers for immune modulation in the tumor microenvironment

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Potentiating the immune response against cancer cells is a proven approach to cure disease. Dramatic examples that target adaptive immune pathways include T cell checkpoint inhibitors and CAR-T cells. However, these current therapies are effective in relatively small populations of eligible patients. There is considerable interest in expanding immune modulatory therapies to new targets beyond T cells and to innate immune pathways. This presentation will focus on the roles that glycan binding proteins play in immune modulation in the tumor microenvironment. Synthetic glycopolymers are central tools for our research. Recent work suggests that glycopolymers capable of activating innate immune pattern recognition receptors have therapeutic value in cancer immune therapy.



POLY 496: Multivalent displays for cancer immunotherapy

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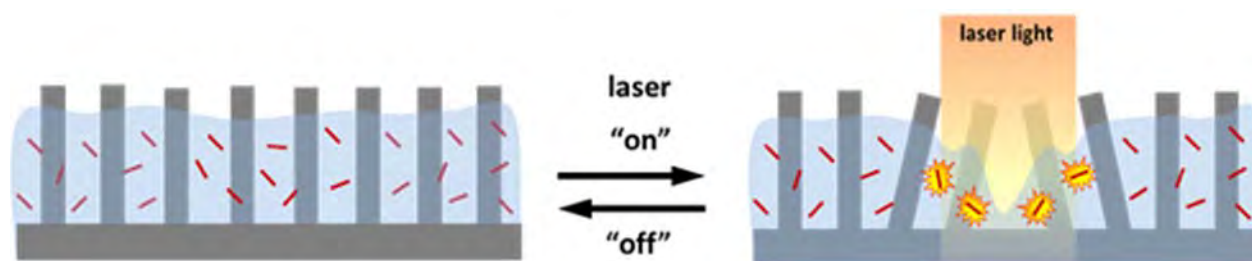
In comparison to live, attenuated or killed vaccines, synthetic vaccines can have superior safety and efficacy. Applying such vaccines to cancer is challenging as they often fail to elicit robust activation of cytotoxic T lymphocytes – an essential response for cellular immunity against cancer. Cellular immune responses have been especially difficult to obtain from carbohydrate-based vaccines. To address these issues, we are targeting antigens to dendritic cells. Specifically, we are designing multivalent scaffolds that can deliver carbohydrate-displaying antigens via lectin-mediated uptake. One such dendritic cell lectin is DC-SIGN. This endocytic receptor has been proposed to function in pathogen uptake and has been postulated to be a useful target for vaccine design. Designed antigens that can bind this receptor undergo internalization and elicit output cellular responses indicative of cellular immunity. By directing antigens to lectin receptors and dissecting the molecular features that give rise to specific responses, we expect to afford a blueprint for the design of more efficacious, carbohydrate-based cancer vaccines.



POLY 497: Design principles for a hybrid polymeric materials system capable of photothermally-triggered actuation and its application as a new platform for in vitro cell manipulation

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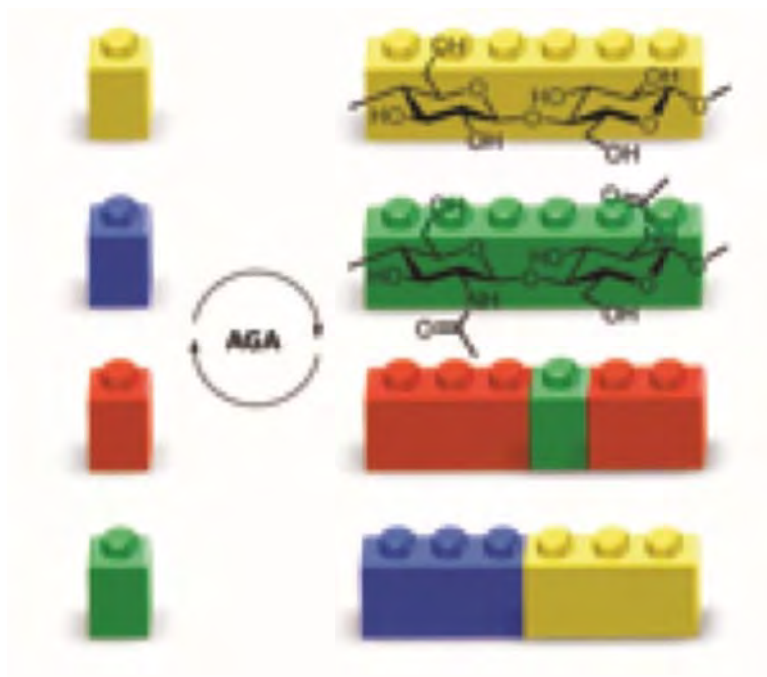
Mechanical forces in the cell's natural environment have a crucial impact on growth, differentiation and behavior. Few areas of biology can be understood without taking into account how both individual cells and cell networks sense and transduce physical stresses. However, the field is currently held back by the limitations of the available methods to apply physiologically relevant stress profiles on cells, particularly with sub-cellular resolution, in controlled in vitro experiments. We will report a novel 2D active material platform built hierarchically using a materials genome approach, which permits directional, remotely controlled, and highly localized surface deformation in the μN force range and allows reversible deformation of the cell growth substrate, with control at scales ranging from the entire surface to the subcellular, and response times on the order of seconds. This material is a new type of Hydrogel-Actuated Integrated Responsive System (HAIRS), which is designed to undergo photothermally triggered actuation of user-selected regions. We established a method to remotely control localized microstructure actuation using temperature-responsive hydrogel muscle loaded with light-sensitive gold nanorods, and exercising control over the location of the microstructure actuation by patterning the light stimulus. The capabilities of this active system is not matched by any other method, and this versatile material has the potential to bridge the performance gap between the existing single cell micro-manipulation and 2D cell sheet mechanical stimulation techniques.



POLY 498: Novel materials created from synthetic polysaccharides: Synthesis, structure and function

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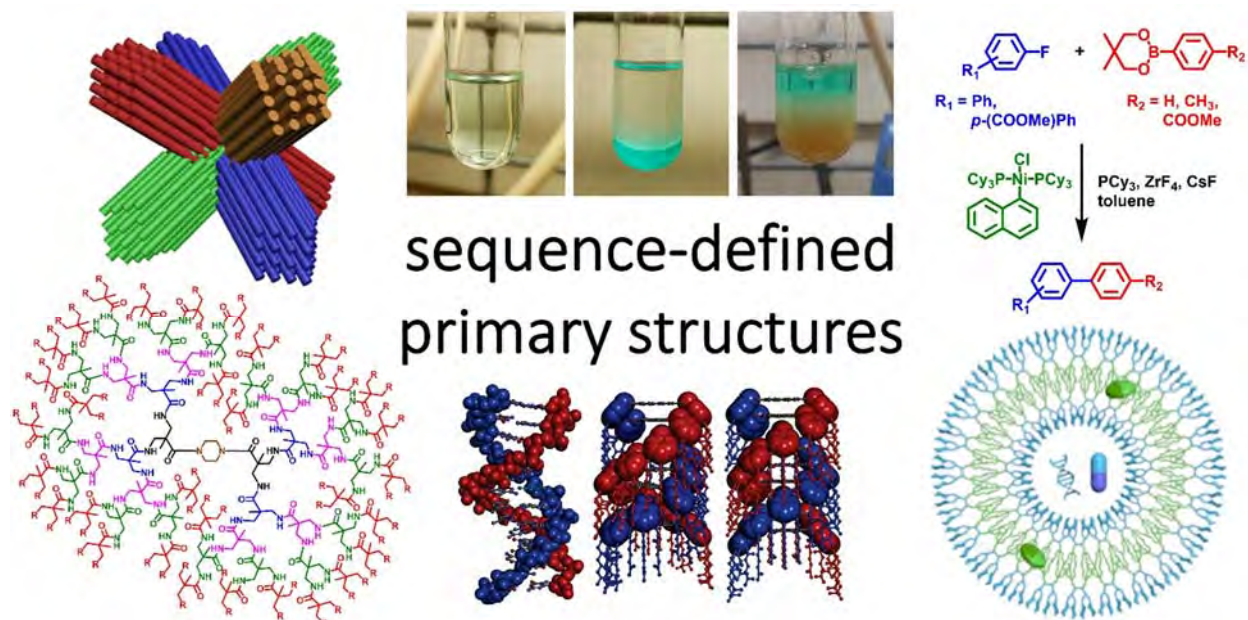
Rapid access to pure glycans by automated glycan assembly (AGA)¹ allows now for the rapid assembly of polysaccharides as long as 50-mers² using a commercial synthesizer.³ These synthetic polysaccharides can be combined much like “molecular LEGO”⁴ to create even larger oligosaccharide assemblies to address fundamental questions of carbohydrate structure, folding and material science applications. The synthetic work is combined with molecular modelling calculations and physical methods to characterize carbohydrate structure.



POLY 499: Complex supramolecular systems and functions from programmed sequence-defined primary structures

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Function arises from the hierarchical transfer of structural information from programmed primary structures to self-organized assemblies. However, the mechanism of this transfer in biological, biological-like, and synthetic systems remains poorly understood. Our laboratory investigates this mechanism via a rational library approach, which uses accelerated synthesis of constitutional isomeric libraries of self-assembling building blocks and structural and retrostructural analysis of their periodic and quasiperiodic assemblies. This approach has been applied to diverse systems including: Janus glycodendrimers and their assembly into biological membrane mimics; an all Ni-catalyzed approach to sterically hindered self-assembling dendrons; sterically congested polyamide dendrimers reaching the limits of organic synthesis; dendronized perylene bisimides and their chirality-invariant assembly; and crown-like dendrimers exhibiting a *supramolecular orientational memory* effect. In all cases, defining the sequence of the primary structure has proven critical to obtaining desirable material functions. In this presentation, a selection of these examples will be discussed.



POLY 500: Star-shaped glycopolymers with ability to manipulate cytokine secretion in human dendritic cells

David M. Haddleton, *D.M.HADDLETON@WARWICK.AC.UK. Chem Dept, Coventry, United Kingdom*

Human C-type lectin DC-SIGN (CD209) is a significant receptor on the surface of dendritic cells - crucial components of host defense that bridge the innate and adaptive immune systems. A range of linear glycopolymers, constructed via controlled radical polymerization techniques have been shown to interact with DC-SIGN with affinities in the physiologically active range. This presentation will describe the use of star-shaped mannose functionalised glycopolymers with 5 and 8 arms for targeting the clustered domain arrangement of DC-SIGN showing binding with acceptable affinity. Incorporating star polymer architecture into glycopolymers could be key to developing selective and very high-affinity therapeutic materials.

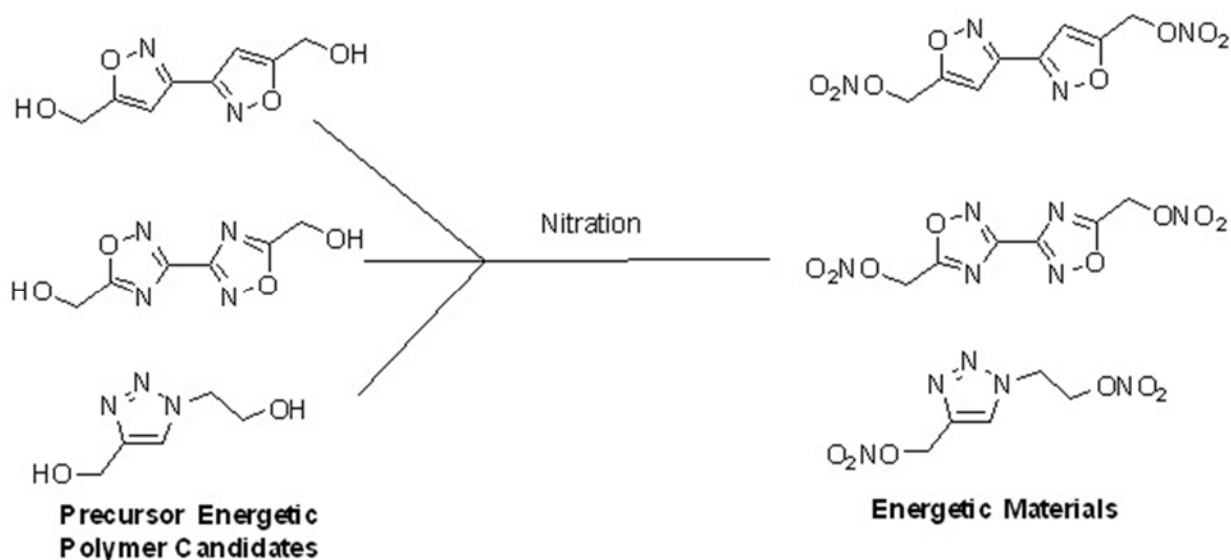


POLY 501: Synthesis of energetic propellant and explosive ingredients for potential polymer applications

Jesse Sabatini, jesse.j.sabatini.civ@mail.mil. Department of Defense, US Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

The development of high-energy-density materials (HEDMs) with good performance and reasonable sensitivity is a common goal amongst those with an interest in the field of energetic materials. Explosive and propellant materials contain a significant amount of potential energy that produces a significant amount of light, heat, sound, and pressure when this energy is released suddenly. Discussed will be the synthesis, characterization, and performance properties of several standalone melt-castable explosive materials, as well as energetic propellant plasticizer candidates; both of which should be considered for broader use in a formulation. Reasons as to why these materials should be considered for formulation use will be explained.

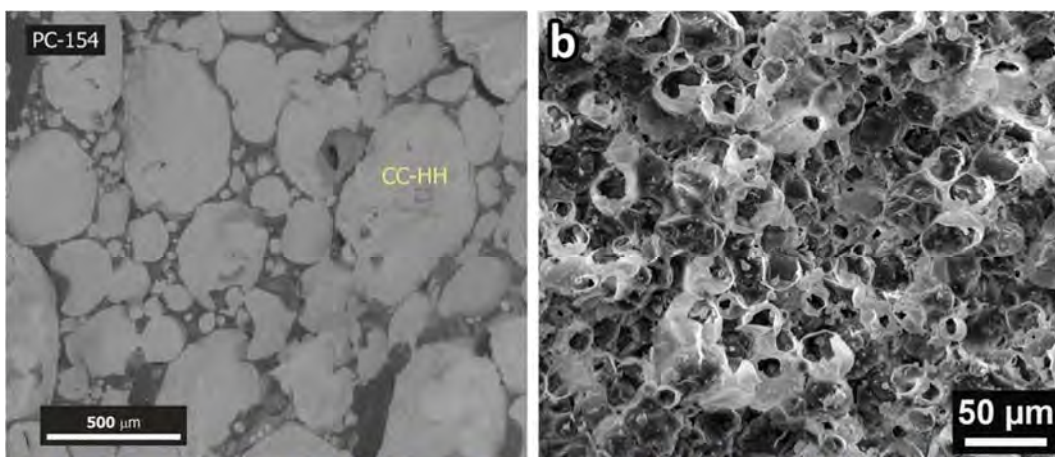
In addition, the non-nitrated (i.e. energetic precursor materials) explosive and propellant materials will also be presented for their potential uses in the pursuit of energetic polymers. While these materials lack the nitro group, they do contain various heterocyclic rings, which in most cases, impart a significantly positive heat of formation. Thus, it is the heat of formation of these precursor molecules, not their nitrated derivatives, which could serve as the foundation for a new class of energetic polymers for potential defense-related applications.



POLY 502: Encapsulation of phase change materials within emulsion-templated polymer monoliths for thermal energy storage/release applications

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High heat of fusion phase change materials (PCMs) are being intensively investigated for thermal energy storage/release for both defense and civilian applications. In PCMs, which can be broadly classified as inorganic (e.g. salt hydrates) or organic (e.g. paraffins), a relatively large amount of thermal energy is absorbed during melting and is then released during freezing. PCMs must be encapsulated for effective application and minimal amounts of encapsulant must be used for efficient application. In this work, PCM contents as high as 90% were achieved by encapsulating within polyHIPE (PH) monoliths produced by templating within high internal phase emulsions (HIPEs). The heat storage and release in the resulting PCM-containing monoliths was studied using thermal cycling. The advantages of salt hydrate PCMs include a sharp melting point, non-toxicity, non-flammability, and the availability of wide range of transition temperatures. Here, calcium chloride hexahydrate (CC-HH) was encapsulated within elastomeric acrylate-based polyHIPEs (Figure, left) that were produced by templating within water-in-oil Pickering HIPEs. The HIPE stabilization, the monomers, the crosslinking comonomer content, and the presence of a nucleating agent were used to modify the thermal behavior and the extent of leakage. The advantages of paraffin PCMs include minimal undercooling on freezing, congruent melting, self-nucleation, and low density. Here, octadecane (OD) was encapsulated within "green" polyHIPEs based on polyphenols such as tannic acid (TA) (Figure, right) that were produced by templating within oil-in-water HIPEs. The nature of the polyphenols and the presence of fillers were used to modify the thermal behavior, the extent of leakage, and the mechanical behavior.



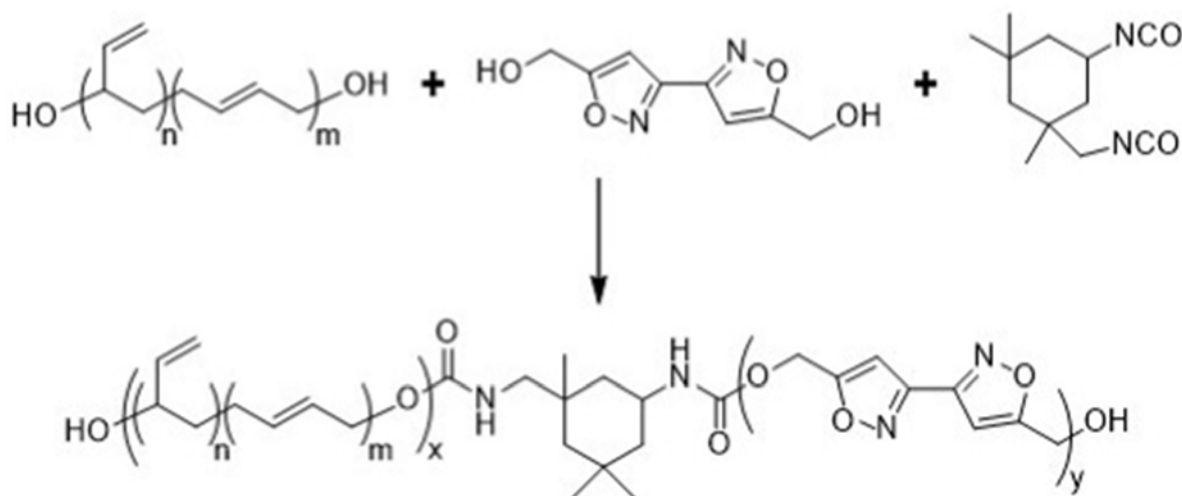
CC-HH in an elastomeric acrylate-based PH.

OD in a "green" TA-based PH.

POLY 503: Strategies to improve binder performance for energetic materials

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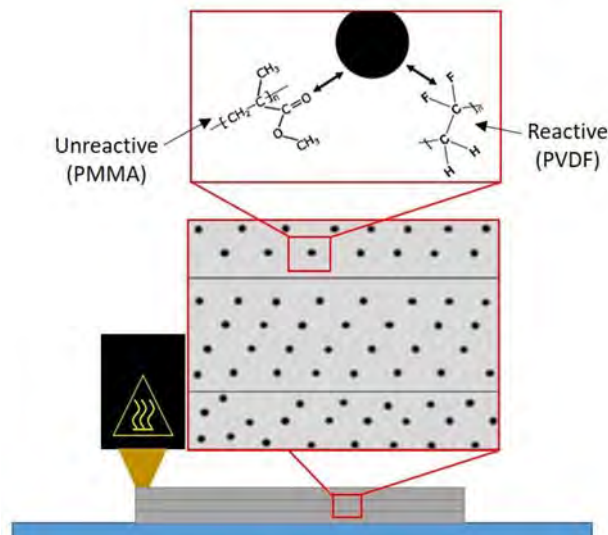
Elastomeric binders are used to host energetic materials in formulations that range from explosives to propellants. The binders typically exhibit low energetic properties, and must also possess a low glass transition temperature and reasonable strength. Two routes were evaluated to modify the characteristics of hydroxyl-terminated polybutadiene (HT-PBD) in a urethane formulation commonly used in binder applications. In the first approach, HT-PBD was modified using triazolinedione chemistry to functionalize the polymer backbone and alter the chemical composition. These materials were evaluated for their impacts on the neat HT-PBD properties such as T_g and calorimetric contribution. The second route altered the urethane characteristics by incorporating promising new diols based on isoxazole compounds. Despite incorporating a stiff diol segment, the resulting urethane exhibited a decrease in T_g and equivalent or improved mechanical properties relative to the baseline material.



POLY 504: Inert binder effects on interface and reaction kinetics of 3D printed reactive composites

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Reactive materials are used heavily in defense applications for localized energy generation. One drawback to these materials in their current form is that compositional control is not easily attainable. This limits shelf life and performance in sensitive applications. Advances in additive manufacturing technologies may help to bridge this technological gap. One approach to join these research areas is to exploit a reactive binder, which eases rheological limitations by reducing solid loading. Aluminum nanopowders (fuel) were melt blended with a poly(vinylidene fluoride) (PVDF) binder to produce reactive filaments. However, due to melt flow and surface energy limitations, these materials are not a reasonable candidate for transition to AM fabrication. To resolve these limitations, poly(methyl methacrylate) (PMMA) was added to the binder to improve processability by increasing binder surface energy and melt flow rate. Although processability is improved with PMMA addition, the use of an inert binder (e.g., PMMA) will impact particle kinetics during processing and polymer decomposition once these materials undergo thermal ignition. This talk details the impact of PMMA on the processability and reaction kinetics of composites produced by fused deposition modeling.

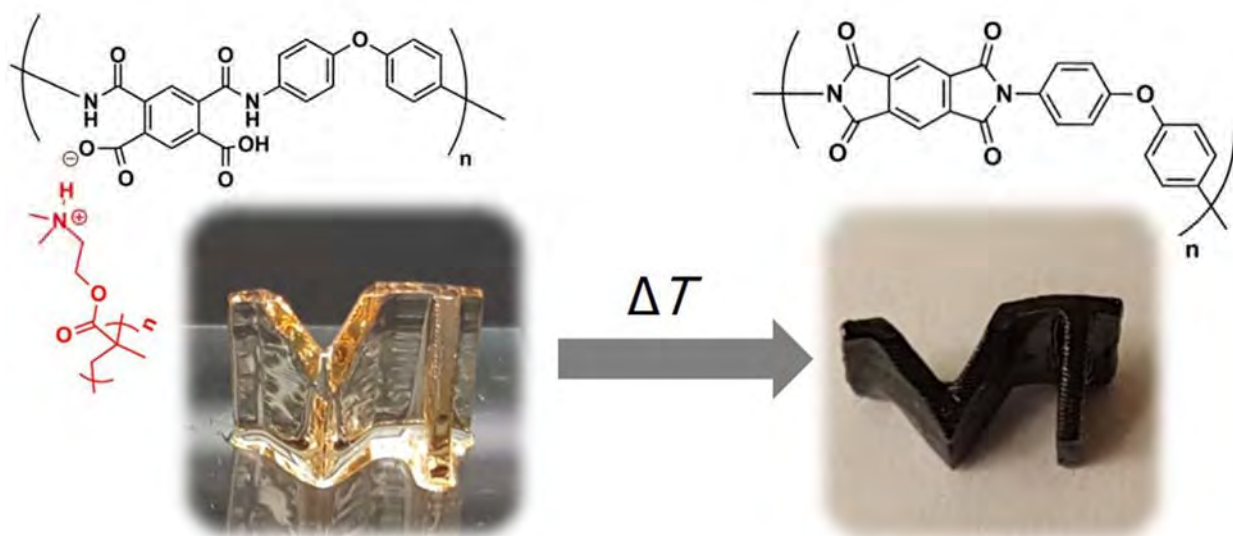


POLY 505: High performance polymers for additive manufacturing: 3D Printing of Kapton®

Jana Herzberger¹, herzberger.jana@gmail.com, **Viswanath Meenakshisundaram**², **Christopher B. Williams**², **Timothy E. Long**¹. (1) Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Department of Mechanical Engineering and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA PI), commonly known by the trademark Kapton®, is a high performance polymer with exceptional thermomechanical properties from -269 °C to 400 °C. Unfortunately, its all-aromatic structure results in insolubility, prohibiting traditional manufacturing processes. This limits commercial PMDA-ODA PI products mainly to films and coatings, which are processed in a 2-step procedure. The advent of additive manufacturing (or 3D printing) revolutionized modern manufacturing and motivated reinvestigation into overcoming the processing challenges of Kapton®.

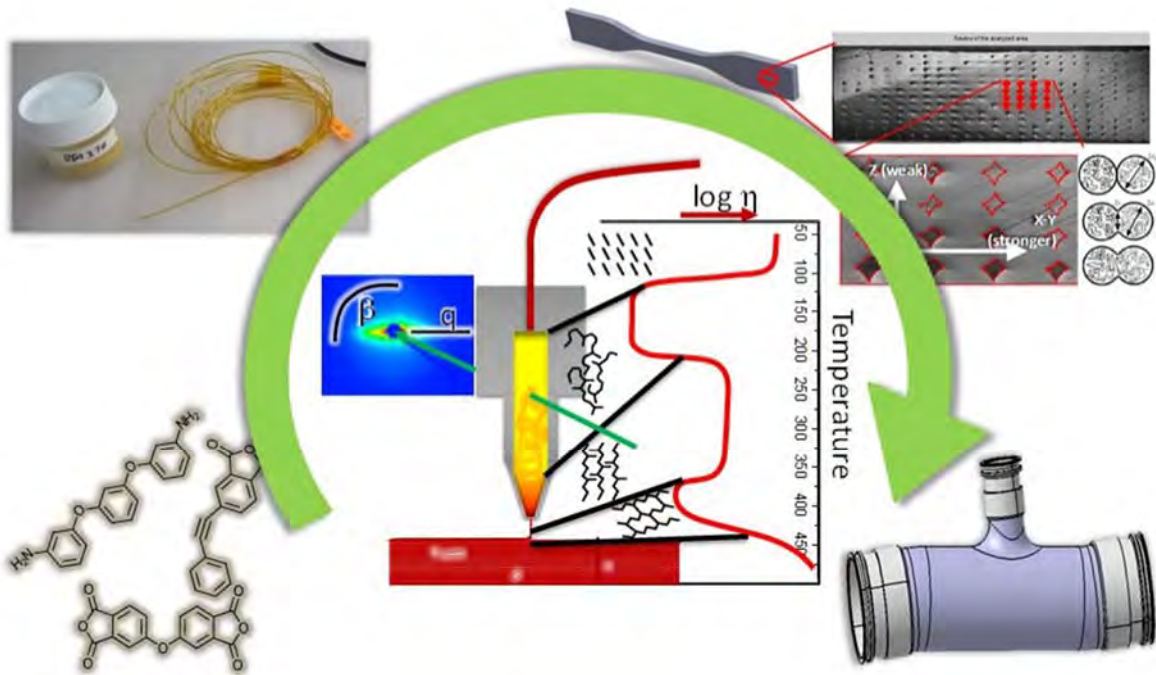
Here, we will present a facile chemical modification of PMDA-ODA PI, which allowed for the development of Kapton® into 3D shapes. In particular, attaching methacrylate moieties to soluble PMDA-ODA precursors enabled their processing using vat photopolymerization (VP). VP utilizes UV light to photo-crosslink the polymeric precursor solution layer-by-layer, resulting in 3D objects. Subsequent drying and thermal treatment of the organogel yielded 3D parts consisting solely of PMDA-ODA PI. This processing strategy expands PMDA-ODA PI products from films to complex 3D objects, thus opening the door to create previously unimaginable parts for applications including spacecrafts/satellites, electronics and automotive.



POLY 506: Old thermoset chemistries for a new process. High temperature thermosetting resins for additive manufacturing

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All services are investing in additive manufacturing of metals, polymer-based materials and composites due to the attractive opportunities in prototyping, parts reduction and complexity. However, current off-the-shelf materials do not exhibit the properties necessary for demanding defense applications, in which durability, thermo-oxidative stability and low creep under extreme conditions (high temperature, humidity, oxygen) are key requirements. This presentation will discuss several routes that enable the use of state-of-the-art chemistries known from conventional polymer matrix composites to be used in additive manufacturing processes, including selective laser sintering and fused deposition modeling. The newly designed resin systems allow 3D printing of parts with service temperatures well above 300C and excellent thermo-oxidative stability. Synthesis, formulation, feedstock development and 3D printing of these new materials and their thermo-mechanical properties will be presented.

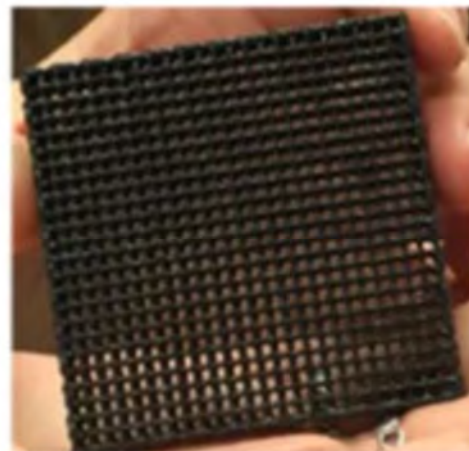
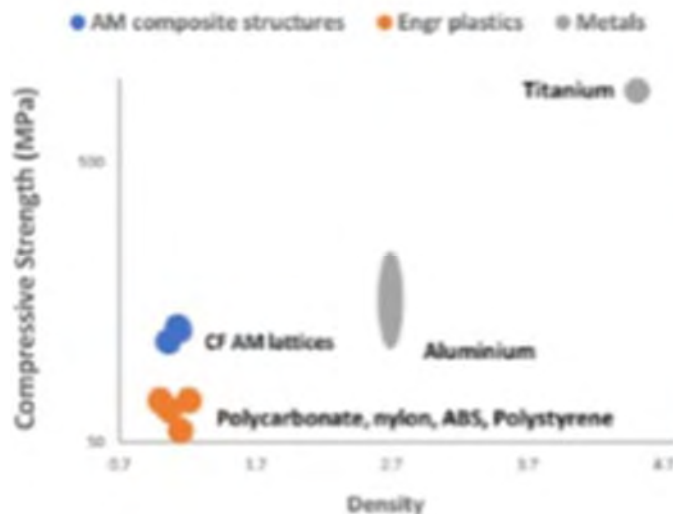


From molecules to parts. Development of new feedstock materials for additive manufacturing processes and understanding material properties at all levels of processing is required to turn additive manufacturing into a robust technology.

POLY 507: Towards additive manufacture of high performance thermoset polymeric composites

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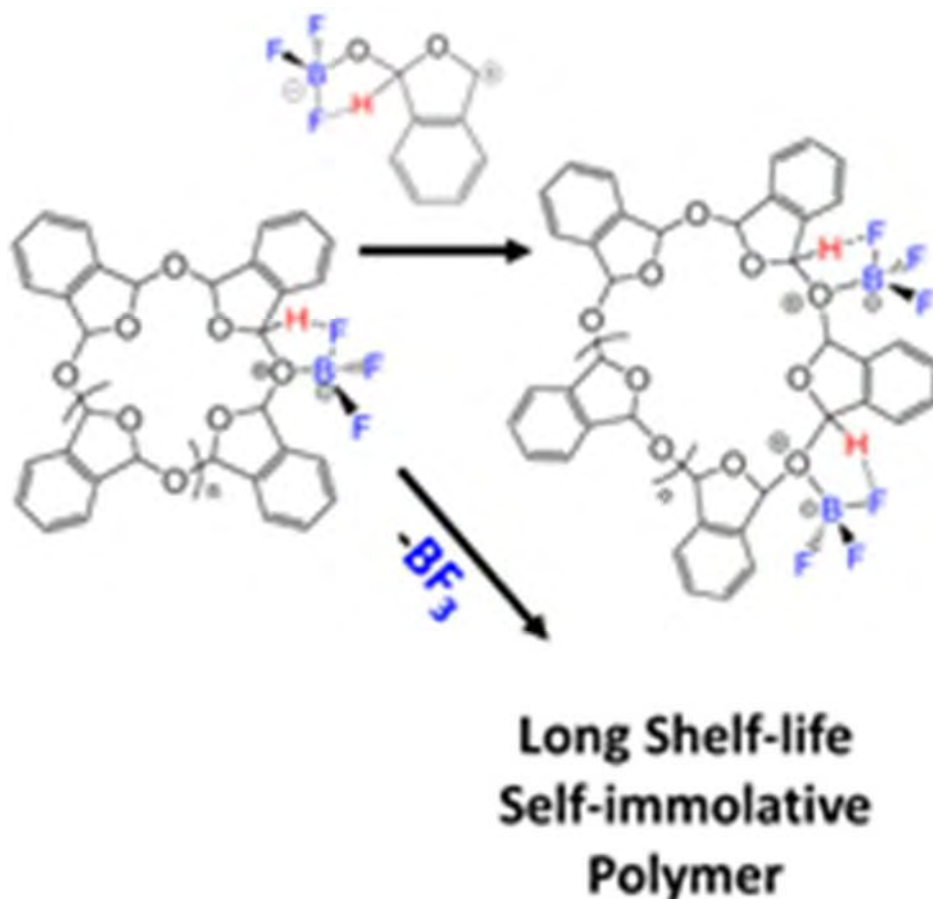
Additive manufacture (AM) of Polymeric composite materials to form parts, structures and devices with enhanced materials property sets and novel functionality is a rapidly growing area of materials science. Lawrence Livermore National Laboratory develops and utilizes polymer formulations, composites and foams for a variety of applications. We manufacture these components using traditional processes such as casting, machining and coating. However, increasingly we are investigating a range of new additive manufacturing methods of both extend the functionality and reduce the process footprint of polymeric parts. Here we present an overview of our recent efforts in the Additive manufacture of non-acrylate based, high performance thermoset polymers based on epoxide and cyanate ester resins and fiber composites. We discuss our efforts in the maturation of a multi-scale technology for additively manufacturing (AM) high performance thermoset composites that are based on aromatic thermoset resins and Direct Ink Write (DIW) 3D printing technology. With our novel '3D-printable' Carbon Fiber (CF)-polymer feedstocks and a range of computational design tools, we have demonstrated control over fiber alignment in 3-dimensions within a thermoset matrix. Furthermore, we are developing the hardware technology to enable high volume fractions of CF to be 3D printed within a complex build volume. Our results show that with improved control of CF-composite mesostructure, it is possible to make materials with truly orthotropic physical properties that significantly outperform equivalent volume fraction CF composites manufactured through conventional means. Simulation, computational design optimization, and toolpath planning approaches will be discussed in the context of manufacturing composites with optimally designed mesostructures for a given property set. We predict that such rational additive manufacturing approaches will ultimately lead to the design of truly polymer hybrid materials having locally programmable complex electrical, thermal and mechanical response.



POLY 508: Phototriggerable transient devices based on polyaldehydes

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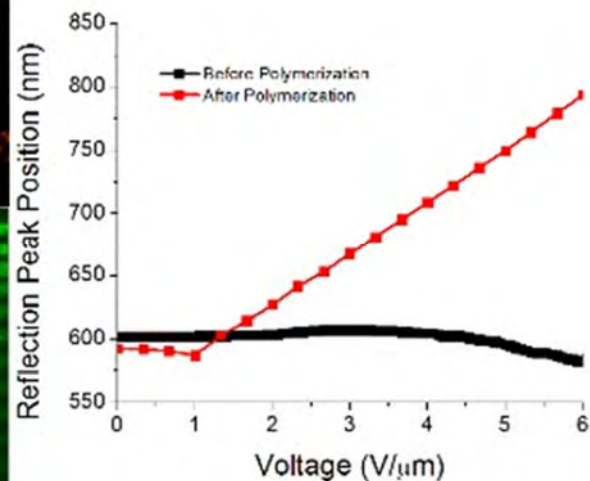
Transient devices are those where the controlled, programmable disappearance of a device is needed because retrieval is not possible or a different form of disposal is desired. The devices include electronic components such as sensors, and delivery vehicles, such as rigid-wing gliders and parachutes. Low ceiling temperature polymers are of interest for construction of such devices because their depolymerization from the solid to liquid or vapor can be triggered at and occur at ambient conditions. Triggering can occur by a photo, chemical or thermal activation. Low ceiling temperature polyaldehydes have been evaluated for transience devices. The mechanism of polymerization, triggering conditions and incorporation of volatile components into the polymer will be discussed. The stimulus for disappearance by a photochemical reaction has been extended from the ultraviolet to the visible region.



POLY 509: Using polymers to affect the behavior of liquid crystals

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The unique combination of birefringence and liquid-like properties make liquid crystals an ideal material system for creating dynamic optical behavior. Unfortunately, by depending solely on the self-assembly of short-chain liquid crystals, the functional properties of liquid crystals are fairly limited. On the other hand, the interplay between liquid crystals and polymers provides an avenue for affecting the self-assembly of these soft-matter systems. More specifically, structure can be imparted onto a growing polymer by using liquid crystals as “smart solvents” during the polymerization process, thereby resulting in liquid crystal-swollen polymer networks with macroscopic order. These polymer networks can in turn affect the liquid crystal properties in the vicinity of the liquid crystal network, such as stabilizing thermodynamically unfavorable phases and imparting new stimuli-responsive behavior. This talk will summarize the research activities at the Air Force Research Laboratory in the area of using polymer stabilization as a method to controllably affect the behavior of liquid crystals to enable novel optical and stimuli-responsive properties.



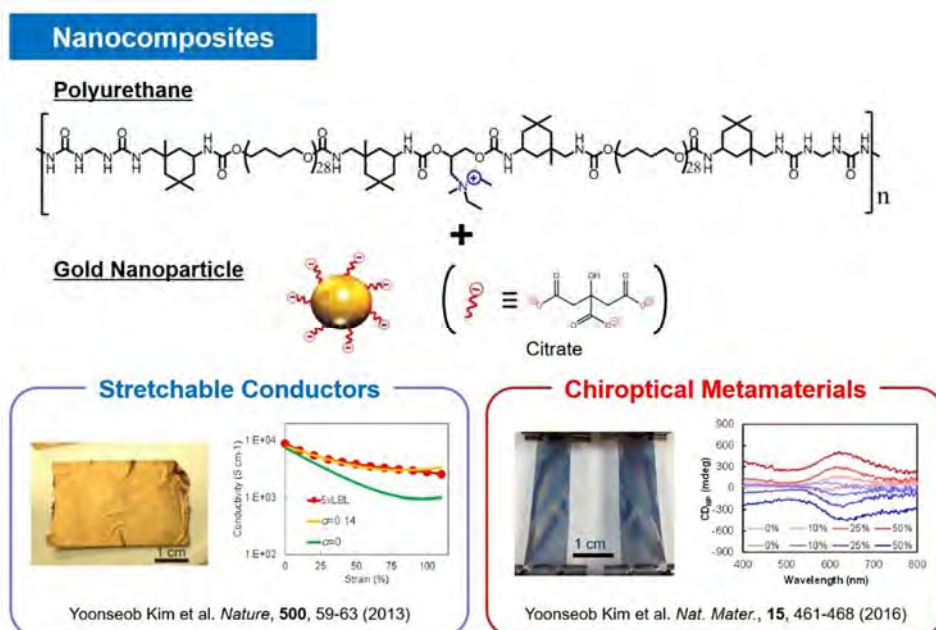
POLY 510: Stretchable electronic and photonic nanocomposites from self-organized nanoparticles

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Polymer chemistry with nanoscale science paved the way for novel composite materials with unique properties. However, incorporation of these properties into macroscale functional applications has been limited due to challenges of scalability, cost effectiveness and homogeneity. Here we explore facile self-assembly of polymer and nanoparticles for discovering fundamental understandings of dynamics for electronic and photonic applications.

An excellent stretchable conductors were demonstrated from self-organized gold nanoparticles (Au NPs) using a highly stretchable polyurethane (PU) matrix. Macroscale free-standing samples were prepared using layer-by-layer assembly of positively-charged PUs and negatively-charged Au NPs. High conductivity and stretchability of the composites originated from dynamic self-organization of polymer-nanoparticle assemblies. The dynamic organization of Au NPs and PU also demonstrated chiroptical nanocomposites for applications of photonic metamaterials. The conformal layer-by-layer deposition on pre-twisted substrates offered a distinctive advantage when producing homogeneous macroscale materials. Chiroptical activity increased up to ten fold (500 mdeg) upon stretching samples and was reversibly tunable.

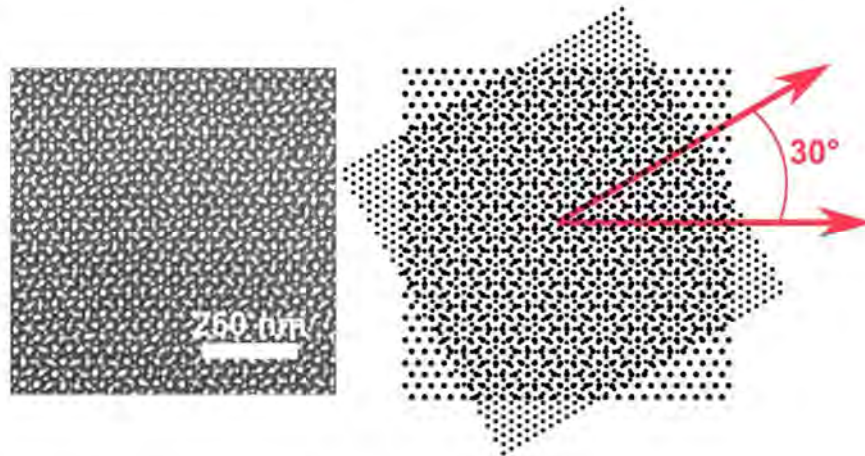
Scalable layer-by-layer methods have distinctive advantages in processing unique polymeric composites such as short preparation time, low-cost, reconfigurability and homogeneity. Layered nanocomposite assemblies at the nexus of mechanics, electronics, and excitonics/plasmonics can be generalized to other nanoscale materials and uniquely applied to composite-based electronic and optic devices.



POLY 511: Sequential annealing of block copolymers for Moiré superstructures

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Self-assembly of block copolymer (BCP) thin films is of great interest for next generation lithography applications.[1] The International Technology Roadmap for Semiconductors (www.itrs2.net) defines block copolymer self-assembly as directed assembly as an innovative technology for solving challenges related to sub-10 nm lithography. As a bottom-up process, the self-assembly of BCP thin films can produce sub-10 nm nanopatterns on surfaces, including lines, dots, bends, jogs, and circles, with features as small as 3 nm, with low cost per unit.[2] These nanostructures have already been demonstrated for the fabrication of high performance semiconductor transistors and high capacity disk storage devices.[3] In this work, we discovered a new method to access an entirely new family of highly complex nanopatterns previously not known for BCP nanostructures, termed Moiré patterns.[4] The Moiré comprise two layers of hexagonal BCP dots, with a distinct rotation angles between two BCP arrays that were measured by analysing large-scale helium ion microscope images (up to 20 μm * 20 μm in size). The influence of two BCP pitch ratios, the details of the annealing sequence, the influence of grain boundaries and other details that affect these remarkable structures will be discussed.

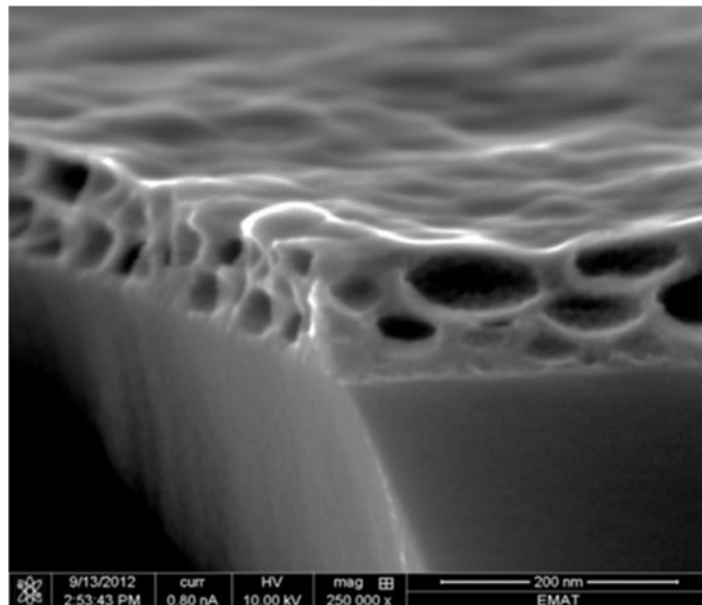


POLY 512: Applications of colloidal core-shell nanoparticles as precursors to porous thin film coatings in photovoltaic applications

Damien Reardon, damien.reardon@dsm.com. DSM, Geleen, Netherlands

The use of hollow nanoparticles has recently gained considerable attention with applications in many field ranging from drug delivery to filtration membranes. DSM has developed a single layer nanoporous antireflective cost-effective coating which can be deposited / processed from solution on a wide variety of substrates such as glass to bypass the costly traditional interference-type multilayer coating currently available in the market. To obtain a one-layer coating with good antireflective properties, very low refractive index materials are necessary. The optimum refractive index n for a one-layer antireflective coating is 1.23 @ 700nm. There are, however, very few low index inorganic solid materials that display a refractive index lower than 1.37, therefore the best method to realize materials with a low n , is to reduce their packing density or increase porosity.

DSM managed to develop a coating technology based on silica / latex core-shell nanoparticle colloidal dispersion. The resulting antireflective coating is mechanically robust, with a transmission of 98% or higher, and shows excellent outdoor durability. Added functionalities to the anti-reflective coating for PV applications will also be discussed.

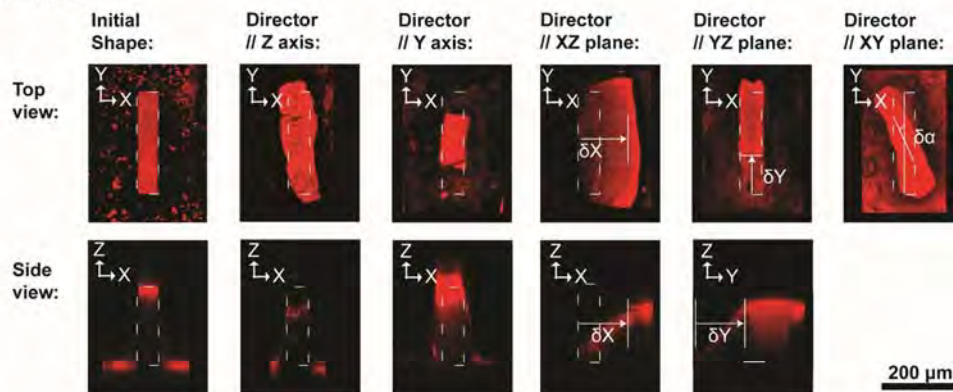


POLY 513: Design of polymeric microstructures showing active, dynamic and hierarchical deformations

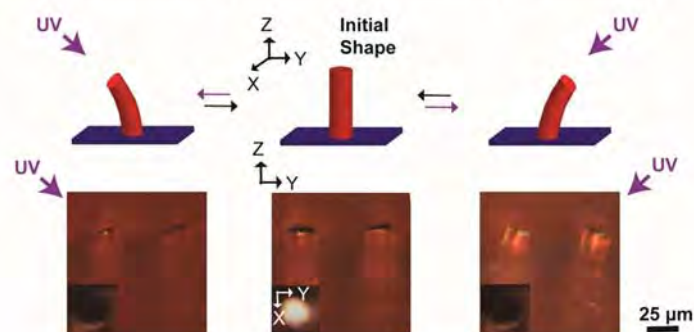
Yuxing Yao, *yuxing.george.yao@gmail.com*, Jiaxi Cui, Xiaoguang Wang, Anna V. Shneidman, Nikolaj K. Mandsberg, Joanna Aizenberg. Harvard University, Cambridge, Massachusetts, United States

In nature, adaptive microstructures are widely used to dynamically change the topography of a macroscopic object that results in a material with novel static and dynamic functions. Here we report a design of active and dynamic microactuation systems based on liquid crystalline elastomers (LCEs). Specifically, the deformation of LCE microactuators is driven by the anisotropic mechanical response parallel and perpendicular to the alignment of their mesogenic components, during nematic-isotropic phase transition. Interestingly, a rich palette of deformation types, including mechanically unfavored motions (e.g., in-plane tilting) and their hierarchical assembly, can be achieved by programming the internal orientation of the mesogens. Pre-determined and self-regulated locomotion can be achieved and controlled by applying different external stimuli. By incorporating other functional materials, we can create hybrid systems showing adaptive light-material interactions utilizing the control over microscale self-regulated deformation. Overall, these results provide the basis of a versatile class of active microstructures that enable the deformations in ways that are not possible with passive systems, and by creating hybrid materials, they can be optimized for a range of potential applications, including self-regulated antenna, controlled adhesive system, and information encryption.

Pre-determined deformation:



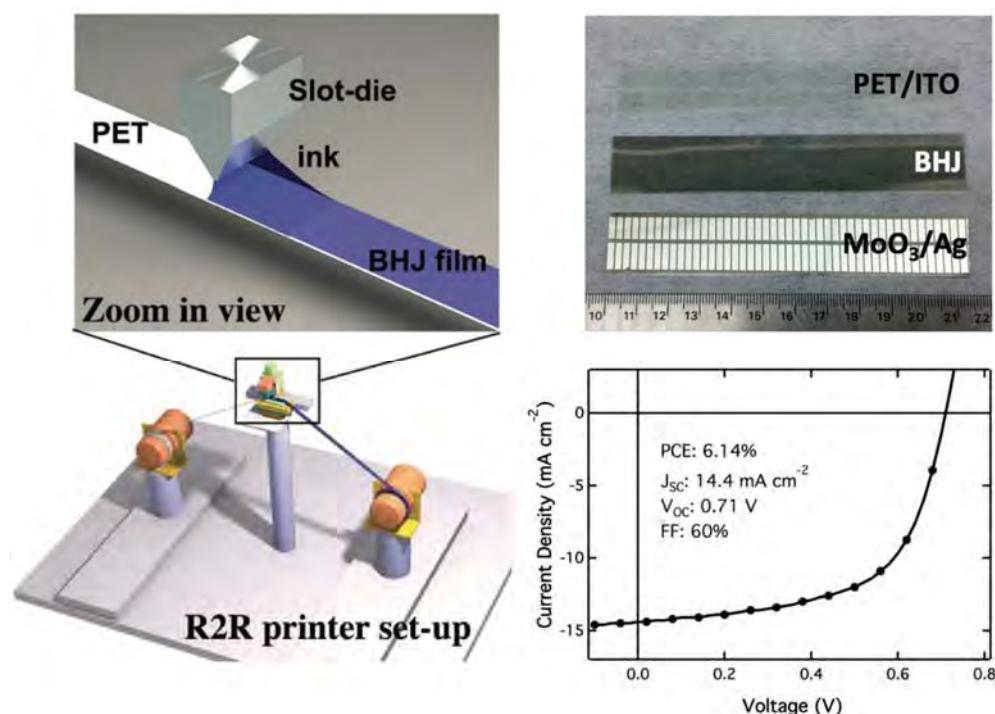
Self-regulated deformation:



POLY 514: High performance roll-to-roll printed PTB7-Th/PC71BM organic solar cells

Kevin Gu¹, klg@stanford.edu, Xiaodan Gu^{1,2}, Yan Zhou¹, Hongping Yan¹, Zhenan Bao¹. (1) Chemical Engineering, Stanford University, Stanford, California, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Despite having surpassed 10% power conversion efficiency (PCE), widely held as the threshold for commercial viability, high performance organic photovoltaics (OPVs) are still mostly constrained to lab-scale devices fabricated by spin coating. Efforts to produce scalable continuously printed OPVs trail significantly in efficiency, highlighting the need to better understand the processing-morphology-performance relationship in the context of linear printing processes. Here we investigate the promising OPV system PTB7-Th/PC71BM, which has demonstrated >10% PCE via spincoating but only exhibits ~1% PCE when roll-to-roll printed due to differences in drying dynamics. Of particular interest is the ubiquitous alcohol post-treatment wash applied to the active layer and its crucial role for printed films. Although it is commonly believed to simply remove the processing additive, 1,8-diiodooctane (DIO), from the dried film, we find that the wash process itself dramatically impacts film morphology and performance. By employing hard and soft x-ray characterization techniques we determine that isopropanol induces significant donor polymer alignment, enhanced relative degree of crystallinity, and increased domain purity. Through the understanding gained in this study, we are able to achieve a roll-to-roll printed OPV exceeding 6% PCE (5.1% avg), which is to our knowledge the highest reported performance for a continuous roll-to-roll printed single junction photoactive layer on a flexible substrate.



POLY 515: Investigating new sources for and applications of cellulose nanocrystals

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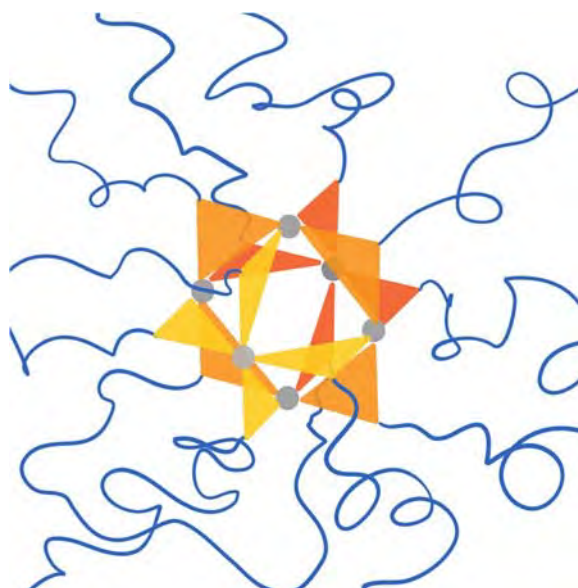
Cellulose nanocrystals (CNCs) have attracted attention in recent years as potential green nanomaterials. CNCs are highly crystalline nanofibers that can be isolated from a variety of renewable biosources, including cotton, sisal, wood, and sea tunicates. The diameters range from 5 to 30 nm and the lengths range from 100 nm to several micrometers depending on the biosource and method of isolation. CNCs have several advantages as a nanomaterial, including biosustainability, biorenewability, relatively low production cost, and low cytotoxicity. They generally have high surface area, low density, low coefficient of thermal expansion as well as high elastic moduli of about 80-150 GPa, depending on the biosource. We have been investigating the use of CNCs to access mechanically-dynamic composites, reinforcing agents for aerogels and to access stable nano-emulsions and latexes. We have also been investigating new possible sources for CNCs and have targeted the large, perennial grass hybrid *Miscanthus Giganteus*, which is a commercial crop currently used for energy production, as a new potential commercially viable source of cellulose nanomaterials.



POLY 516: PolyMOC gels formed from M_6L_{12} coordination cubes

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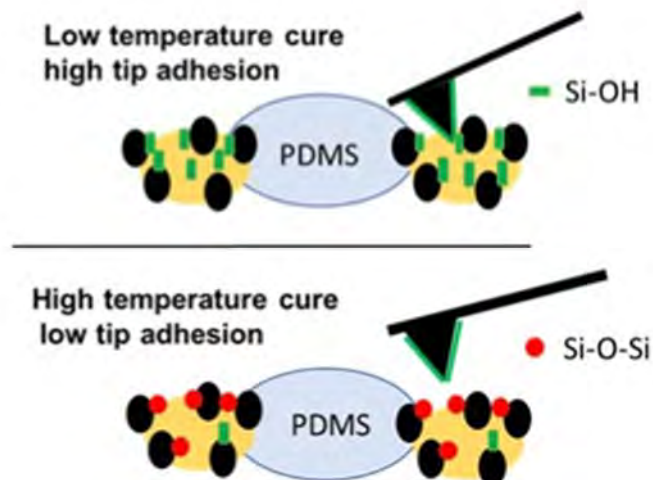
Polymer metal-organic cage (polyMOC) gels are polymer networks with well-defined, supramolecular junctions formed from multiple metal ions (M) and ligands (L). Previous work has shown that these networks behave like different classes of materials based on junction architecture: polymers connected using $M_{12}L_{24}$ MOC junctions form more robust networks with higher branch functionality and network defect tolerance compared to gels with M_2L_4 MOC junctions. In this work, we have modified an existing M_6L_{12} coordination cube to form a new type of polyMOC gel with anticipated rheological properties and loop defect density intermediate to those of previously studied systems.



POLY 517: AFM peakforce QNM mode for measurement of nanosurface mechanical properties of Pt-cured silicones: Evidence for a double network

Kenneth J. Wynne, *kjwynne@vcu.edu*, *Sithara Nair*, *Chenyu Wang*. *VCU Dept of Chem Engr, Richmond, Virginia, United States*

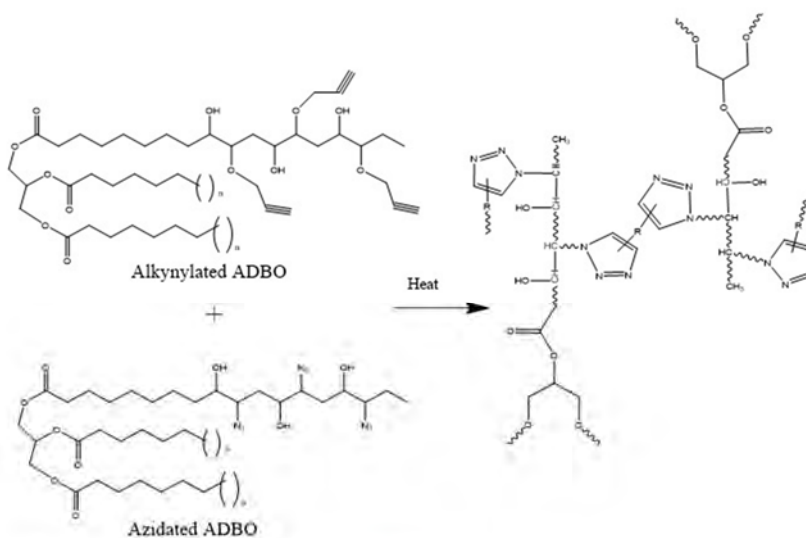
Sylgard 184 is used for diverse applications including nanoimprinting, micro-electronic and mechanical systems (MEMS), soft robots and tactile and epidermal sensors. For such applications, understanding effects of processing conditions on nanoscale mechanical properties is essential for performance, but little attention has been paid, especially to effects on surface properties. To begin understanding the complex relationships among hydrosilylation, autoxidation of Si-H to Si-OH and secondary network formation by condensation, processing conditions and composition were varied followed by measurements of nanomechanical properties. Peakforce Quantitative Nanomechanical Mapping (PF-QNM), an atomic force microscopy (AFM) mode provided a nanoscale map of deformation, adhesion, dissipation, modulus and morphology as a function of varying cure temperature and base-to-crosslinker ratio. The interaction of the Si-OH rich AFM tip with the outermost 20-40 nm provided modulus and adhesion measurements that revealed important effects of cure conditions and composition. Results were interpreted in terms of a model for the concentration of near surface Si-OH from autoxidation and a double network due to condensation at high temperature cure. Moduli were found to be comparable with dynamic mechanical analysis (DMA), validating PF-QNM as a tool for mechanical property measurements. The dependence of nanosurface mechanical properties on composition and network formation conditions provides guidance for future work using Pt-cured silicones.



POLY 518: Studies into the preparation of *Adenopus breviflorus benth* oil cast resin via catalyst and solvent free thermal click chemistry

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Adenopus breviflorus benth oil (ADBO) monomer bearing azide moiety was prepared by nucleophilic addition of sodium azide to the epoxidised ADBO to yield azidated ADBO and the oil monomer bearing alkyne moiety was prepared by reacting epoxidised ADBO with propargyl alcohol in the presence of Zinc Chloride catalyst. Polymers series were then prepared by reacting the alkynylated ADBO as well as other suitable aliphatic and aromatic diynes with the azidated ADBO by thermal 'Click' reactions under solvent and catalyst free conditions to yield cross-linked biopolymers. Characterization of the biopolymers was by FTIR, ¹HNMR, DSC, TGA, GPC and DMA. Addition of a terminal triple bonds or azide group to the fatty acid chain of ADBO by ring opening nucleophilic addition was facile. Monomers of azidated ADBO and alkynylated ADBO readily underwent polymerization with each other and with suitable cross-linkers by simply heating at 100°C. While curing of azidated ADBO with either aliphatic or aromatic diyne happened in six hours, that of azidated ADBO with alkynylated ADBO took eighteen hours. Polymers prepared using aromatic diyne showed higher glass transition, cross-link density and stiffness compared to that prepared using aliphatic diyne. Polymer prepared from azidated and alkynylated ADBO though possessed shorter network chains and thereby lower tensile strength; however displayed better damping characteristics compared to those prepared from azidated ADBO and organic diynes cross-linkers. There is a strong correlation between crosslinking density and thermal and surface properties of the biopolymers.



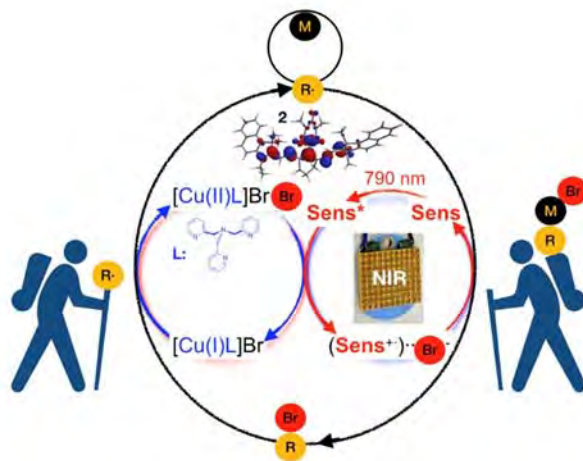
Formation of cross-linked polymer from azidated ADBO and alkynylated ADBO via thermal click chemistry

POLY 519: NIR-sensitized photoinduced ATRP with ppm of Cu catalyst

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Among the controlled radical polymerization methods, ATRP has become the most used strategy for tailor-made synthesis of macromolecular structures. Due to the requirement of low-oxidation state transition metal complexes, strict precautions need to be taken to prevent the formation of metal oxides. Therefore, in situ generation of Cu(I) complexes by the reduction of the corresponding Cu(II) conjugates has been suggested by chemical reduction or photochemical reduction using radical photoinitiators or photosensitizers.

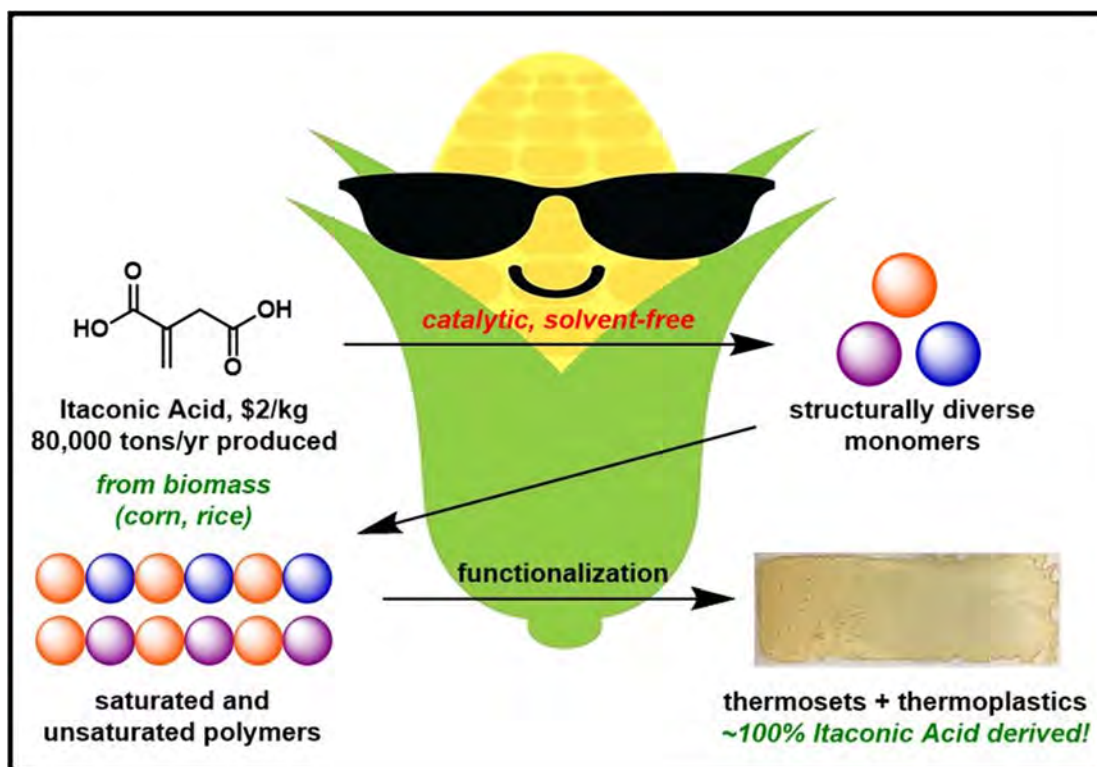
A novel methodology reports about NIR-sensitized photo-ATRP by using ppm of Cu(I)/tris(2-pyridylmethyl)amine (TPMA) as catalyst, a polymethine as photosensitizer and α -bromophenylacetate (EBPA) as alkyl halide initiator, respectively. Among the polymethines investigated with cationic (**1**), zwitterionic (**2**, **3**) and anionic (**4**) structures, only **2** carrying a barbital group in the meso-position exhibited sensitization activity under NIR light at room temperature resulting in the formation of polymers with controlled molecular weight characteristics (dispersities between 1.15-1.25) and well working chain end functionalities. The barbital group placed at the meso-position of **2** responsibly caused the activity in this photo-ATRP framework while the squaring type, which also depicts a neutral pattern, did show any polymerization activity. Compounds **1** and **4**, which bear a cationic and anionic pattern, did show any polymerization activity either. The chain-end fidelity of the obtained polymers was approved by chain extension and block copolymerization experiments resulting in narrow disparities as well. The polymerization system exhibits high photostability under NIR light exposure taking anaerobic or aerobic conditions demonstrating the high photo stability of this new photocatalytic system. For comparison, fast bleaching was observed without Cu(II) and replacement of another radical initiator; that is an iodonium salt. Several light on/off experiments approved the function of the system comprising **2** with barbital group, Cu(II), TPMA and EBPA.



POLY 520: Renewable thermosets and thermoplastics from itaconic acid

Jacob T. Trotta¹, jttrotta@gmail.com, **Brett P. Fors**². (1) Cornell University, Peabody, Massachusetts, United States (2) Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States

Itaconic Acid (IA) is a well established renewable resource, produced inexpensively and on large scales worldwide. Herein, we report catalytic, solvent-free transformations of IA into structurally diverse monomers. Subsequent polymerization through a step-growth process gives rise to both saturated and unsaturated polymers that can be further modified through crosslinking or chain extension to give almost 100% IA-derived thermosets and thermoplastics. Characterization of these materials with a variety of methods including tensile testing and dynamic mechanical thermal analysis provides insight into their behavior, establishing them as green alternatives to petroleum-based materials for various renewable applications.

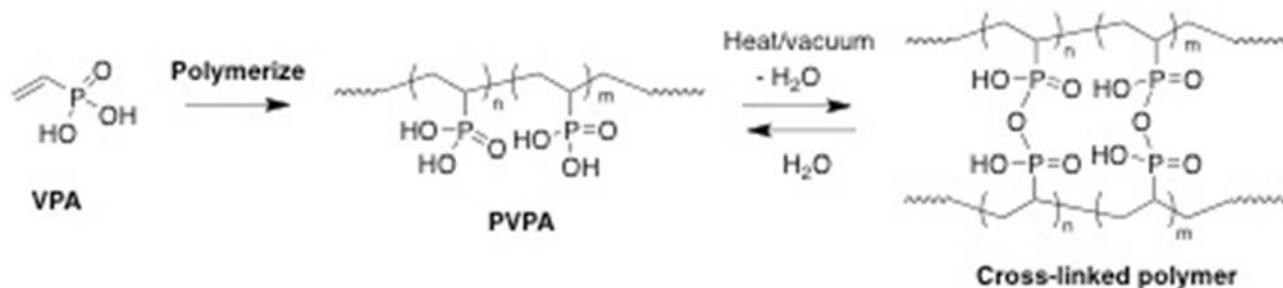


Synthesis of thermosets and thermoplastics from biorenewable Itaconic Acid.

POLY 521: Synthesis of poly(vinyl phosphonic acid)-based polymers and their potential applications

Sarah L. Lilholt¹, lilholst@clarkson.edu, **Ishah Alshehri¹**, **Kelly Tillman²**, **Devon A. Shipp¹**. (1) Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States (2) Chemistry and Biomolecular Science, Clarkson University, Potsdam, New York, United States

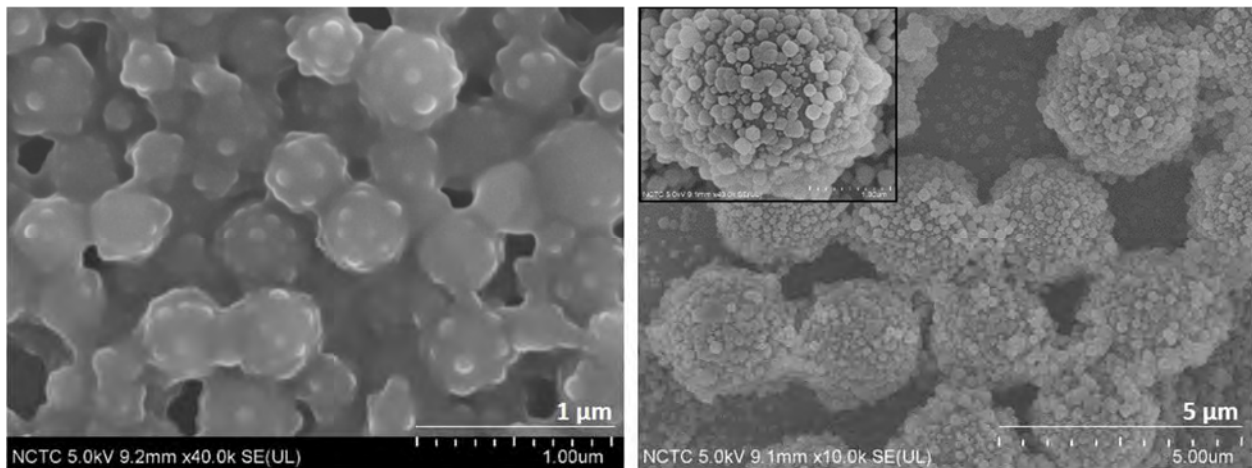
Phosphonic acid functionalized (co)polymers have been identified as a potential candidates for use in many biomedical applications such as bone tissue engineering. Among the many phosphonic acid functionalized monomers, particular attention has been recently paid to vinyl phosphonic acid (VPA), which is a low cost industrial monomer. It is hypothesized that VPA homopolymerization and the potential crosslinking agents of VPA after polymerization leads to significant changes in polymer solubility and biocompatibility. Here we report use of radical polymerization to produce VPA-based polymers. This is achieved using both conventional radical polymerization (CRP) and reversible addition-fragmentation chain-transfer polymerization (RAFT) in homogeneous aqueous conditions. In addition we describe demonstrate that reversible crosslinking is achievable with these polymers. The polymers were characterized using gel permeation chromatography (GPC) and ¹H NMR spectroscopy.



POLY 522: Synthesis and characterization of nanoZIF-8 loaded polystyrene composite particles

Sineenat Thaiboonrod¹, sineenat@nanotec.or.th, Warayuth Sajomsang¹, Chalita Ratanatawanate², Pattarapond Gonil¹. (1) National Nanotechnology Center, Klong Luang, Phatumthani, Thailand (2) National Nanotechnology Center, Thailand, Klong Luang, Pathum Thani, Thailand

Zeolitic imidazolate frameworks (ZIF-8) is a kind of metal organic framework (MOF). Basically, they can be made from zinc ions coordinated with four imidazolate rings. They have chemical and thermal stability which make ZIFs capable of diverse applications, such as gas storage, separation, heterogeneous catalysis and chemical sensing. However, the ZIF-8 in form of nano-sized powder is difficult to handle and collect after used. The aim of project is to improve the stability of individual ZIF-8 by incorporating with polymeric particles. Polystyrene (PS) has been selected since its simple preparation method, size variation and functionalization ability. NanoZIF-8 loaded PS composite particles are prepared via two methods (i) dispersion polymerization of styrene with ZIF-8 and PVP in one step and (ii) polystyrene particles are prepared prior surface functionalization of PS particles and generate ZIF-8 on the PS particle surface. The composite particles prepared via one step method exhibited the ZIF-8 embedded in the particles surface, while two step method created the ZIF-8 attached on the particles surface as shown in Fig. 1. XRD patterns confirmed the present of ZIF-8 on the composite particles surface. This composite particles can be used as absorbent materials or applied for waste water treatment.

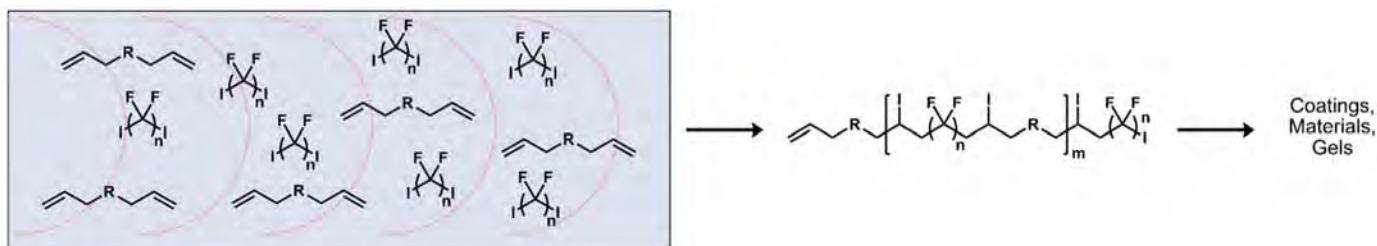


SEM micrographs of ZIF-8 loaded PS composite particles prepared via one step (left) and two step method (right)

POLY 523: Green synthesis of functional fluoropolymers

Joseph Jaye, jaye4028@g.ucla.edu. Chemistry, University of California-Los Angeles, LOS ANGELES, California, United States

Fluoropolymers are widely used in many different industries due to the desirable physical properties of these polymers, such as high melting points and maximum operation temperatures, high electric chemical resistance. The inert nature of the carbon-fluorine bonds surrounding the carbon backbone is what gives these materials their outstanding properties, but also make the resulting materials difficult to characterize and manipulate into functional products. The reaction conditions to generate many of these fluoropolymers involve high pressure with toxic and highly reactive gases. We have developed a safe and scalable method to produce high molecular weight fluoropolymers from a diene and perfluorodiiodide monomers. The resulting polymers maintain desirable fluorous properties while having increased solubility and processability. This method allows for the incorporation of functional dienes to result in chemically responsive fluorous materials. Furthermore, we have shown these polymers can readily undergo post-polymerization modification. Collectively, this new methodology sets the stage for the creation of functional fluorous materials.

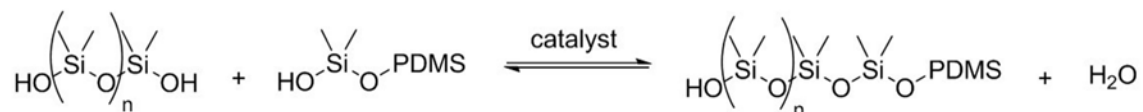


POLY 524

Lewis acids as highly active silanol condensation polymerization catalysts

Matthew Belowich, MEBELOWICH@DOW.COM, Evelyn Auyeung, John Roberts, Thomas Peterson, Shuangbing Han, Vladimir Pushkarev, Wen-Sheng Lee. The Dow Chemical Company, Midland, Michigan, United States

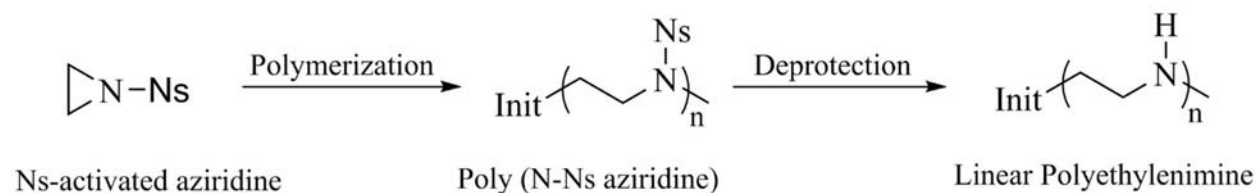
Silanol condensation polymerization is one of the most important reactions for the production of silanol-terminated polysiloxanes and is involved in the manufacturing of many silicone products. While typical condensation catalysts include potassium hydroxide or Bronsted acids, Lewis acids have remained largely unexplored. Herein, we explore several trends that govern the activity of a series of metal complexes as silanol condensation polymerization catalysts – namely, the electrophilicity of the metal center and the donicity of the ligands.



POLY 525: Anionic polymerization of nitrophenylsulfonyl-activated aziridines

Pierre Canisius Mbarushimana, *pambarushimana@crimson.ua.edu*. Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama, United States

The synthesis of polyethyleneimine (PEI) via anionic ring opening polymerization of aziridines has been intensively studied for the past couple of decades due to their use in gene transfection and CO₂ capture. There are two forms of PEI, linear and branched PEI (LPEI & BPEI). BPEI is easily obtained by electrophilic ring opening polymerization of unsubstituted aziridine with a Lewis acid or a cationic catalyst, whereas LPEI is usually synthesized by post-modification of cationically obtained poly (2-oxazoline)s (POXs). Herein, we report the synthesis, polymerization, and characterization of nitrophenylsulfonyl-activated aziridines. The synthesized poly(N-nitrophenylsulfonyl aziridine)s showed good solubility in DMF and DMSO, and can be used as precursor to linear PEI.



Init. : Initiator
PG : Protecting group
Ns : Nitrophenylsulfonyl group

POLY 526: Transition metal mediated ATRP of butadiene

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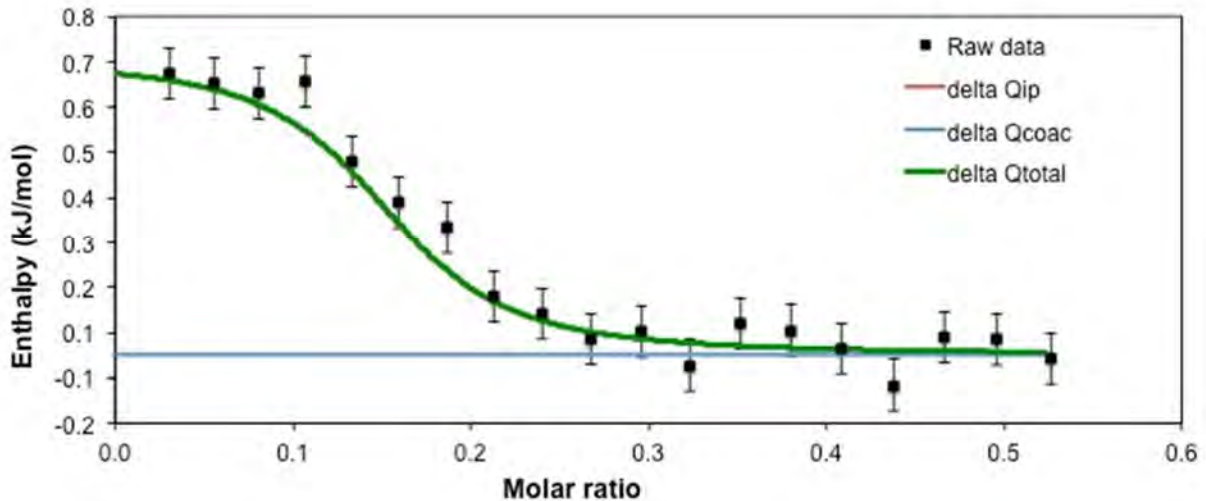
By contrast with the controlled radical polymerization (CRP) of styrene and (meth)acrylates the metal mediated CRP of gaseous dienes remains challenging. To this end, we have carried out comprehensive investigations of the effect of the reaction variables in the ATRP of butadiene mediated by group 8 (Fe, Ru), 10 (Ni, Pt, Pd) and 11 (Cu) transition metals, including the ATRP method, the nature of the halide, initiator, ligand, solvent and temperature. The rational selection of these parameters affords the synthesis of well defined polybutadiene with low polydispersity and high chain end functionality, suitable for the ATRP synthesis of complex architectures including stars and block copolymers.



POLY 527: Thermodynamic investigation of hyaluronic acid-chitosan coacervates

Fatma Akcay Ogur¹, Fatma A. Akin¹, **Ayşe B. Kayitmazer**^{1,2}, *bkayitmazer@gmail.com*.
(1) Department of Chemistry, Bogazici University, Istanbul, Turkey (2) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Hyaluronic acid (HA) and chitosan (CHI) are weak, semi-flexible biopolymers which have found interesting applications in biomaterials due to their biocompatibility and biodegradability. The interaction between anionic HA and cationic CHI system was investigated with isothermal titration calorimetry (ITC). By increasing the mole ratio, HA/CHI system went through a sequence of two stages: First, soluble (colloidal) complexes were formed when the association was weaker. As the system approached charge complementarity, these complexes associated to go into phase separation; polyelectrolyte-rich (coacervate) and polyelectrolyte-poor (dilute) phase. While enthalpic contributions for the stages of both soluble complexes (sc) and coacervates (coac) were endothermic, HA/CHI interaction was found to be predominantly entropic due to the release of small ions. Furthermore, the effects of various parameters (pH, ionic strength, temperature and polymer molecular weight) were investigated by ITC to determine binding constant of soluble complexes (K_a), stoichiometry of soluble complexes and coacervation (n_{sc} and n_{coac}), and molar heat capacity (ΔC_p).

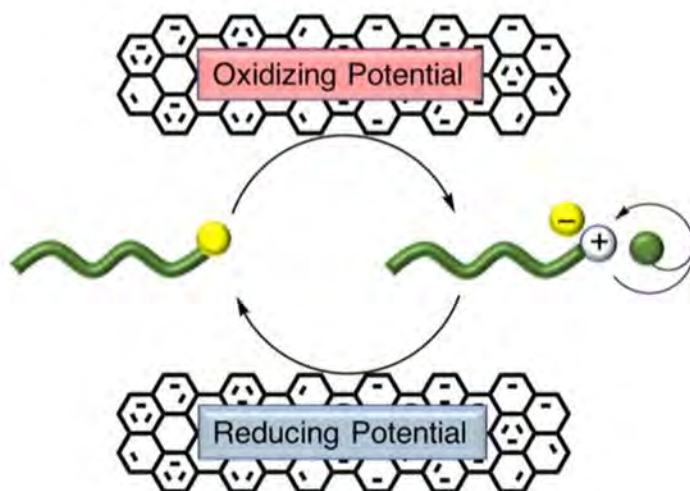


Experimental raw data and plots of curve fitting to two-step model for interaction of hyaluronic acid-chitosan. pH = 4.0, I = 0.15 M, T = 25°C. "IP" stands for soluble complexes while "coac" stands for coacervation.

POLY 528: Electrochemically controlled cationic polymerizations

Brett P. Fors, bpf46@cornell.edu. *Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States*

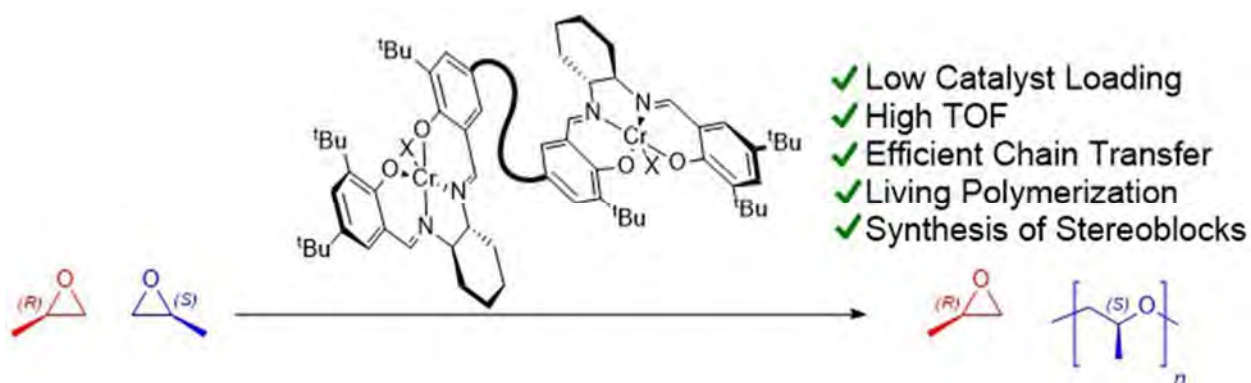
Cationic polymerizations that are initiated by an external stimulus are widely used in industrial processes. Importantly, going beyond initiation and obtaining external control over polymer chain growth would expand the utility of these methods and allow the synthesis of novel complex architectures. This presentation will detail the use of electrochemistry to gain temporal control over cationic polymerization, where an oxidizing potential can initiate chain growth and a reducing potential can reversibly terminate the propagating cation. Using an appropriate mediator, excellent control over polymer molar mass and dispersity is demonstrated for a wide variety of vinyl ether and styryl monomers.



POLY 529: Bimetallic chromium catalysts with chain transfer agents: A new route to isotactic poly(propylene oxide)s with narrow dispersities

Lilliana S. Morris, lsm227@cornell.edu, Ian Childers, Geoffrey W. Coates. Cornell University, Ithaca, New York, United States

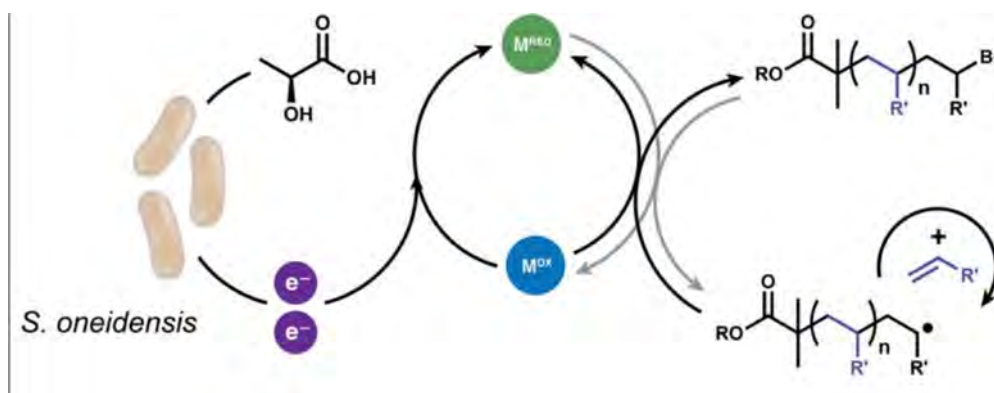
Herein we describe the investigation of bimetallic chromium catalysts for the enantioselective polymerization of propylene oxide. The catalyst is composed of two salen chromium species linked by an alkyl chain, the length of which significantly impacts the rate of polymerization. While the use of a chloride initiator on the catalyst resulted in bimodal molecular weight distributions, switching to a trifluoroacetate initiating group and adding a diol chain transfer agent afforded a living polymerization system. This system enabled access to both isotactic and stereoblock polymers with low, unimodal dispersities from racemic monomer.



POLY 530: *S. oneidensis* as a living electrode for controlled radical polymerization

Gang Fan, danielgangfan@gmail.com, Christopher Dundas, Austin Graham, Nathaniel A. Lynd, Benjamin Keitz. Mcketta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas, United States

Bacteria produce a variety of soft materials, but they are limited in their structure and function. A synthetic system in which the power of bacterial engineering is combined with traditional organometallic catalysis could pave new avenues to polymer synthesis. Here we demonstrate that electroactive bacteria, *S. oneidensis*, can control the activity of a transitional-metal catalyst in atom-transfer radical polymerization (ATRP) through extracellular electron transport (EET) machinery. This polymerization features characteristics of controlled radical polymerization, such as first-order kinetics, narrow molecular weight distribution and block-polymer synthesis. Catalyst performance and polymer microstructure were a strong function of bacterial metabolism, specific electron transport machinery, and catalyst design. Overall, our results demonstrate that targeting biological electron transport pathways may combine the advantages of metabolic engineering with traditional organometallic catalysis.

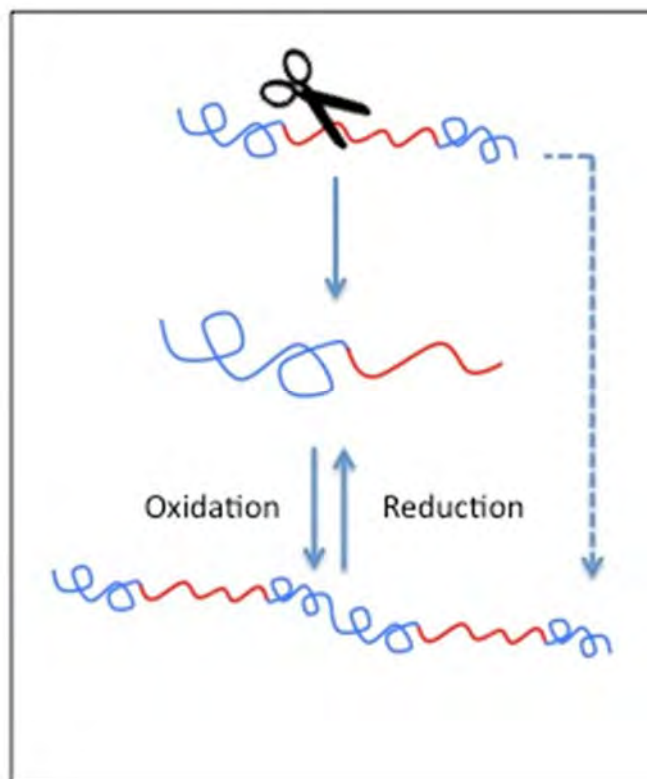


***S. oneidensis* enabled atom-transfer radical polymerization (ATRP)**

POLY 531: Convenient synthesis of redox responsive block polymers

Debbie K. Schneiderman, *schne643@umn.edu*, Tania Ruiz Velasco, Ron Miranda, Stuart J. Rowan. *Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States*

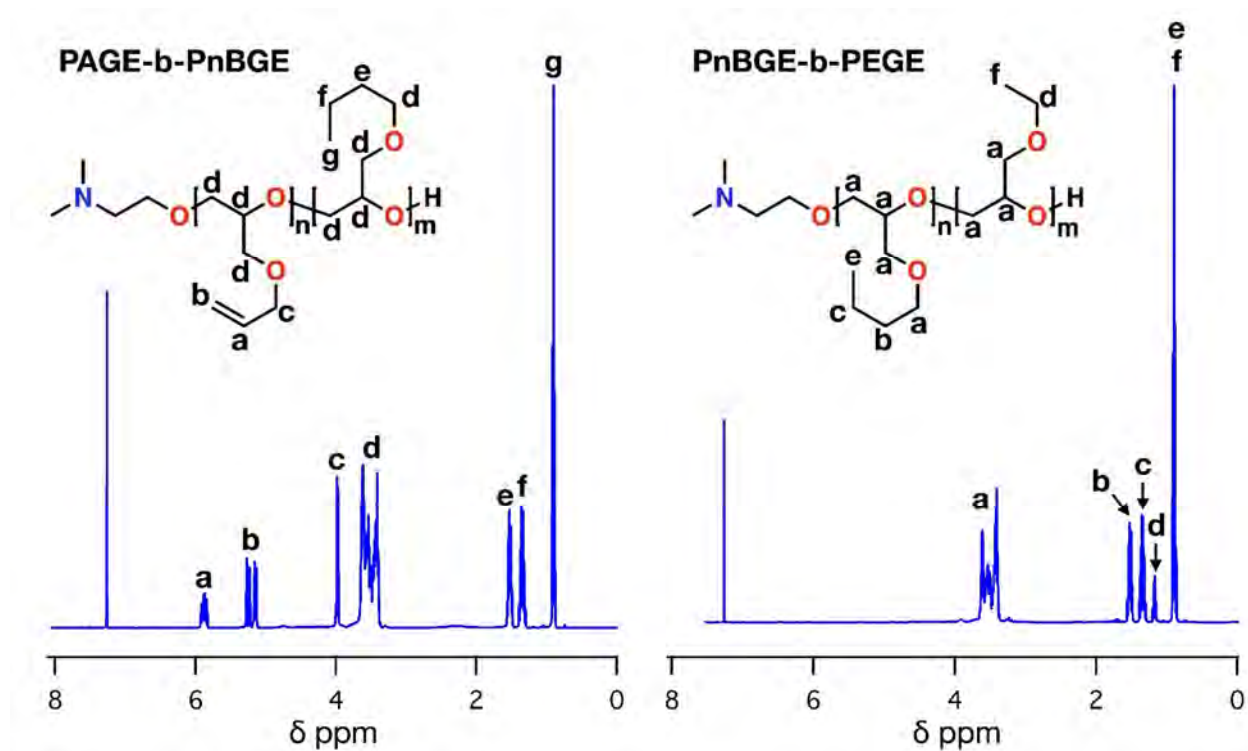
Changes in block polymer architecture directly impact phase behavior and thus the properties of the bulk material. For example, while ordered ABA triblocks may behave as tough plastics or elastomers, ordered AB diblocks of a similar compositions have little tensile strength. This difference is due to the ability of individual triblock polymer chains to bridge multiple domains. For the same reasons, linear $-(AB)_n-$ multiblock polymers display even greater toughness than ABA triblocks. However, linear multiblock polymers prepared by coupling necessarily have larger molecular weights and higher viscosities than their parent prepolymers, which can limit their processability. To combat this problem, we have synthesized linear redox responsive block polymers that can be reversibly reconfigured from a triblock to diblock to multiblock over multiple cycles. Using a small library of samples, we study the role embedded dynamic bonds play in influencing the phase behavior, mechanical, and rheological properties of linear block polymers in the bulk. Finally, we also discuss the synthesis of non-linear (branched, brush, and comb) architectures with reconfigurable bonds.



POLY 532: Synthesis and self-assembly of polyether-containing block polymers

Nathaniel A. Lynd, nate.lynd@gmail.com. Department of Chemical Engineering, University of Texas at Austin, Berkeley, California, United States

Polyethers derived from epoxides represent a versatile class of polymeric materials. Recent developments in polymerization catalysis have enabled the synthesis of new architecturally and compositionally controlled block polymer materials. In this presentation I will describe the development of new organoaluminum catalysts for epoxide polymerization and their application for block polymer synthesis.



POLY 533: Reversible-addition fragmentation chain transfer (RAFT) mediated depolymerization of brush polymers

Michael J. Flanders, **William Gramlich**, william.gramlich@maine.edu. Department of Chemistry, University of Maine, Orono, Maine, United States

Brush block polymers can form nanostructures with greater than 100 nm domains through block polymer microphase separation, enabling advanced materials such as photonic crystals. Synthesis of brush block polymers by a “grafting-through” (i.e. polymerization of macromonomers) has had the most success using techniques such as ring opening metathesis polymerization. Controlled radical polymerization techniques such as reversible-addition fragmentation chain transfer (RAFT) polymerization face challenges creating high molecular weight materials due what has been typically referred to as the “low reactivity” of the macromonomers used for polymerization; however, the origins of these challenges has not been explored fully. Explorations into RAFT polymerized brush polymer behavior discovered that these polymers undergo depolymerization when heated at typical polymerization temperatures (ca. 70 °C) in the absence of initiator. This depolymerization followed pseudo first ordered kinetics while heated in 1,4-dioxane, reaching macromonomer concentrations of circa 30 mM for both oligo-ethylene glycol methacrylate (OEGMA) and oligo-dimethylsiloxane methacrylate (ODMSMA) polymers (Figure 1a). Since the liberated monomer concentration ([M]) plateaued with time, polymerization thermodynamic equilibrium was expected which was confirmed through polymerization of these macromonomers converging to the same [M] as was observed for depolymerization (Figure 1b). The depolymerized polymers still had active RAFT chain transfer agents as they could reinitiate RAFT polymerizations. The origin of radicals required to initiate the external initiator free depolymerization was found to be likely due to low levels of thermal homolytic cleavage of bonds off the polymer chain. These results underscored the importance of selecting appropriate RAFT polymerization conditions to successfully synthesize brush block polymers.

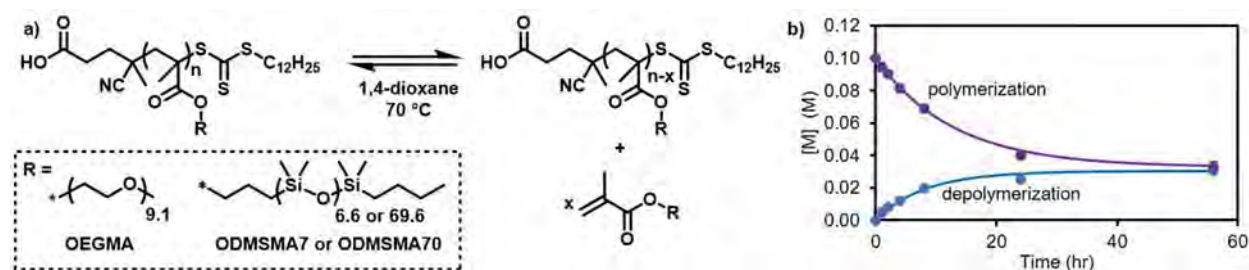
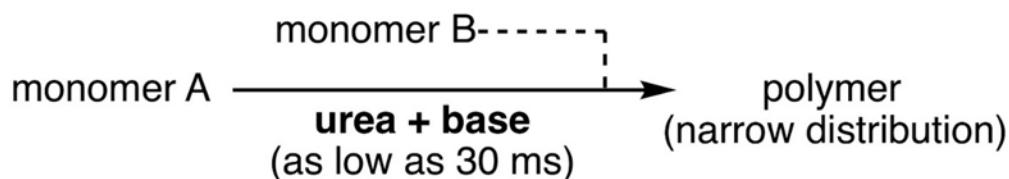


Figure 1. A) Polymerization-depolymerization equilibrium. B) Monomer concentration ([M]) as a function of time for polymerization and depolymerization of ODMSMA.

POLY 534: Organic ring-opening polymerization catalysts: A facile approach to homopolymers and block copolymers

Binhong Lin¹, binhong@stanford.edu, Nathan Park², James Hedrick², Robert M. Waymouth³. (1) Department of Chemistry, Stanford University, Stanford, California, United States (2) IBM Research, San Jose, California, United States (3) Dept of Chemistry, Stanford University, Stanford, California, United States

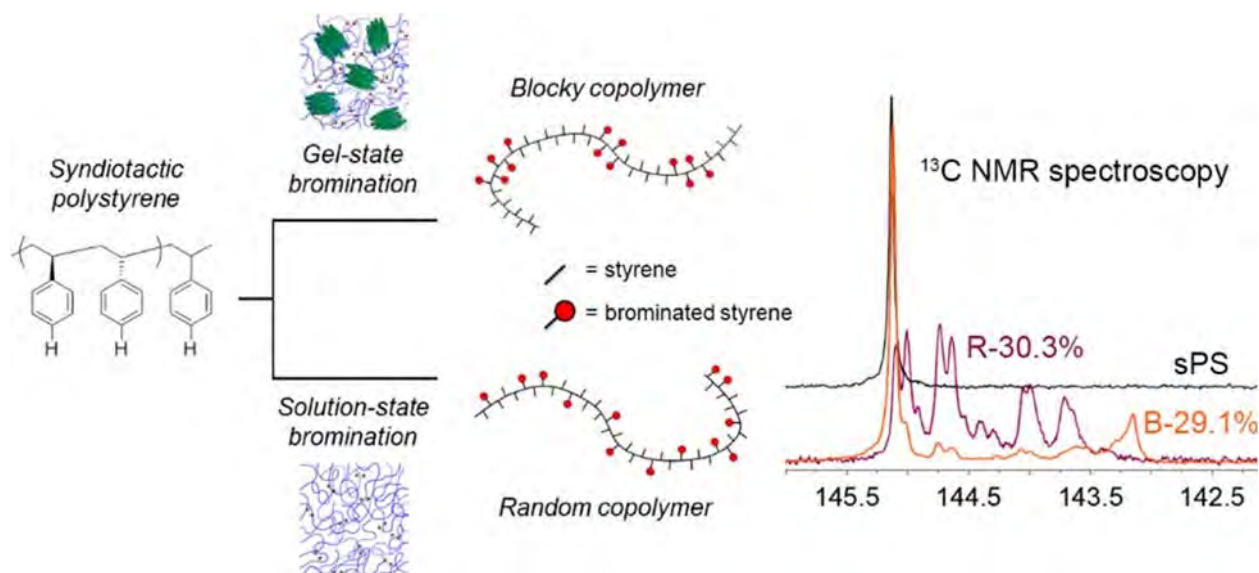
Polyesters and polycarbonates constitute a key class of functional materials as solutions to challenges and new opportunities in chemistry, materials science and medicine. A family of highly selective catalysts, urea anions, lead to the controlled polymerization of a range of monomers in seconds to generate well-defined homopolymers and block copolymers. The observed anion catalytic activity is a function of the acidity of the ureas, which prompted a systematic investigation of the benchmark organocatalyst thiourea/DBU system. The findings not only deliver a suite of catalysts with activities ranging almost 10 orders of magnitude that can cater to various synthetic demands, but also provide useful guidelines for the rational design of catalysts.



POLY 535: Post-polymerization synthesis of blocky copolymers via reactions in the semicrystalline gel-state

Robert B. Moore¹, rbmoore3@vt.edu, Lindsey Anderson², Kristen Felice², Samantha Talley². (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

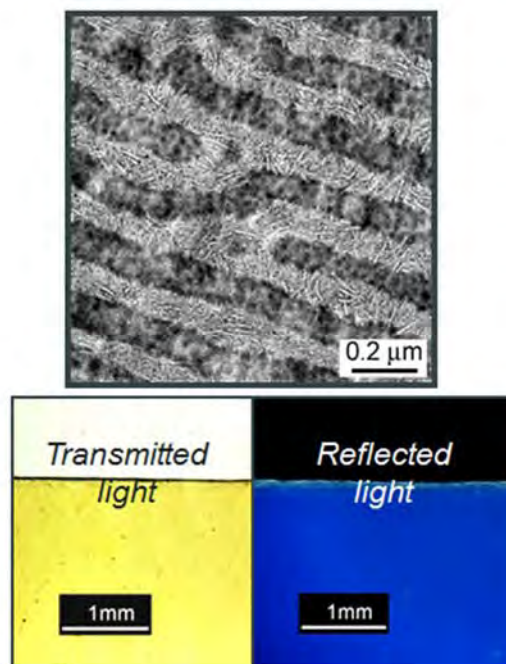
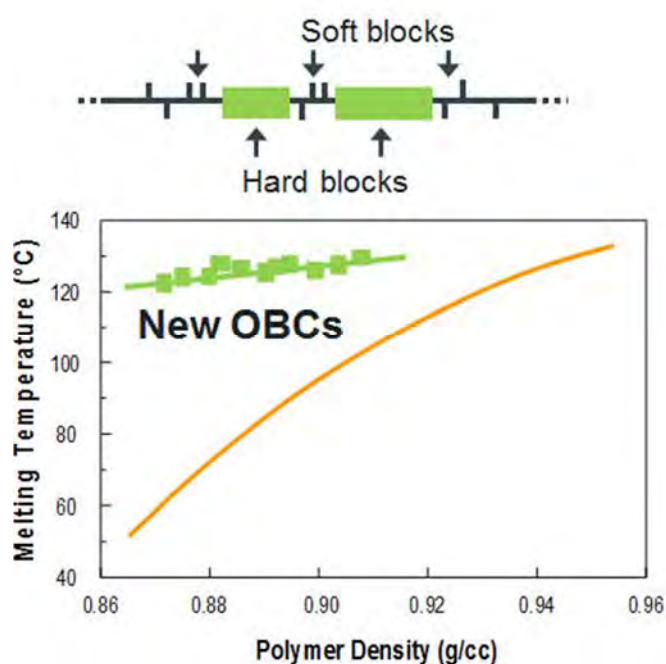
Post-polymerization functionalization is a useful technique to modify existing homopolymers and provide functional handles for further substitution. Recent findings from the ion-containing polymer membrane community have taught us the importance of controlled sequencing of ionic groups along polymer chains in the development of ordered polar domains for enhanced transport properties. When compared on an equal ion content basis, a blocked arrangement of ionic groups along polymer chains tends to produce more ordered nano-phase-separated domains while preserving the inherent properties of the unfunctionalized homopolymer over that of analogous random ionomers. Inspired by these demonstrated enhancements, we are exploring the impact of variable post-polymerization sulfonation and bromination reactions on the spatial distribution of functional groups in blocky copolymers. Very recently, we have discovered a non-functionalizing solvent for PEEK that allows for a homogeneous sulfonation reaction. Surprisingly, this new solvent also allows for the formation of a thermo-reversible gel. Following a method we previously developed to sulfonate syndiotactic polystyrene (sPS) in the gel state, we are now able to prepare blocky forms of sulfonated and brominated sPS and PEEK that have a high degree of functionalization, high degree of crystallinity, and sequence-dependent nanoscale phase behavior.



POLY 536: Synthesis, materials science, and applications of olefin block copolymers prepared by chain shuttling catalysis

Phillip D. Hustad¹, pdhustad@dow.com, **Edmund M. Carnahan**², **Jeffrey Weinhold**³, **Colin Li Pi Shan**¹. (1) The Dow Chemical Company, Lake Jackson, Texas, United States (2) The Dow Chemical Co, Freeport, Texas, United States

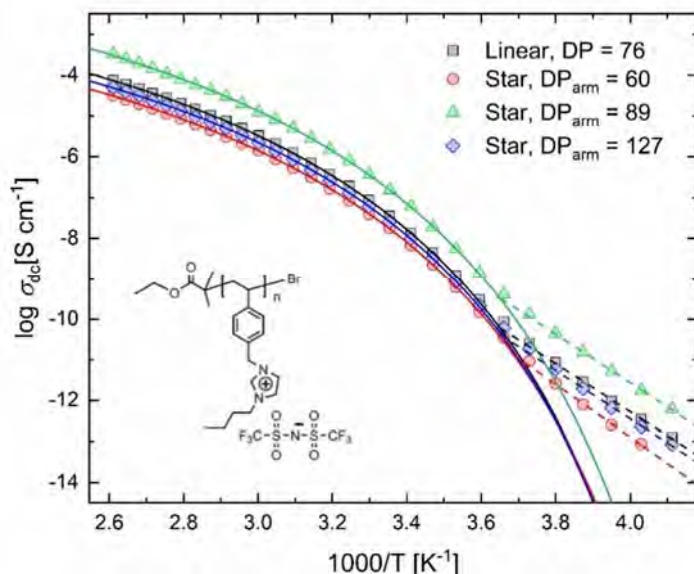
Carbon and hydrogen, organized appropriately, have generated a massive global industry with products touching most aspects of modern life. Three quarters of a century later, scientists are still able to extract additional performance from these diminutive polymer chains. Our search for ways to craft polyethylene with a better balance of flexibility and heat resistance led to some fascinating discoveries in catalysis and polymer materials science. We discovered certain advanced homogeneous catalysts are capable of reversible chain transfer to certain metal alkyl species; this so-called chain shuttling catalysis enables the synthesis of block copolymers from simple olefinic feedstocks in a catalytic fashion. Enabled by these inventions, The Dow Chemical Company commercialized INFUSE™ Olefin Block Copolymers and INTUNE™ Olefin Block Copolymers. These new materials have unique morphologies as a consequence of their block structure. Several aspects of these materials will be discussed with particular emphasis on their unique characteristics that enable them to perform in a range of applications previously inaccessible to polyolefins.



POLY 537: Interactions, organization, and functional properties of star poly(ionic liquid) assemblies

Andrew J. Erwin^{1,4}, aerwin6@gatech.edu, Hongkun He², Krzysztof Matyjaszewski², Alexei P. Sokolov^{3,4}, Vladimir V. Tsukruk¹. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (3) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (4) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States

Star polymers are attractive components for soft nanostructured materials because their heterogeneous segmental densities, soft particle interactions, and anomalous phase behavior generally expand their functionality. While the diverse range of properties and assembly behavior of branched polyelectrolytes have long been explored, poly(ionic liquid)s (PILs) with star architectures have received relatively little attention. Here, the interactions of an imidazolium-based star poly(ionic liquid) with bis(trifluoromethylsulfonyl)imide counterions and different degrees of polymerization are investigated at interfaces and within both nanoscale and microscale films. We find that the amphiphilicity of ionic liquid moieties suppresses association of star PILs at the air-water interface whereas their linear counterparts irreversibly aggregate. Additionally, linear and star PILs are demonstrated to have different responsive internal and surface microstructures in multilayer thin films. Due to their orthogonal solubilities in aqueous solutions and organic solvents, solvent-annealing is demonstrated to control the dewetting at interfaces. Moreover, the role of star architecture and their responsive morphologies on the thermal, mechanical, and ion conducting properties is elucidated. These studies outline the advantages of using branched polymer topologies to guide the organization of ionic liquid materials with tunable functional properties.

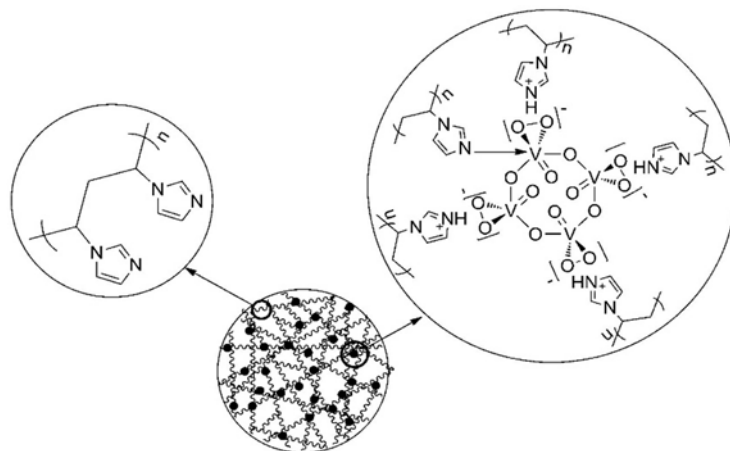
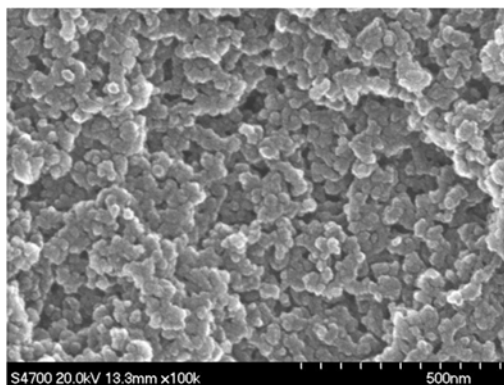


The dc conductivities are plotted against reciprocal temperature for the linear and star PILs. There is a dynamic crossover near T_g separating Vogel-Fulcher-Tammann dependence above (solid lines) and Arrhenius behavior below (dashed lines).

POLY 538: Highly crosslinked PILs as sorbent and catalyst in deep desulfurization of fuel oil

Chunxi Li, *licx@mail.buct.edu.cn*, Hong-yan Song. Faculty of Science, Beijing University of Chemical Technology, Beijing, China

Linear polymers of polyvinyl imidazole (PVIM) and polyvinyl pyridine (PVP) were synthesized via radical polymerization, and then ionized by varying crosslinking reagents, p-xylene dichloride, phosphotungstic acid, and vanadic acid. The structure and morphology of the as-prepared poly ionic liquids (PILs) were characterized by different methods, including XRD, FTIR, elemental analysis, BET analysis, SEM, TG-DSC etc. Their application as sorbent and catalysts for the adsorptive and oxidative desulfurization of fuel oils were studied. The PILs are mesoporous with higher specific area ($100\sim 600\text{ m}^2\cdot\text{g}^{-1}$), and higher adsorptive desulfurization ability than their ionic precursors due to their rich porosity and high specific area. The heteropoly acid based PILs (V-PIL, HPW-PIL) show much better catalytic performance than their heteropoly acids due to the synergic effect of adsorption mesoporous PIL and the in situ catalytic oxidation by the well dispersed active sites. Two oxidative desulfurization processes were studied by using H_2O_2 and CHP as oxidants respectively, both achieves promising desulfurization performance.



POLY 539: Mesoporous poly(ionic liquid)s catalyze the conversion of CO₂ into high-value chemicals

Yu Zhou, njtzhouyu@njtech.edu.cn, Zengjing guo, Jun Wang. Nanjing Tech University, Nanjing, China

Chemical fixation of carbon dioxide (CO₂) into valuable organic compounds has attracted great attention to control the increased CO₂ concentration. Cycloaddition of CO₂ and epoxides is a 100% atom-economical reaction to generate cyclic carbonates and polycarbonates, representing one of the most promising ways for CO₂ fixation. However, it is challenging to construct heterogeneous catalyst for efficient conversion under mild conditions. Mesoporous poly(ionic liquid)s (MPILs) with large surface area and tunable porosity possesses the unique ionic liquids (ILs) moieties in the polymeric framework, which are the internal high performance active sites for the cycloaddition of CO₂ and epoxides.

A double cationic IL monomer with a rigid molecular structure was synthesized and applied in an ionothermal free radical polymerization to afford a hierarchical MPIL with rich macropore and mesopore. The target catalyst led to the first highly active, metal-solvent-additive free heterogeneous catalyst in the cycloaddition of CO₂ and epoxides. (*Chem. Sci.*, 2015, 6: 6916-6924).

Imidazolium based porous hypercrosslinked ionic polymers (HIPs) with rich micro/mesoporosity provided high yield, stable reusability and good substrate compatibility under mild conditions (down to ambient conditions) in the cycloaddition of CO₂ with epoxides. The synergistic adsorption and conversion enabled the efficient low-temperature conversion of diluted CO₂ (0.15 bar CO₂ and 0.85 bar nitrogen, the simulation of flue gas) in the presence of co-catalyst ZnBr₂ (*Green Chem.*, 2017, 19, 2675-2686).

Vicinal dual hydroxyl functional mesoporous poly(ionic liquid)s acted as recyclable heterogeneous organocatalysts in the cycloaddition of a series of epoxides with CO₂ under mild conditions (down to ambient conditions). The remarkable performance was attributable to the abundant mesoporosity and the synergistic effect of vicinal dual hydroxyls as hydrogen-bonding donors and halogen anions as nucleophiles (*ACS Catal.*, 2017, 7, 6770-6780).

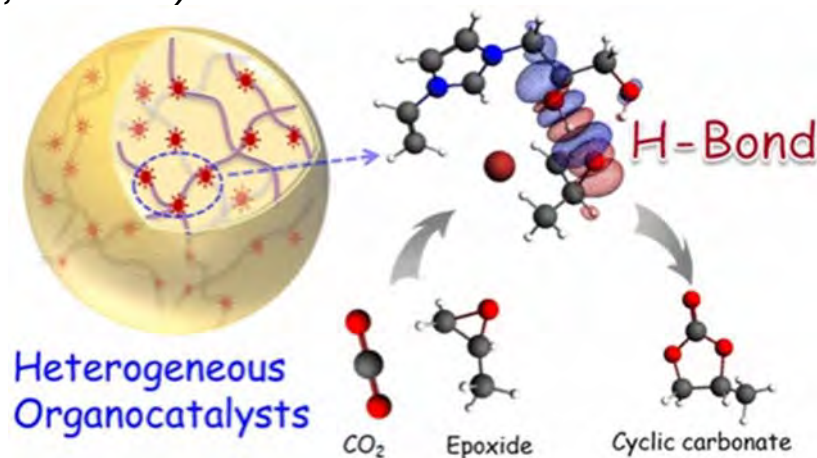
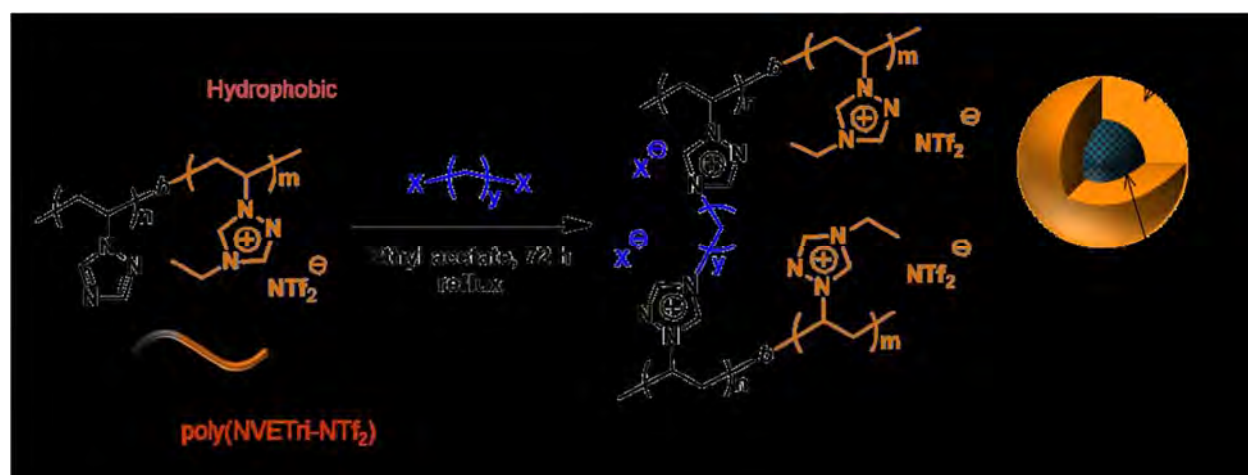


Fig. 1 The application of MPIL in conversion of CO₂.

POLY 540: Design of ion-conductive core-shell nanoparticles via site-selective quaternization of triazole–triazolium salt block copolymers

Chen-Tsyrr Lo, *loxxx148@gmail.com*, Kazuhiro Nakabayashi, Hideharu Mori. Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata, Japan

Triazolium-based ion-conductive nanoparticles (NPs) with cross-linked cores were synthesized using a self-assembled block copolymer comprising *N*-vinyl-4-ethyl-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (NVETri-NTf₂) and *N*-vinyl-1,2,4-triazole (NVTri) and site-selective cross-linking quaternization in a selective solvent. Four different dihalide compounds, namely diiodoethane, diiodooctane, dibromoethane, and dibromooctane, afforded four core–shell NPs NP(C2-I), NP(C8-I), NP(C2-Br), and NP(C8-Br), respectively. DLS analyses demonstrated the formation of stable NPs with uniform sizes ($D_h = 192$ nm for NP(C2-I), 196 nm for NP(C8-I), and 195 nm for NP(C2-Br)). Among these, NP(C2-Br) exhibited the highest ionic conductivities. In the presence of 30 wt.% ionic liquid, high ionic conductivities of 1.26×10^{-3} , 3.31×10^{-4} , and 1.36×10^{-4} S/cm were achieved with solid-state NP(C2-Br) at 90, 55, and 25 °C, respectively, which are due to the enhanced segmental molecular motion and the formation of a preferable ionic-conductive path composed of the hydrophobic ionic-liquid based shell with the added ionic liquid.

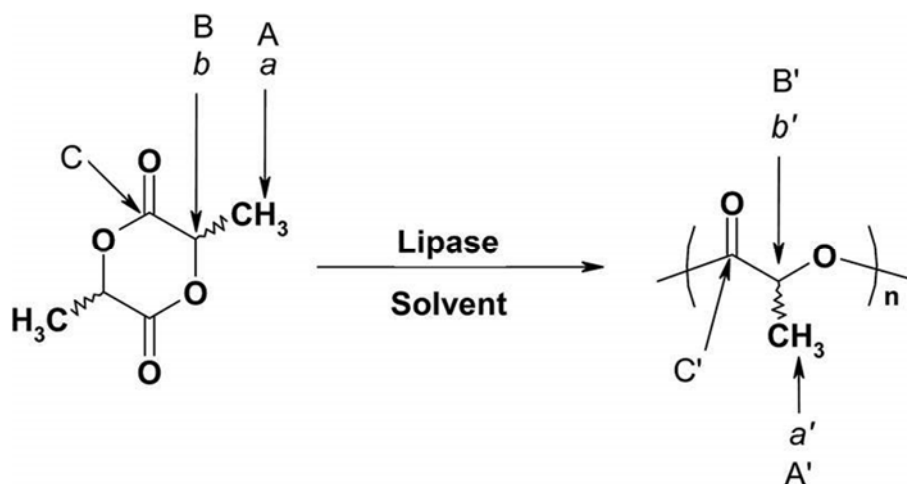


Schematic illustration of the synthesis of core-cross-linked nanoparticles from triazole–triazolium salt block copolymer.

POLY 541: Polyester synthesis via enzymatic ring-opening polymerization (ROP) in ionic liquids

Hua Zhao, *huazhao98@gmail.com*, Lennox Afriyie. Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, Colorado, United States

Enzymatic ring-opening polymerization (ROP) represents a 'greener' approach to the synthesis of polylactides and polylactones. However, there are discrepancies in the literature on the lipase specificity toward a particular monomer (such as L-lactide), and many disagreements on the molecular weights produced by similar methods. To enable a better understanding of the enzymatic ROP reaction, we carried out a systematic evaluation of the polymerization process under various conditions including the water contents in lipases and solvents, and different types of ionic liquids. Our custom-made ionic liquids are designed to be compatible with enzymes and for the high-temperature reaction condition. Our results indicate that these reaction parameters must be finely controlled for the enzymatic ROP reaction although some earlier studies often neglected some conditions (such as the exact water content in enzymes and solvents).

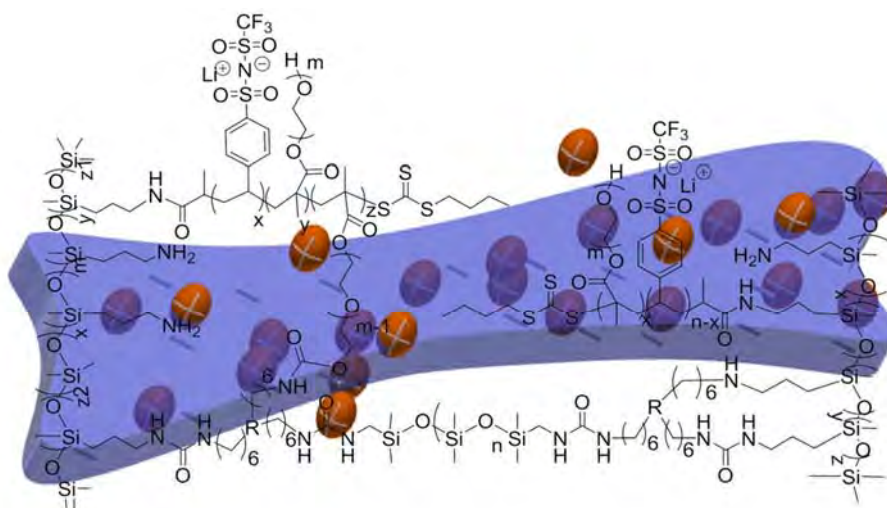


Enzymatic ring-opening polymerization of lactide

POLY 542: Stretchable single-ion conducting block copolymer membranes

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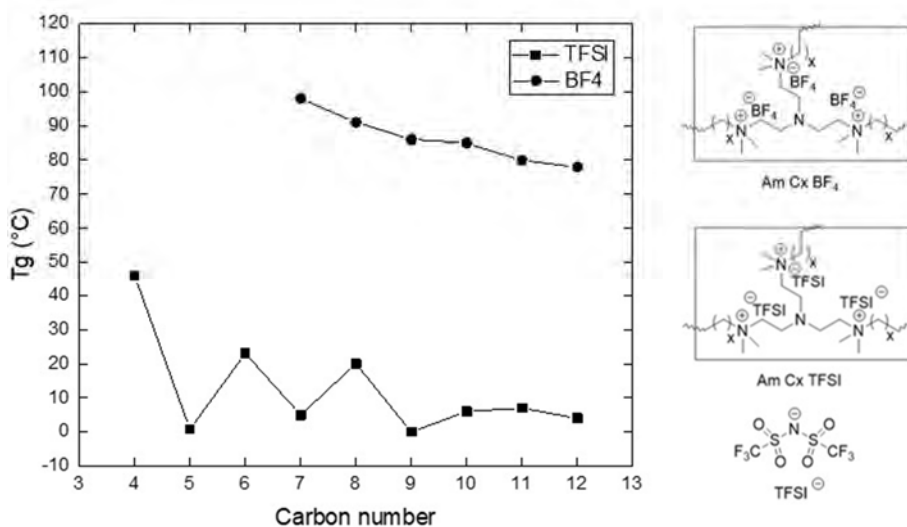
Single-ion conducting polymer electrolytes (SCPEs) are well recognized for increased energy efficiency and prolonged cell lifetime due to their capability to mitigate electrode polarization and reduce electrolyte loss. Stretchable electronics, especially stretchable batteries, have attracted significant interest. Herein, we will report the fabrication of a series of single-ion conducting polymer electrolyte membranes with high flexibility and stretchability that can be used for stretchable electronics. The tailored polymer membrane with polydimethylsiloxane (PDMS) as the polymer backbone and single-ion conducting polymer as the side chains has been fabricated. The investigation revealed that the incorporation of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) plays a significant role in forming the stretchable polymer membranes, which can not only lower the glass transition temperature but also provide additional reactivity. Tensile test shows that the polymer membrane can be stretched up to 250% before breaks. Modifying the molar ratio of PDMS based cross-linker in the polymer matrix enables to tune the Young's modulus of obtained membranes. Broadband dielectric spectroscopy (BDS) has been employed to measure the dc-conductivity of the membrane, and the dc-conductivity can be significantly improved after the addition of the propylene carbonate (PC), i.e., 10^{-4} S/cm.



POLY 543: Ion specific odd-even effects glass transitions in polymerized ionic liquid networks

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The odd-even effect is a well-known phenomenon where various physical properties (e.g. density, melting points) exhibit non-monotonic changes between odd/even structural units and are frequently rationalized in terms of differences in molecular packing ability. Recently, odd-even effects were reported for glass transition temperatures (T_g) in ionic liquid networks of divalent ammonium cations and trivalent citrate anions. Such odd-even T_g effects are less commonly reported and their physical origin is still unclear. Here we report an odd-even T_g effect in amorphous polymerized ionic liquid networks (Figure 1) whose magnitude depends on the specific ions. Initially, the network contains fixed ammonium groups and a mobile BF_4 counterion which shows a monotonic decrease in T_g with increasing length of the linker between network junctions. Upon ion exchange to mobile bis(trifluoromethane sulfonamide) (TFSI) anions which exhibits weaker electrostatic interactions with ammonium, the T_g drops substantially and shows an odd-even effect with linker length. These networks are ion exchanged from the exact same precursor material ostensibly ruling out network topology as a cause of the effect. Wide angle x-ray scattering of the TFSI networks reveals the typical peaks associated with the ionic aggregate formation; however, the scattering peaks exhibit monotonic intensity variations while T_g exhibits a pronounced odd-even effect in the TFSI networks. Thus, in these systems, the scattering data is not a reliable indicator of dynamics. Conductivity measurements of TFSI systems indicate that the networks with odd linker length all have higher conductivities (> 1 order of magnitude) than the even linker lengths providing an important insight into the design of ionic polymers for energy storage applications.



POLY 544: Multifunctional mesoporous poly(ionic liquid)s for the transformation of biomass platform compound 5-hydroxymethylfurfural

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Among the most abundant renewable resources, biomass is a unique carbon-containing renewable resource that is a promising alternative for fossil fuels, chemicals, and energy. 2,5-Diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) are the important platform chemicals with wide potential applications as precursors of furanbased biopolymers, pharmaceuticals, antifungal agents and ligands. Task-specific design of new efficient heterogeneous catalysts plays a crucial role in the transformation of platform compounds.

Mesoporous poly(ionic liquid)s (MPILs) possess both the advantages of mesoporous materials and ionic organic polymer. The ionic exchange ability of MPILs leads to strong affinity to the guest species such as heteropolyacid anion ($\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$) and noble metal anions (PdCl_4^{2-}). The electrostatic interaction between MPILs and guest anions benefits high activity and stability in the reactions like the conversion of HMF. For example, $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ enriched PILs acted as a highly efficient heterogeneous catalyst in the ambient selective aerobic oxidation of HMF into DFF with O_2 , offering a high DFF yield of 86.8% and TON of 121 (*Dalton Trans.*, 2016, 45, 4504-4508). Hydrophilic MPILs supported Au-Pd NPs shown the high activity in oxidation of HMF into FDCA (yield>99%) under the ambient conditions (*Green Chem.*, 2017, 19, 3820-3830). MPILs grafted with different acid groups (carboxylic group and sulfonic group) endow active acid sites in the multifunctional catalysts with potential high performance in the biomass-related tandem reactions. The binary catalytic systems of hydrophilic MPILs with carboxylic groups and $\alpha\text{-CuV}_2\text{O}_6$ got a high efficiency in the conversion of fructose into DFF (*Catal. Sci. Technol.*, 2017, 7, 1006-1016).

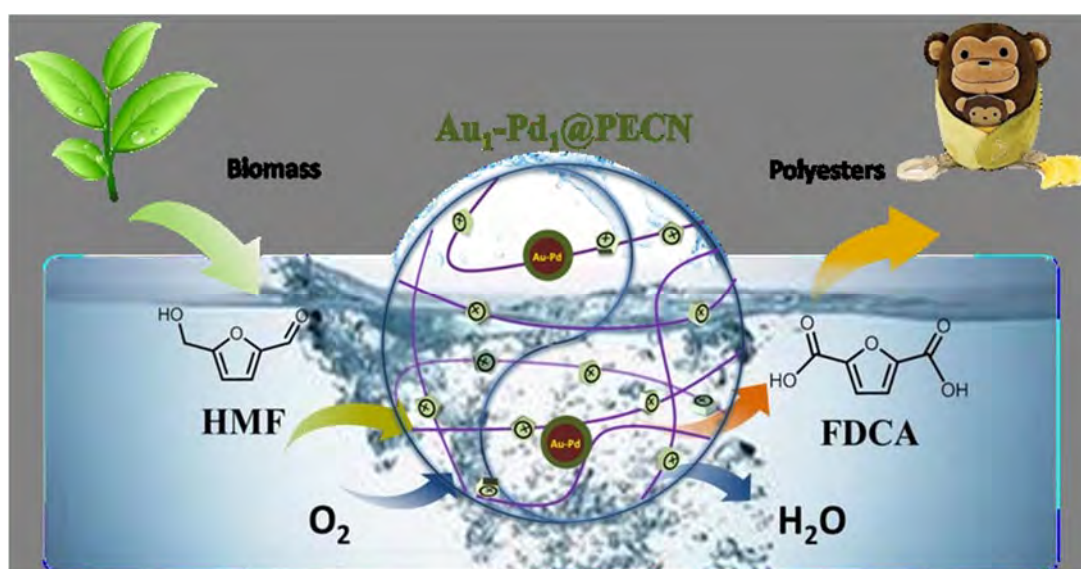


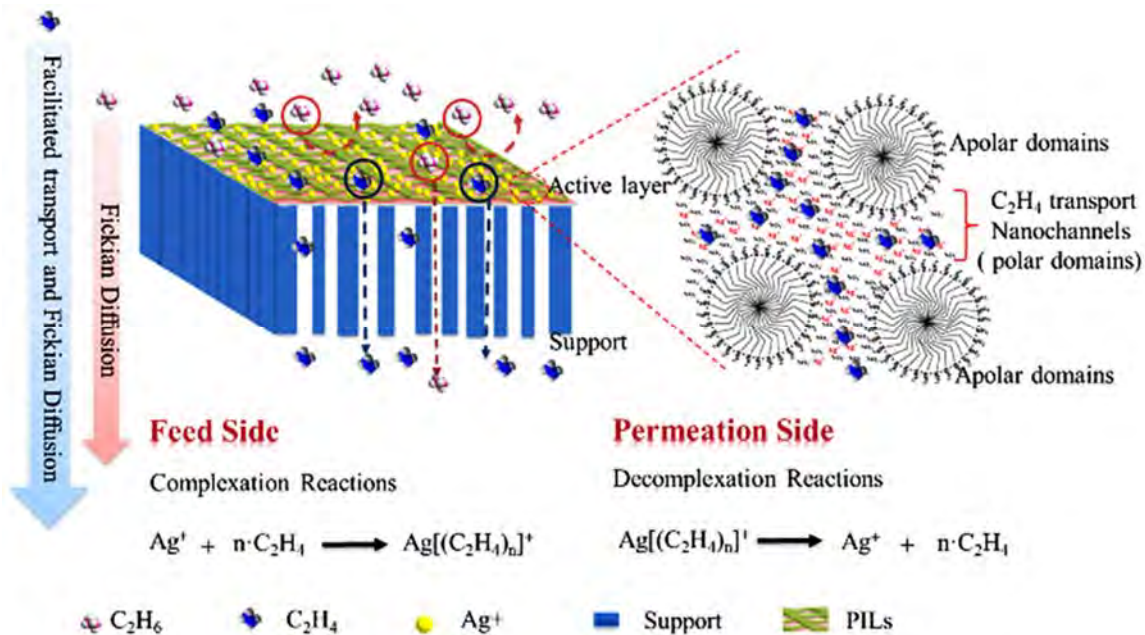
Fig.1 The reaction process of 5-HMF oxidation with Au-Pd@MPIL.

POLY 545: Protic ionic liquids composite membranes with selective gas transport nanochannels: Applications in olefin-paraffin separation

Xiaowei Tantai, tantaixw@tju.edu.cn, Luhong Zhang. Tianjin University, Tianjin, China

The separation of olefin/paraffin is one of the key industrial gas separations, which is challenging due to their similar physical and chemical properties, such as boiling point, solubility, and molecular size. To date, the most common technology for olefin/paraffin separation is cryogen distillation associating with huge capital and operation costs. Extensive researches have been conducted to develop novel materials or alternative techniques for olefin/paraffin separation.

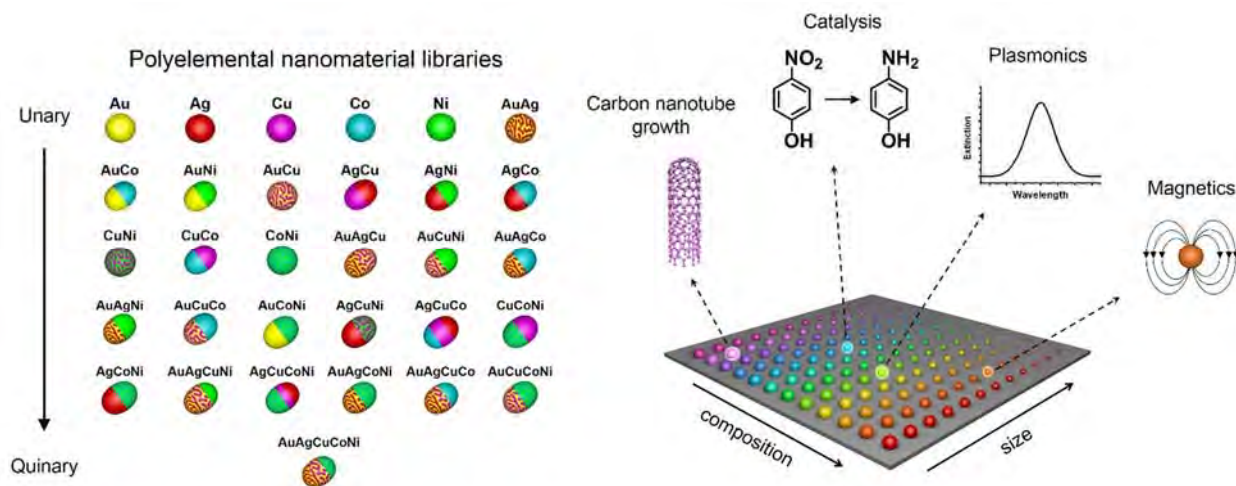
The protic ionic liquids (PILs) were firstly utilized for fabrication of composite membranes containing AgNO_3 as carrier to perform olefin/paraffin separation. The intrinsic nanostructures of PILs were skillfully adopted to construct the fast and selective olefin transport nanochannels. Results suggested apolar domains and polar domains of PILs could be tuned sustainably with the size of cations, thus greatly affecting the separation performances of membranes. The effects of carriers in the facilitated transport were studied, which revealed that the PILs are good solvents for dissolution and activation of AgNO_3 . Due to the excellent solvent properties of PILs, AgNO_3 exhibited comparable ability of facilitated olefin transport compared with the silver salts containing large and weakly electronegative anions such as BF_4^- and CF_3SO_3^- . The C_2H_4 permeability and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity could be greatly boosted with the silver salt concentration increasing. Overall, Ag/PILs composite membranes, which possess good long-term stability, excellent C_2H_4 permeability and high $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity up to 57, may have a good perspective in industrial $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separation.



POLY 546: Combinatorial nanoscience: Expanding the materials genome

Chad A. Mirkin, *chadnano@northwestern.edu*. Chemistry, Northwestern University, Wilmette, Illinois, United States

Multicomponent nanoparticles have many novel chemical and physical properties that are greater than the sum of their parts, which makes them promising for a range of fields including catalysis, magnetics, plasmonics, and electronics. The optimization of multicomponent nanoparticles with desired functionalities requires the development of platforms for systematically studying a broad spectrum of compositions and structures. Combinatorial screening is a common strategy to establish composition-structure-function relationships. To achieve this goal, we developed scanning probe block copolymer lithography (SPBCL), a technique that allows one to print attoliter-size nanoreactors on a substrate. These nanoreactors consist of polymers loaded with metal precursors, which upon thermal treatment can be converted into nanoparticles with sub-nm resolution and precise elemental composition. This technique has been successfully used to synthesize single metal, metal oxide, and metal sulfide nanoparticles, as well as, alloyed and heterostructured particles composed of metals including Au, Ag, Pd, Pt, Ni, Co, Fe, Cd, and Cu. When combined with polymer pen lithography (PPL), a high-throughput cantilever-free patterning technique that utilizes an elastomeric pen array with millions of pens, combinatorial libraries of nanoparticles can be made by varying the ink composition across a 1-million-pen array. The synergy between SPBCL and PPL enables an innovative and robust solution to synthesize new nanoparticles over large areas, which allows for the rapid screening of the properties of multicomponent nanoparticles. This novel approach lays the foundation for generating new combinatorial libraries of materials, where scale, in addition to composition becomes an important library parameter.



POLY 547: Machine learning for colloidal crystal structure and property discovery & inverse design

Sharon C. Glotzer, *sglotzerkjc@umich.edu*. University of Michigan, Ann Arbor, Michigan, United States

Machine learning is quickly revolutionizing materials discovery and design. In soft matter, machine learning can discover hidden correlations linking building block attributes to material structure, autonomously identify and classify from millions of state points dozens of polymorphs comprising a phase diagram, find “sweet spots” in the data where complexity is likely to arise, find new crystal structures with target properties, minimize the number of simulations or experiments needed to map phase boundaries, and more. Here we give examples of each of these using random decision forests, active learning with Gaussian process regression, clustering, and artificial neural networks. For example, using unsupervised Gaussian mixture models (GMMs), supervised artificial neural networks (ANNs) and local environment descriptors, we identify and classify complex polymorphs arising from two-parameter interaction potentials. We combine recently developed techniques in inverse design called “digital alchemy” with random forest techniques to construct a model that correctly classifies the colloidal crystals of more than ten thousand polyhedral shapes into 13 different crystal structures with a predictive accuracy of 96% using only two geometric shape measures. We address the problem of efficient phase diagram sampling using active learning techniques and achieve an 80% reduction in the number of state points needed to establish the phase boundary up to a given precision in example applications. We also show how batch sampling can be used to better utilize parallel computing resources in active learning. Finally, we show how our data management framework **signac** supports our data-intensive research.

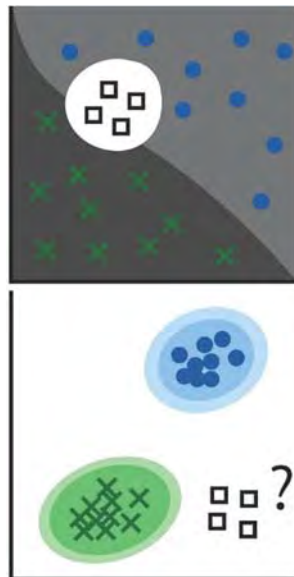


Image by M. Spellings, University of Michigan.

POLY 548: Mechanically robust but healable polymer materials

Takuzo Aida^{2,1}, aida@macro.t.u-tokyo.ac.jp. (1) U of Tokyo Chem Biotech Dept, Tokyo, Japan (2) Center for Emergent Matter Science, RIKEN, Tokyo, -, Japan

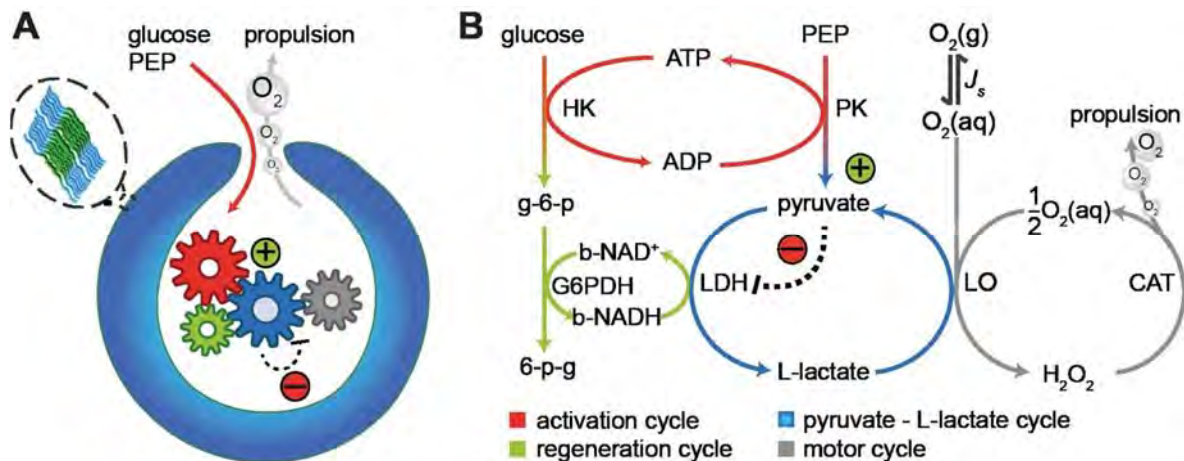
Expanding the range of healable materials is an important challenge for sustainable societies. Noncrystalline, high-molecular-weight polymers generally form mechanically robust materials, which, however, are difficult to repair once they are fractured. This is because their polymer chains are heavily entangled and diffuse too sluggishly to unite fractured surfaces within reasonable time scales. Here we report that low-molecular-weight polymers, when cross-linked by dense hydrogen bonds that do not induce crystallization, yield mechanically robust yet readily repairable materials, despite their extremely slow diffusion dynamics. A key was to utilize thiourea, which anomalously forms a zigzag hydrogen-bonded array that does not induce unfavorable crystallization. Another key was to incorporate a structural element for activating the exchange of hydrogen-bonded pairs, which enables the fractured portions to rejoin readily upon compression. In the present lecture, these new strategies for the realization of mechanically robust, healable materials will be presented.



POLY 549: Active, autonomous and complex life-like molecular systems with adaptive behaviour

Daniela A. Wilson, *d.wilson@science.ru.nl*. Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, Gelderland, Netherlands

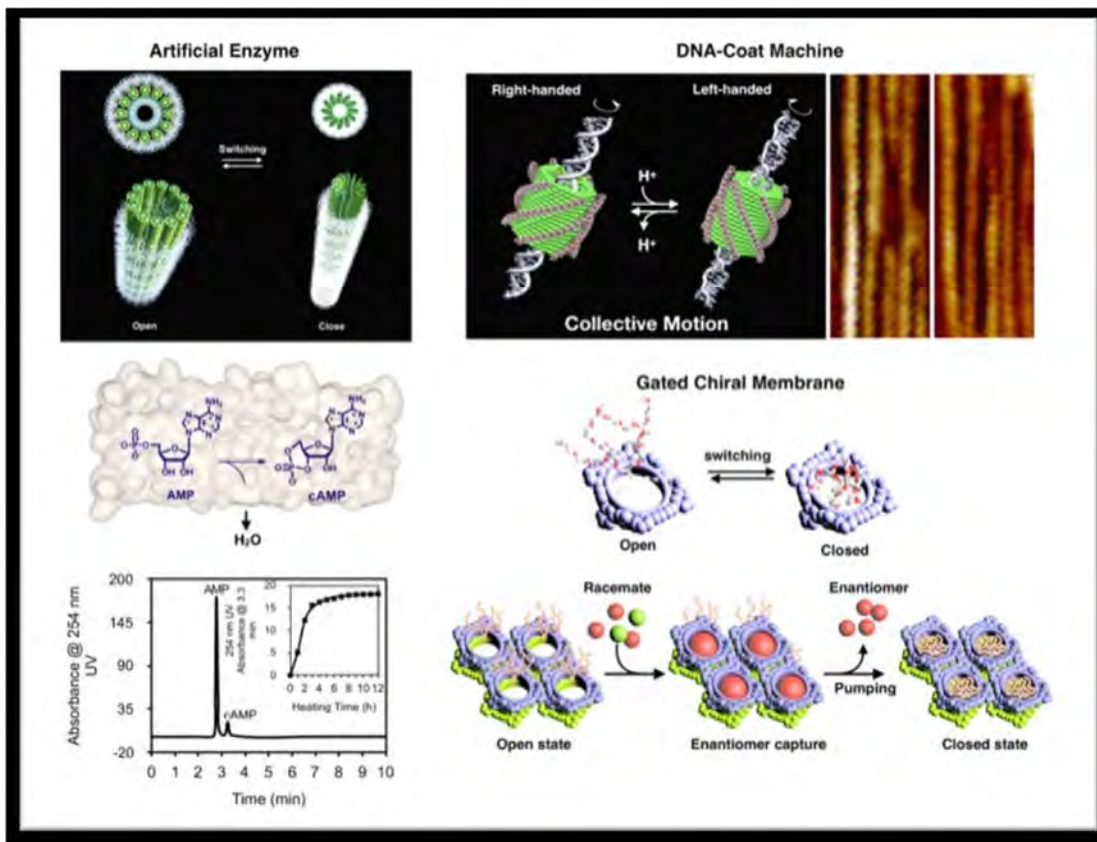
Self-powered artificial motile systems are currently attracting increased interest as mimics of biological motors but also as potential components of nanomachinery, robotics, and sensing devices.¹ We have recently demonstrated a supramolecular approach to design synthetic nanomotors using self-assembly of amphiphilic block copolymers into polymersomes and the controlled folding of the vesicles under osmotic stress into a bowl shape morphology.² The folding process can be precisely controlled to generate different complex architectures³ with adjustable openings and selective entrapment of inorganic catalysts^{4,5} enzymes or multiple enzymes working together in a metabolic pathway.^{6,7} Control of the speed and behaviour of the nanomotors is possible due to integration of regulatory feedback and feedforward loops in the enzyme networks. The nanomotor is now not only running at low concentrations of fuel but also able to regulate its fuel consumption to achieve the same output speed showing adaptive behaviour. Recent developments on greater control over the movement of the nanomotors under chemical gradients or temperature will be presented^{4,7}. Additional manipulation of the nanomotors under external stimuli and their biomedical applications will be discussed.^{6,7}



POLY 550: Dynamic self-assembly for life-inspired systems

Myongsoo Lee, mslee@jlu.edu.cn. Jilin University, Changchun, China

In this symposium, I will introduce our recent results how to construct dynamic self-assembled nanostructures exhibiting switchable functions, inspired by life systems. For example, synthetic tubular pores are able to undergo open-closed switching driven by an external signal. The pore-switching mediates a water pumping action for the dehydrative cyclization of AMP nucleotide. When self-assembled tubules embed DNA inside the hollow cavities, the chirality of DNA is able to transfer accurately to the coat assembly. The DNA-coat assembly undergoes simultaneous helicity switching in physiological conditions. In the case of toroid assembly, the discrete toroids are able to reversibly propagate in a helical sense by nucleating with an activator through allosteric switching, similar to TMV virus coat assembly. Moving from 1-D to 2-D structures, the internal pores are able to form chiral interior which selectively capture one enantiomer in racemic solution with perfect pore performance. Remarkably, the pores are closed with simultaneous pumping of the captured molecules driven by environmental changes. I will discuss recently discovered these results with their biological implications.



POLY 551: Harnessing artificial molecular machines in slide-ring polymer synthesis

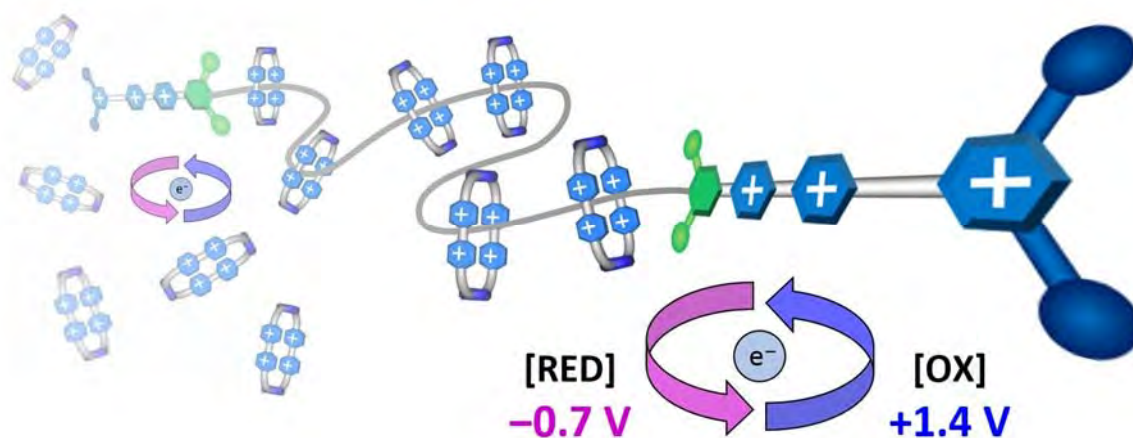
Cristian Pezzato, Yuanning Feng, Yunyan Qiu, Indranil Roy, **James F. Stoddart**, stoddart@northwestern.edu. Department of Chemistry, Northwestern University, Evanston, Illinois, United States

The rise of artificial molecular machines (AMMs) is accompanied with the promise of establishing new molecular functions. In this talk, following an introduction on the nature of the mechanical bond, I will discuss our recent advances on AMMs capable of operating by pH- and/or redox-controlled oscillations, putting emphasis on those that make use of electricity for producing polyrotaxanes.

Controlling relative movements of the components of machines on the molecular scale represents a milestone for current research on AMMs. Although unidirectional motion has been established in diverse artificial systems, inverting the process-direction in response to different stimuli represents a formidable challenge. We are developing a dual responsive molecular motor capable of working in either clockwise or anti-clockwise directions, simply depending on how pH- and redox-oscillations are synchronized during a four-stroke cycle.

Performing work at the nanoscale without generating and accumulating waste products is an appealing aspect regarding the applications of AMMs. Recently, we reported on the use of controlled potential electrolysis driving the operation of artificial molecular pumps in solution. We have used prototypes bearing two molecular pumps at the termini of polymeric chains, which act as collecting chains for multiple cyclobis(paraquat-*p*-phenylene) (**CBPQT**⁴⁺) rings. We show that enthalpically and entropically demanding, slid-ring polyrotaxanes can be made progressively through the controlled supply of electricity (see the Figure).

Developing artificial counterparts of RNA polymerases is a seductive prospect encompassing our current research efforts. In this regard, we envision incorporating molecular pump segments into monomers, and engineering **CBPQT**⁴⁺ ring-bearing catalysts capable of binding and linking them sequentially, in concert with controlled redox-oscillations.

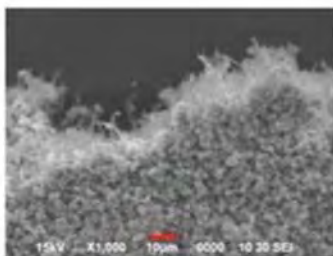
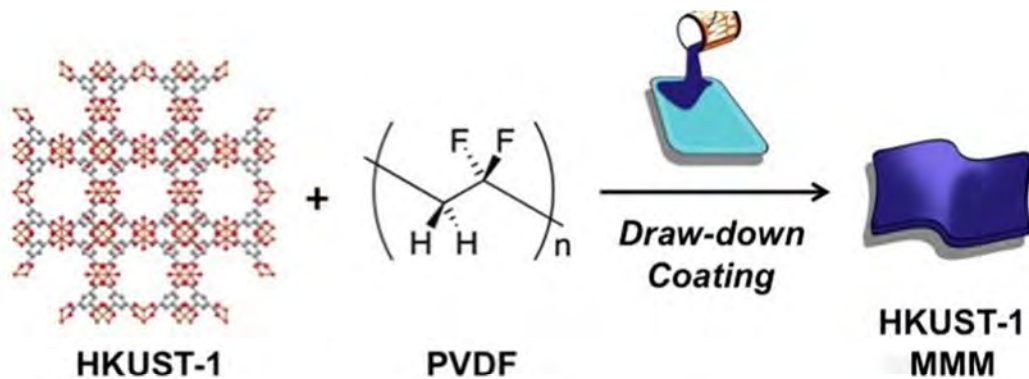


Electrochemically-controlled production of polyrotaxanes

POLY 552: Unexpected synergy in engineered metal-organic frameworks and polymer membranes for military protection applications

Jared B. DeCoste¹, jdecost1@gmail.com, **Michael S. Denny**², **Trenton Tovar**¹, **Ivan Iordanov**¹, **Gregory Peterson**¹, **Seth Cohen**². (1) US Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland, United States (2) Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States

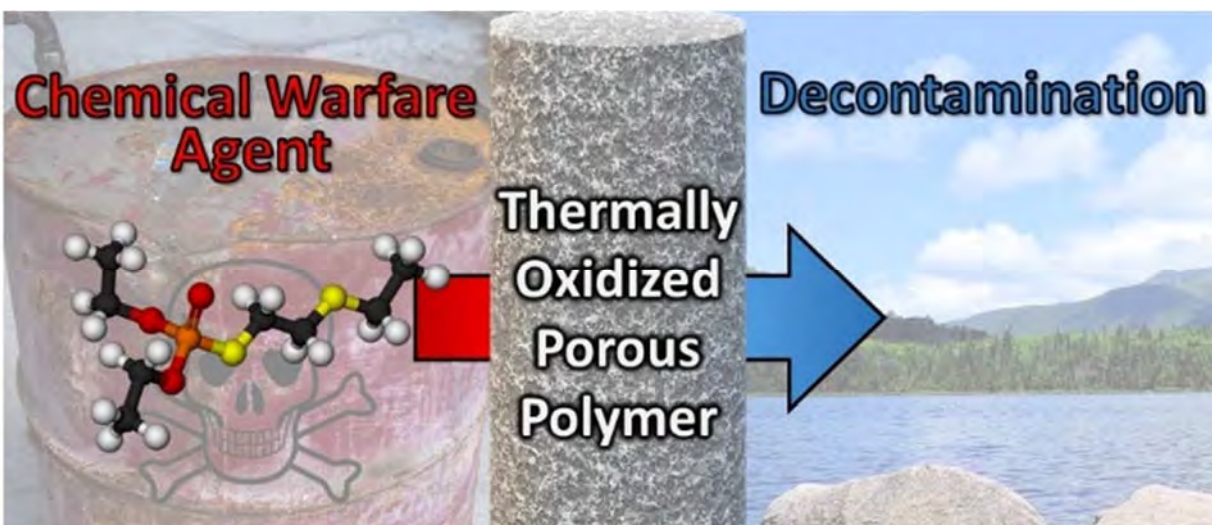
Much research in the area of metal-organic frameworks has been in the area of chemical adsorption of the primitive materials. However, real-world applications typically call for an engineered material and not a powder or crystalline solid. We will discuss here the incorporation of MOFs into various polymeric matrices including thin films and electrospun nanofibers. While the incorporation of MOFs into polymeric films can have an adverse effect on the polymer's physical properties, previously unachievable adsorption qualities of a film can be achieved. We will specifically discuss here the incorporation of the MOF HKUST-1 into poly(vinylidene fluoride) (PVDF) membranes for the adsorption of ammonia, and the positive effect that the hydrophobic polymer can have on the water stability of the MOF. Interestingly, controlling the PVDF phase also exhibits an unexpected synergistic effect for the non-polar gas (oxygen, carbon dioxide, nitrogen) adsorption capacity of the MOF. We will discuss these effects, among others, and the tradeoffs that incorporation of MOFs into polymeric matrices can have.



POLY 553: Improved sequestration and decomposition of chemical warfare agents *via* low-temperature thermal treatment of porous poly(dicyclopentadiene) foams

Robert Balow¹, bobbybalow@gmail.com, **Spencer L. Giles**², **Christopher McGann**³, **Grant C. Daniels**², **Jeffrey Lundin**⁴, **Pehr E. Pehrsson**⁵, **James H. Wynne**². (1) Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States (2) Chemistry Division, Naval Research Laboratory, Lorton, Virginia, United States (4) Naval Research Laboratory, Washington, District of Columbia, United States

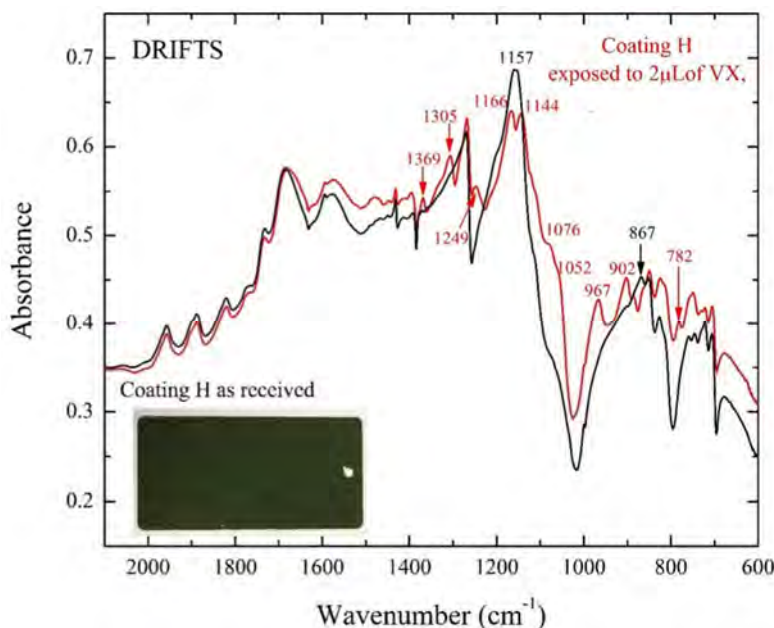
Recent events in London, Syria, and Malaysia confirm that chemical warfare agents (CWAs) continue to pose an immediate threat to warfighters and civilian populations. As a result, there remains a critical need for innovative materials and sorbents to quickly sequester and neutralize toxic chemicals and CWAs. This presentation will discuss a cheap and industrially scalable polymer foam that can sequester and decontaminate such threats. The polymer foam, comprising poly(dicyclopentadiene) (pDCPD), was synthesized *via* emulsion templating to produce a porous microstructure that aided in wicking and sequestering toxic chemicals. Additionally, the pDCPD foam oxidized in air to form carbonyl, hydroxy, and highly reactive peroxy oxidation products. The bound peroxy groups rapidly oxidized the CWA simulant demeton-S, a chemical surrogate for the extremely toxic nerve agent VX. Heating the pDCPD polymer foam in air accelerated the formation of bound peroxy species and improved the decontamination efficiency of the porous pDCPD foam.



POLY 554: N-Substituted polyurea-silane polymers for coatings with enhanced CWA resistance

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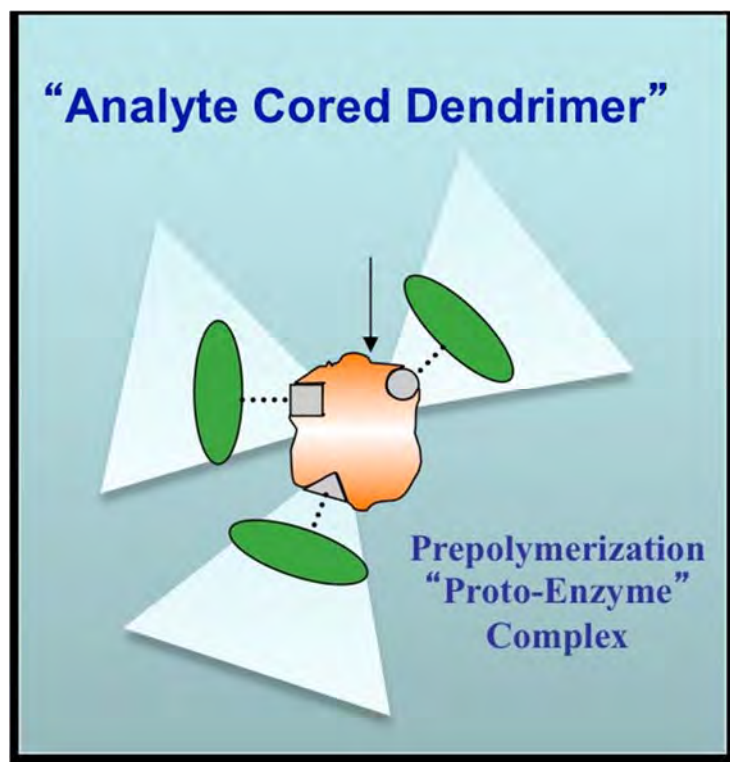
Organosilicon polymers offer several advantages over the traditional polycarbamate (polyurethane) polymers used in commercial coating applications. For example, organosilicons provide enhanced resistance to moisture and are lower in viscosity compared to polyurethane polymers of similar size, in addition to possessing greater resistance to degradation from ultraviolet (UV) radiation in sunlight. Recently, NRL has developed alkoxy-silane-terminated N-substituted polyurea polymers that hydrolyze with atmospheric moisture and condense to form inorganic/organic networks. These polymers were formulated as clear and pigmented systems, then applied on substrates to generate highly cross-linked, yet flexible, coatings. The coatings were evaluated by ECBC against toxic chemicals, specifically chemical warfare agents (CWAs), in an effort to assess their interactions and resistivity towards harmful chemicals. Several techniques, such as diffuse reflectance infrared spectroscopy (DRIFTS), reflection absorption infrared spectroscopy (RAIRS), and contact angle (CA), were used to determine the surface interactions, as well as the degree of resistivity. The new polymers have demonstrated a marked decrease in reactivity and increased resistivity compared to the polyurethane polymers used in commercially available chemical agent resistant coatings.



POLY 555: Detection of threats and sensors via electrochemically molecularly imprinted polymers (E-MIPS)

Rigoberto C. Advincula, *rca41@case.edu*. *Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States*

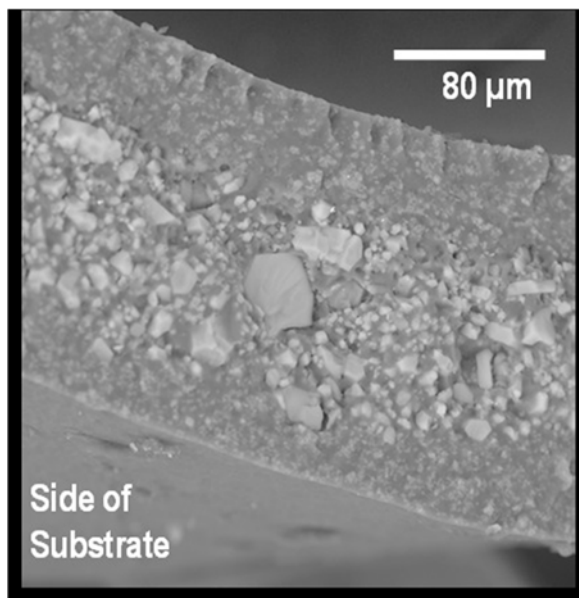
Detectors and sensor are needed for advanced capabilities in the military. The detection of analytes, nerve agents, pollutants is a challenge especially when present in very low quantities. There are a number of methods to improve sensitivity and selectivity but usually, this requires more elaborate instrumentation methods. The key is the use of high-performance sensor elements and a highly efficient transducer element that can be put in a portable device to enable on-site usability. In this talk, we will show the effective detection of nerve agent analogs, pathogen analogs, and explosive and highly energetic materials analogs via polymerized sensor materials. We will focus on the demonstration of electropolymerized molecularly imprinted polymer (E-MIP) sensor elements and its ability to utilize transduction methods such as surface plasmon resonance (SPR) spectroscopy or quartz crystal microbalance (QCM) to enable high sensitivity and selectivity. The monomer and molecular design for optimized analyte interaction enable effective templating protocols in a conducting polymer matrix with tunable oxidative states to enable a high volume of analyte-cavity sites. Optimized electropolymerization methods are important for film deposition and surface characterization.



POLY 556: MOFwich: Sandwiched metal-organic framework-containing mixed matrix composite polymers for chemical warfare agent removal

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Traditional materials used for handling chemical warfare agents (CWAs), such as butyl rubber, are effective barriers but suffer from low moisture vapor transport, a property that affects the thermal burden experienced by the user. Without the ability to transport moisture effectively through the barrier, evaporative cooling does not occur. In this work, a new layering strategy for fabricating mixed matrix composites (MMCs) from elastomeric block copolymers and metal-organic frameworks (MOFs) was developed for use as functional barriers against CWAs. MMCs were fabricated using two layers with low MOF loading encasing a core layer with high MOF loading. We term these new materials “MOFwiches” as the MMC resembles a sandwich-like structure. Utilizing elastomeric outer layers also protects the core layer from catastrophic failure, enabling new robust membrane-based technologies. Several MMCs had moisture vapor transport rates two orders of magnitude higher than butyl rubber and one order of magnitude higher than latex. Furthermore, multiple MMCs provided effective reactive barriers against several classes of CWAs whereas current materials simply slow penetration without detoxification. Beyond barrier applications, we demonstrated the effectiveness of several MOFwich materials in areas such as gas separations and sensing.

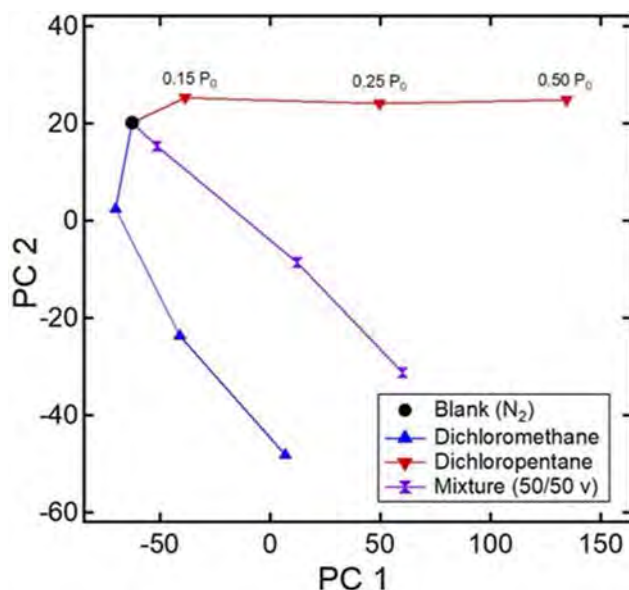


A core layer of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) with high HKUST-1 metal-organic framework (MOF) loading is sandwiched between two SIS layers with low UiO-66-NH₂ MOF loadings

POLY 557: Sensing chemical warfare agent simulants via natural and synthetic photonic crystals

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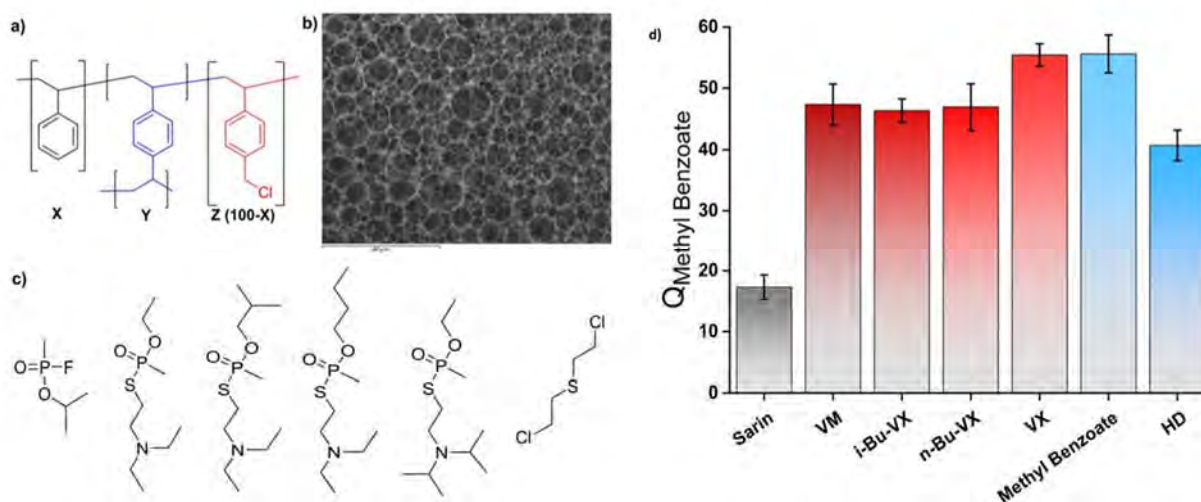
Natural polymeric photonic crystals (PhCs), such as those found in the wing scales of the *morpho didius* butterfly, offer a rapid means to distinguish between vapors of similar refractive index and polarity. Fundamental studies into natural PhCs has shown that their complex nanoarchitecture and polarity gradient leads to aggregation of vapor analyte within different regions of the PhC, altering the wavelength of reflected light in a manner that is specific to that analyte. Our work has shown that chemical warfare agent (CWA) simulant vapors can be detected at the ppm level in both binary and tertiary vapor mixtures by processing visible light reflected from these natural PhCs. To explore increases in sensitivity, a porous silicon PhC was also studied in conjunction with the natural system. Collectively, these results were used to refine a PhC model that suggests an array of synthetic PhCs with variable nanoarchitecture and surface functionalization could be used to improve CWA simulant sensitivity while retaining the selectivity of natural PhCs.



POLY 558: Poly high internal phase emulsions for the absorption and immobilization of chemical warfare agents

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We present a facile method for the absorption (weight/weight; $Q > 40$, 4400 wt%) of a variety of organic liquids and chemical warfare agents (CWAs) using a poly(styrene-co-vinyl benzyl chloride-co-divinylbenzene) lightly cross-linked poly-high internal phase emulsion (polyHIPE). By varying the vinyl benzyl chloride (VBC) content and the volume of the internal phase of the precursor emulsion we demonstrate that absorption of organic liquids is facilitated both by the swelling of the polymer and the uptake of liquid in the pores. In particular the sample prepared from a 95% internal emulsion water content showed rapid swelling taking less than 5 minutes to reach total absorption. Furthermore the pHIPEs could be compressed from their expanded state to significantly higher densities (from $\sim 0.064 \text{ g cm}^{-3}$ to $\sim 0.377 \text{ g cm}^{-3}$) without losing absorption capacity thereby reducing the volume occupied by the absorbent. These high absorption values, the facile synthesis, the low cost of raw materials and the control over density and form makes these systems ideal practical candidates for the rapid immobilization of CWAs. This was demonstrated by absorption studies on the physical HD simulant methyl benzoate and the subsequent absorption of the CWAs; GB (isopropyl methyl phosphonofluoridate); VM (diethylaminoethyl O-ethyl methylphosphonothioate); *i*-Bu-VX (diethylaminoethyl O-isobutyl methylphosphonothioate); *n*-Bu-VX (diethylaminoethyl O-*n*-butyl methylphosphonothioate); VX (diisopropylaminoethyl O-ethyl methylphosphonothioate); and HD (bis(2-chloroethyl) sulfide).

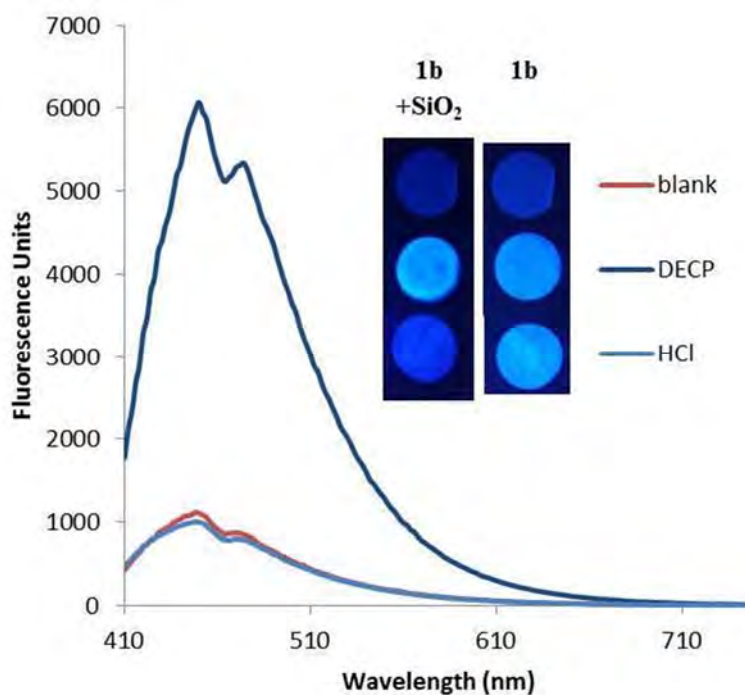


a) General polyHIPE structure, b) electron micrograph of the 5% VBC, 95% internal phase polyHIPE, c) (from left to right) the chemical structures of the CWAs; sarin (GB), VM, *i*-Bu-VX, *n*-Bu-VX, VX and sulfur mustard (HD), d) Swelling performance of a polyHIPE in the CWAs: sarin (GB), VM, *i*-Bu-VX, *n*-Bu-VX, VX and HD, shown alongside the original simulant result.

POLY 559: Detection of organophosphates using a new generation of polymer-incorporated fluorescent sensors

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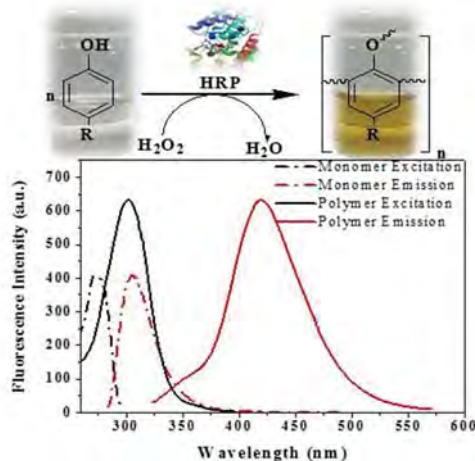
A new generation of sensors for detection of organophosphates have been developed. Based on platinum sensors that exhibit increased fluorescence response to organophosphates, novel 2-pyridyl-1,2-butenyl-4-ol structures have been assembled focusing on a thiazole core. These reactivity-driven phosphate sensors were previously plagued by acids generated by phosphoryl halide degradation. Therefore, the structures could not be directly polymer-bound for incorporation into a detector. In order to circumvent this limitation, a new class of reactivity-based sensor structures has been prepared. They contain functional groups that allow the sensor to be incorporated into or directly bound to a polymer (e.g., polystyrene). Incorporation of acid-scavenging additives mitigates acid sensitivity and promotes selectivity for organophosphoryl halide simulants in both liquid and gas-phase samples.



POLY 560: Enzymatic synthesis of fluorescent conjugated polymers and their application in sensing

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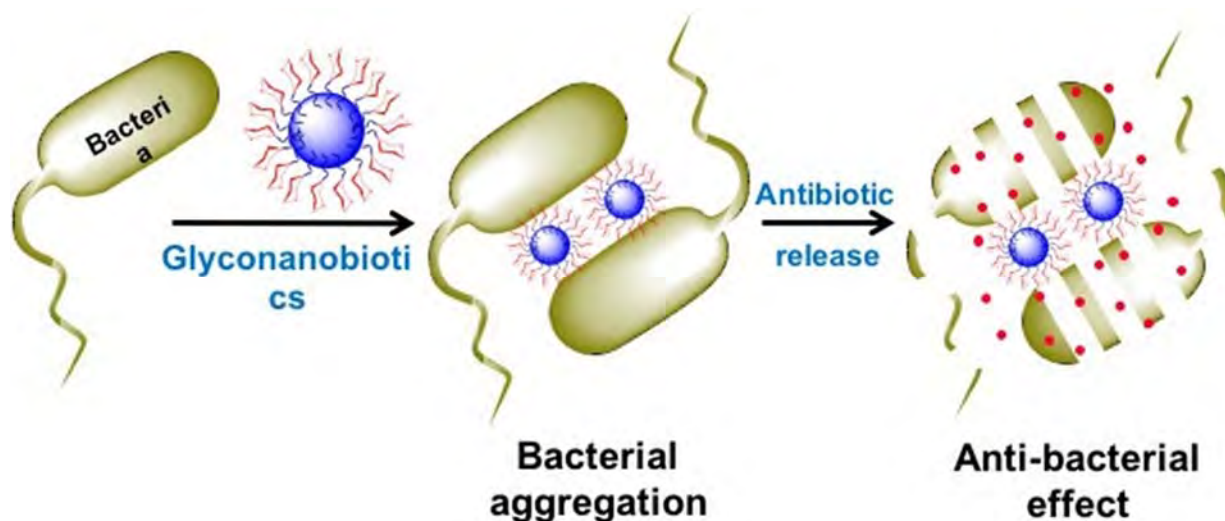
With large varieties of explosives with increasing level of sophistication being fielded, there is an immediate need for highly sensitive analytical techniques for the detection of explosives. Fluorescence based sensors are simple, extremely sensitive, versatile and adaptable for detection of different types of analytes. Typically synthetic fluorescent polymers [such as poly(p-phenylene ethynylene)s and polythiophenes] are used in the detection of explosives. Multi-step synthesis using toxic chemicals followed by purification is often required for obtaining these fluorophores. Moreover, the residual catalyst can inhibit the fluorescence and therefore extensive purification of the product is essential to obtain the product in the fluorescent form. Here we demonstrate the possibility of utilizing enzymes as the catalyst, for the one step polymerization of naturally occurring monomers to yield fluorescent conjugated polymers. The metal in the active site of the enzyme remains chelated during the synthesis allowing the polymers to be fluorescent as synthesized without the need for extensive purification. Four monomers, 4-Hydroxyphenylacetic acid, Hydroxytyrosol, Chlorogenic acid and Serotonin were polymerized using Horseradish peroxidase as the biocatalyst. Spectroscopic techniques, UV-Vis, FTIR-ATR and Fluorescence, are used to characterize these polymers. These polymers exhibit fluorescence with significant Stokes shift around 100 nm rendering them useful in fluorescence quenching-based sensors. Preliminary studies on the use of these polymers, in the detection of nitro-aromatic compounds in solution through fluorescence-quenching are presented. In addition, the use of these polymers for the detection of other analytes such as metal ions will also be presented.



POLY 561: Bioactive nano- and microstructures from self-assembling amphiphilic glycopolymers

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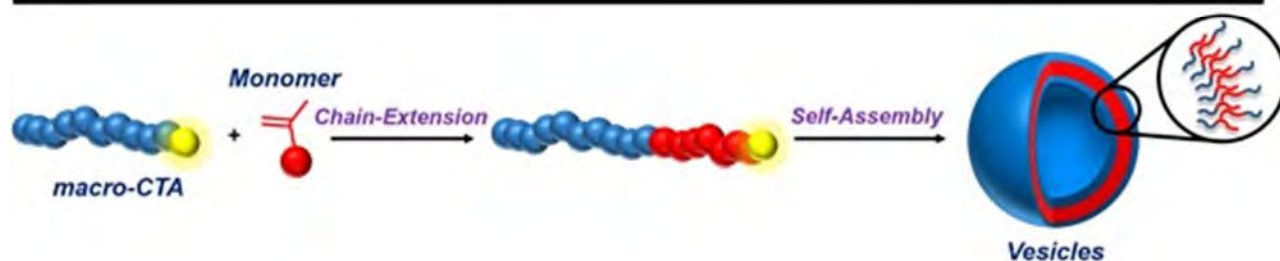
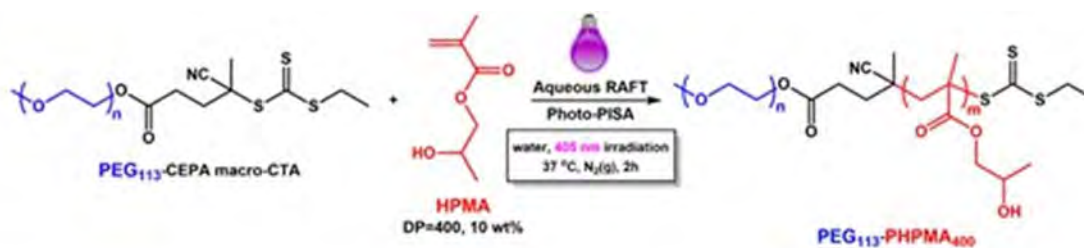
Carbohydrates mediate many processes in biology, particularly those that involve contacts between surfaces (for example cell-cell and cell-virus particle contacts). Nature overcomes the intrinsic weakness of individual carbohydrate-protein (lectin) interactions by means of multivalency, of both the carbohydrate ligand and the lectin. Thus the preparation of multivalent, high-affinity carbohydrate-bearing macromolecules, including glycopolymers, is an attractive strategy for investigating and inhibiting such interactions, leading to applications in therapeutics, diagnostics, protein purification and other areas of biotechnology. We present our work on the development of biologically active, amphiphilic glycopolymers from simple monosaccharide-containing monomers. Depending on the exact molecular characteristics of the polymers and the self-assembly process employed, the polymers can be assembled into a variety of bioactive nano- and microstructures, including micelles, nanoparticles and polymersomes. The presentation will discuss two recent projects in our lab: 1. The production of self-assembled glyconanoparticles for the delivery of antibiotics ('glyconanobiotics'); and 2. The development of glycosylated giant polymersomes as simple minimal cell mimics.



POLY 562: Advances in PISA

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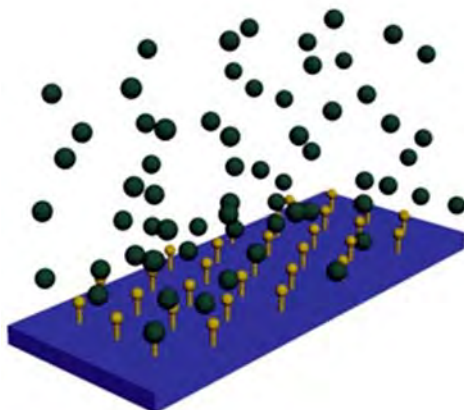
There is great current interest in the synthesis of well-defined and functional nanostructures using polymerization induced self-assembly (PISA) techniques. The advances in the development of these techniques has enabled access to a wide range of functional and responsive nanomaterials for a diverse range of applications.



POLY 563: Polymers at Interfaces

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Surface-initiated polymerization (SIP) techniques are powerful tools for the preparation of thin, surface tethered polymer films. Surface grafted polymer films produced via SIP are often colloquially referred to as polymer brushes. SIPs are characterized by a number of unique features, which include the ability to (i) prepare polymer brushes with precise control over chemical composition and film thickness; (ii) generate polymer films that present very high surface concentrations of functional groups; (iii) conformally coat both simple, planar substrates as well as complex, 3D structured or porous substrates and (iv) tune the conformation of the surface grafted polymer chains by engineering the average distance between neighboring anchoring points. This presentation will highlight recent work from our laboratory that illustrates the use of SIP to generate thin polymer films with sensory or responsive properties as well as results from recent work, which shows that the stretched conformation of these surface grafted polymer chains also has an impact of their chemical reactivity, potentially opening avenues towards novel mechanically responsive surfaces.

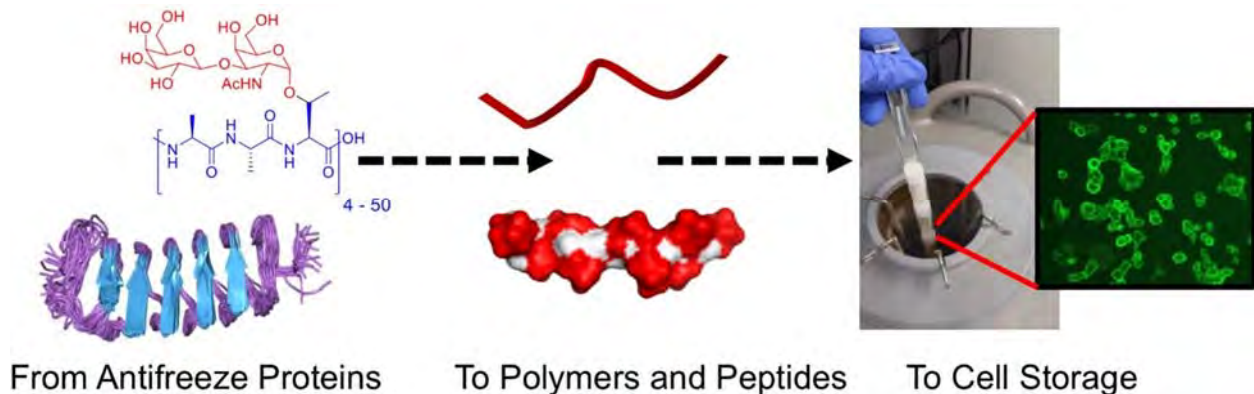


POLY 564: New materials inspired by antifreeze proteins to enable cell and biologic storage

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All biotechnology, basic biology, drug delivery, biomaterials science and regenerative medicine is reliant on high-quality cells and tissue. However there exists a major logistical challenge in how these cells are transported, to avoid cellular degeneration. Cryopreservation is the state of the art for this, but requires large volumes of organic solvent 'antifreeze'. Low numbers of cells are often recovered post-thaw, and the solvents can induce phenotypic changes, reduction in cell function or in many cases simply no cells are recovered.

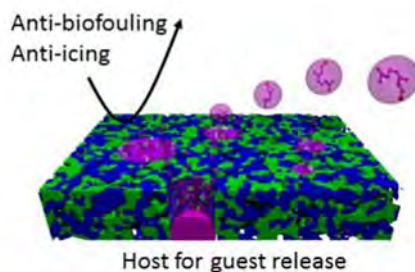
In this talk, I will introduce the progress the Gibson Lab has made in the past few years in developing synthetic polymer mimics of antifreeze proteins (AFPs) found in extremophile species. AFPs have many effects on ice crystals, but their property of ice recrystallization inhibition (IRI) (slowing ice growth) has huge potential applications. I will discuss our progress in identifying the key structure motifs which are essential for IRI activity in synthetic polymer materials, using a combination of polymer synthesis as well as recombinant protein expression. I will then demonstrate that this is a platform technology for enhance the cryopreservation of a vast range of nucleated cells, micro-organisms, biologics and more.



POLY 565: Complex, amphiphilic hyperbranched fluoropolymer poly(ethylene glycol) crosslinked networks: Unique characteristics for broad applications from anti-biofouling coats, to hosts for promoted guest release, to anti-icing materials

Karen L. Wooley, *wooley@chem.tamu.edu*. 3255 TAMU, Texas AM University, College Station, Texas, United States

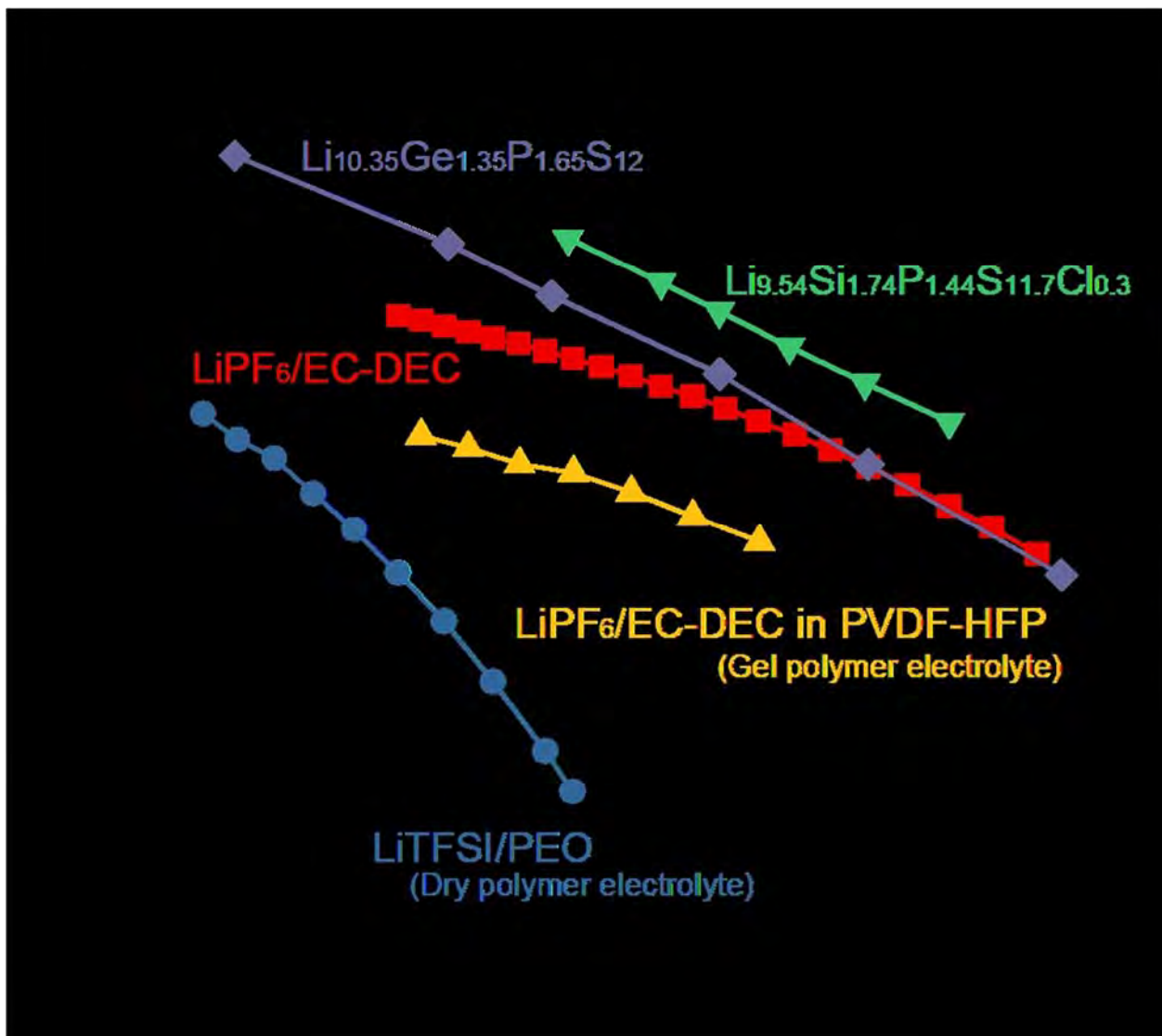
This presentation will highlight a body of research that relates to both of the 2018 Biomacromolecules/Macromolecules Young Investigator Awardees, has been conducted over the past couple of decades, and has progressively investigated the unique characteristics of amphiphilic crosslinked networks comprised of hyperbranched fluoropolymers and linear poly(ethylene glycol)s (HBFP-PEGs). As an undergraduate student, Jeremiah Johnson contributed to key experiments that identified unusual physical and topographical properties for these HBFP-PEG materials, which allowed for their performance as anti-biofouling coatings. More recently, the ability of HBFP-PEGs to organize water molecules has led to their study as anti-icing materials, which is an area of research that is of keen interest to Matt Gibson.



POLY 566: Why polymer electrolytes less conductive than liquids and inorganic solid electrolytes?

Yang Shao-Horn, shaohorn@mit.edu. Dept Mech Eng Rm 3-334, MIT, Cambridge, Massachusetts, United States

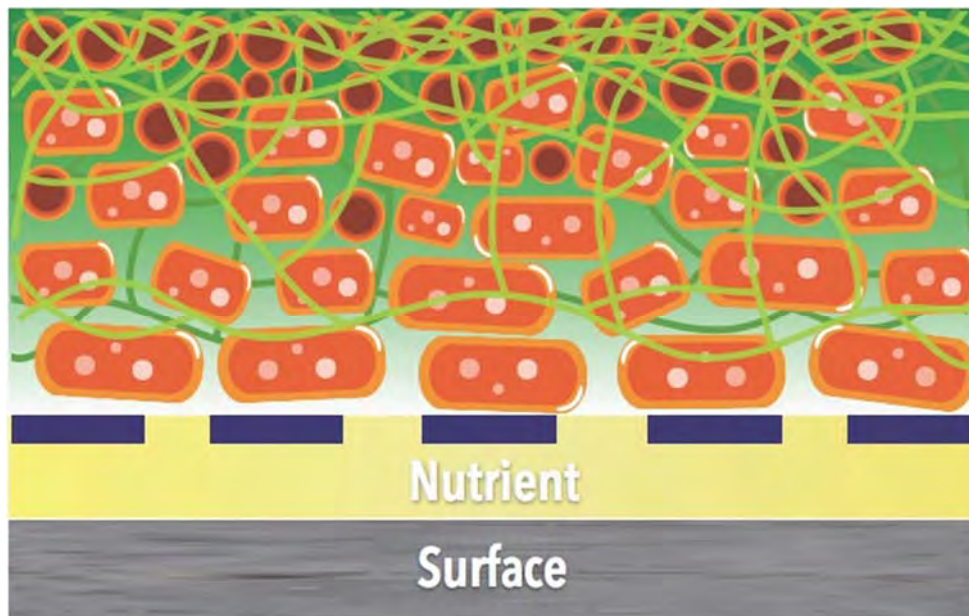
Polymeric materials with their structural and functional tunability, and processability at low temperatures open immense opportunities to transform electrochemical energy storage technologies including batteries and fuel cells. For example, replacing aprotic liquid electrolytes in Li-ion batteries with conducting polymer electrolytes can greatly increase battery safety and form-factor characteristics. Unfortunately, current polymer electrolytes have much lower ion conductivity, interfacial charge transfer kinetics and (electro)chemical stability than liquid and solid ceramic electrolytes. Here we will discuss processes that potentially limit the ion conductivity of polymer electrolytes, from which highlight opportunities to design polymer electrolytes for electrochemical devices.



POLY 567: Engineered living materials

*Hanwei Liu, Seunghyun Sim, Yue Hui, **David A. Tirrell**, tirrell@caltech.edu. MC 210-41, Caltech, Pasadena, California, United States*

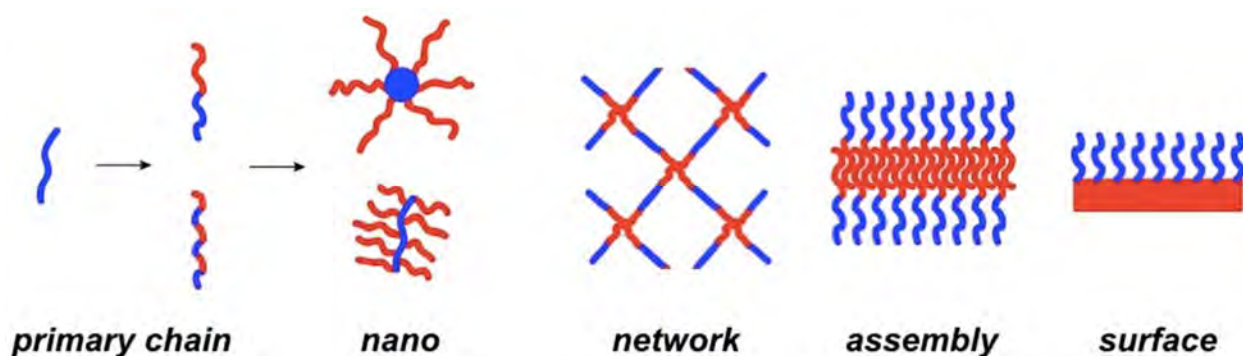
We are exploring the preparation and properties of soft materials constituted from mixtures of macromolecules and bacterial cells. Issues of interest include the roles of cell identity, cellularity, intercellular interaction, macromolecular composition and concentration, and macromolecular-cellular adhesion in determining the physical and biological behavior of such systems.



POLY 568: Toward increased precision and efficiency in macromolecular synthesis: New strategies and enabling functions

Jeremiah A. Johnson, *jaj2109@mit.edu*. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

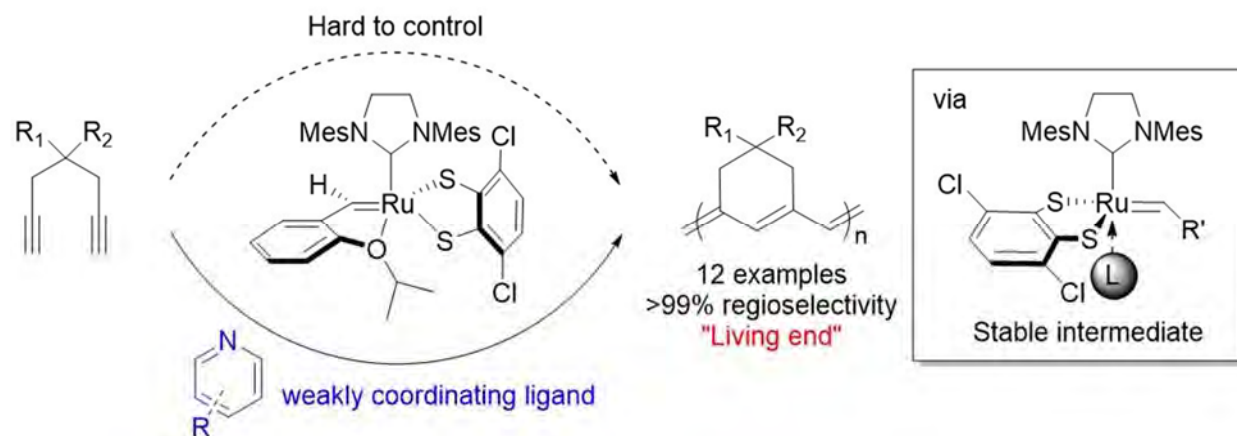
Motivated by nature, polymer chemists have long sought methods and strategies for the synthesis of macromolecules with precise structures. Existing approaches typically require a trade-off between structural control and atom economy/scalability. Driven by specific functional targets, we have developed techniques that offer enhanced precision and efficiency in macromolecular synthesis, and that enable new or otherwise difficult-to-access polymer functions.



POLY 569: β -selective cyclopolymerization using Ru-dithiolate olefin metathesis catalysts by controlled manner

Kijung Jung, *kjjung@snu.ac.kr*, Tae Choi. School of Chemistry, Seoul National University, Seoul, Korea (the Republic of)

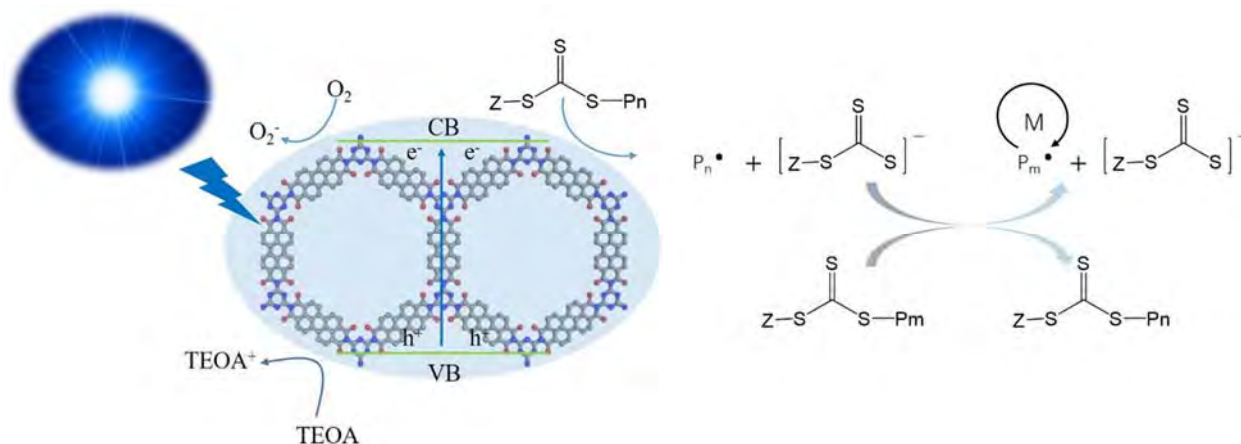
Ru-based Grubbs catalysts employed in cyclopolymerization (CP) of diyne derivatives have promoted selective α -addition, forming the conjugated polyenes containing exclusively five-membered repeat unit in the case of 1,6-heptadiynes. Along with our recent achievement on β -selective CP using a Ru Z -selective olefin metathesis catalyst, we have pursued a higher efficiency and more selective regiocontrol to produce conjugated polymers with only six-membered rings with broader substrate scope. Herein, we demonstrate a very β -selective CP by applying another type of Ru-based Z -selective dithiolate catalyst, and discovering the prominent effects of pyridine additives to improve the conversion and the selectivity. In-depth observation and monitoring on the reactive carbene species enabled us to understand the plausible role of pyridine ligands, such as stabilizing the propagating carbenes and control k_i/k_p values. All of the investigation led the living/controlled CP and further diblock copolymerization to be possible, which became the first example for CP in a completely β -selective and living manner using Ru-based catalysts.



POLY 570: Porous polyimide network as a new photoactive organocatalyst for PET-RAFT polymerization with oxygen tolerance

Lei Zhang, zhlei_thu@163.com, Gang Ye, Shengming Xu. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China

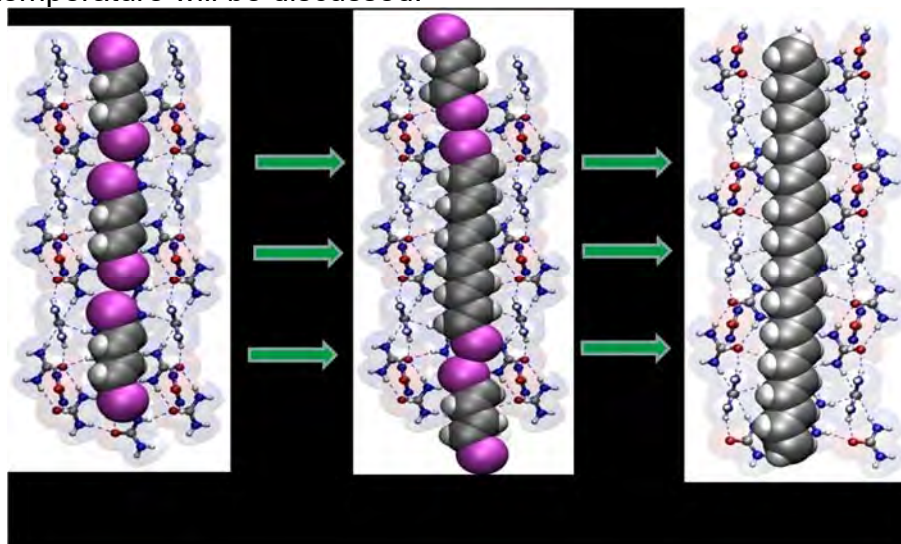
Metal-free photo-induced electron transfer reversible addition fragmentation chain transfer polymerization (PET-RAFT), as one of the most promising controlled/living polymerization technologies, has aroused worldwide interest recently. In this study, a microporous polyimide (PI) network was synthesized and used as the photocatalyst for PET-RAFT polymerization of methyl methacrylate (MMA) with oxygen tolerance. The microporous polyimide (PI) network was synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and 1,3,5-triazine-2,4,6-triamine (melamine) using a Lewis acid catalyst zinc acetate/imidazole complex. Because of the π - π conjugated structure, the PI network exhibited favorable fluorescent properties which were highly influenced by the solvent effect. PET-RAFT polymerization of MMA monomers was carried out, by using the PI network photocatalyst, in different solvents, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), methylbenzene, and Petroleum ether. PMMA products with controlled molecular weights, narrow dispersity, and high conversion were obtained. Besides, the effects of RAFT agents (i.e., trithiocarbonates), catalyst concentrations, and residue oxygen in this system were investigated. The mechanism of deoxygenation and the PET-RAFT polymerization was discussed.



POLY 571: Solid state photoelimination polymerization: Structure change with guest species in urea inclusion

Michael Moskowitz¹, Bo Wang², Steluta Dinca⁴, Mark Hollingsworth³, Michael B. Sponsler¹, **Bruce S. Hudson**¹, bshudson@syr.edu. (1) Syracuse Univ, Syracuse, New York, United States (2) Kansas State University, Manhattan, Kansas, United States (3) Chemistry Dept., Kansas State University, Manhattan, Kansas, United States (4) Syracuse University, Syracuse, New York, United States

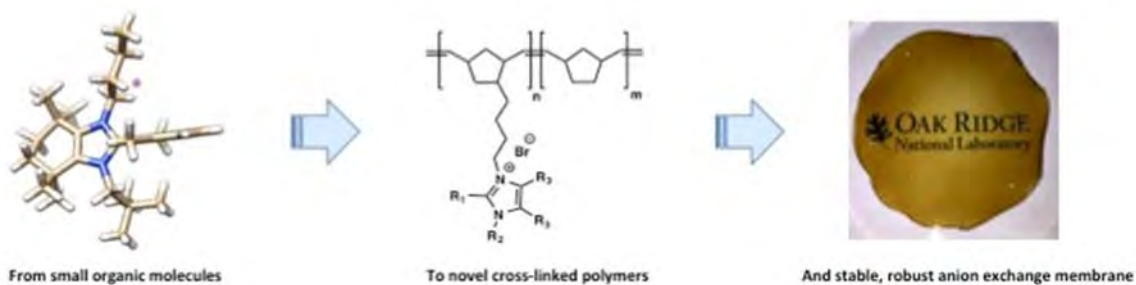
Urea inclusion compounds (UICs) containing E,E-1,4-diiodobutadiene (DIBD) and E,E,E-1,6-diiodohexatriene (DIHT) are described in terms of their structural chemistry and the photochemical polymerization of the guest species. This involves breakage of the terminal C-I bonds and the elimination of iodine from the crystalline material. Raman spectroscopy shows the formation of the expected diiodopolyene oligomers following the Raman frequency and relative intensity changes observed for finite species of known length (Schaffer 10.1063/1.460649). The Raman signal disappears with extensive irradiation as anticipated due to lack of the dominate Condon contribution for very large species. Inelastic neutron scattering vibrational spectroscopy shows continued evolution of the polymer at longer time of irradiation. A key observation is that broadband radiation results in a mass loss that is close to the expectation based on the crystal stoichiometry indicating complete conversion of reactants to products. DIBD inclusion crystals are commensurate, fully-ordered structures with “stacked-loop” host H-bonding networks, uncommon for UICs. Changing the guest to DIHT results in UICs that have the standard helical host H-bonding network. Diffraction data show that the guests are significantly disordered and that in ordered regions, $\Delta_g = c_g/3$, as seen earlier with certain α,ω -dibromoalkanes and α,ω -diiodoalkanes. This maximizes the distance between the terminal halogens in adjacent channels. The photochemical elimination process results in considerable loss of material within each channel. UICs that are filled end to end with polymeric product may be obtained by local irradiation/reactant diffusion or, if necessary, by diffusional refilling (Marti-Rujas 10.1021/jp806380p). The electrical conductivity of the resulting hybrid oriented insulated polyacetylene UIC arrays as a function of temperature will be discussed.



POLY 572: Towards exceptionally stable imidazolium cations for anion-exchange membrane applications

Jiun-Le Shih¹, p389426@hotmail.com, Vincent de Paul N. Nziko², Vyacheslav Bryantsev¹, Jan-Patrick Melchior¹, Radu Custelcean³, Santa Jansone-Popova¹. (1) ORNL, Oak Ridge, Tennessee, United States (3) MS 6119, Oak Ridge National Lab, Oak Ridge, Tennessee, United States

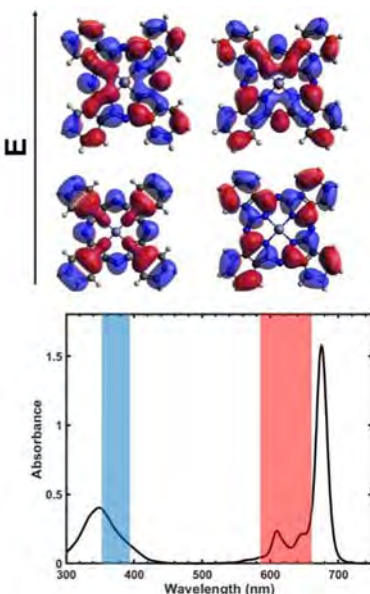
Anion exchange membranes (AEMs) are the crucial components of alkaline fuel cells. Insufficient alkaline stability of AEMs at high temperatures limits the commercialization of AEM fuel cell technology. Herein we report the design, synthesis, and stability measurements of novel imidazolium-based anion exchange membranes for alkaline fuel cell applications. Degradation rates and mechanisms of small organic cations were analyzed by NMR spectroscopy and rationalized using density functional theory (DFT) calculations. The most stable imidazoliums were polymerized to produce robust AEMs. The stability of membranes was examined using dynamic vapor sorption (DVS) technique. The stability profiles of small organic cations and AEMs will be correlated and discussed in detail.



POLY 573: Investigation of a dual-role, two-color photosensitive molecule for oxygen removal and radical generation

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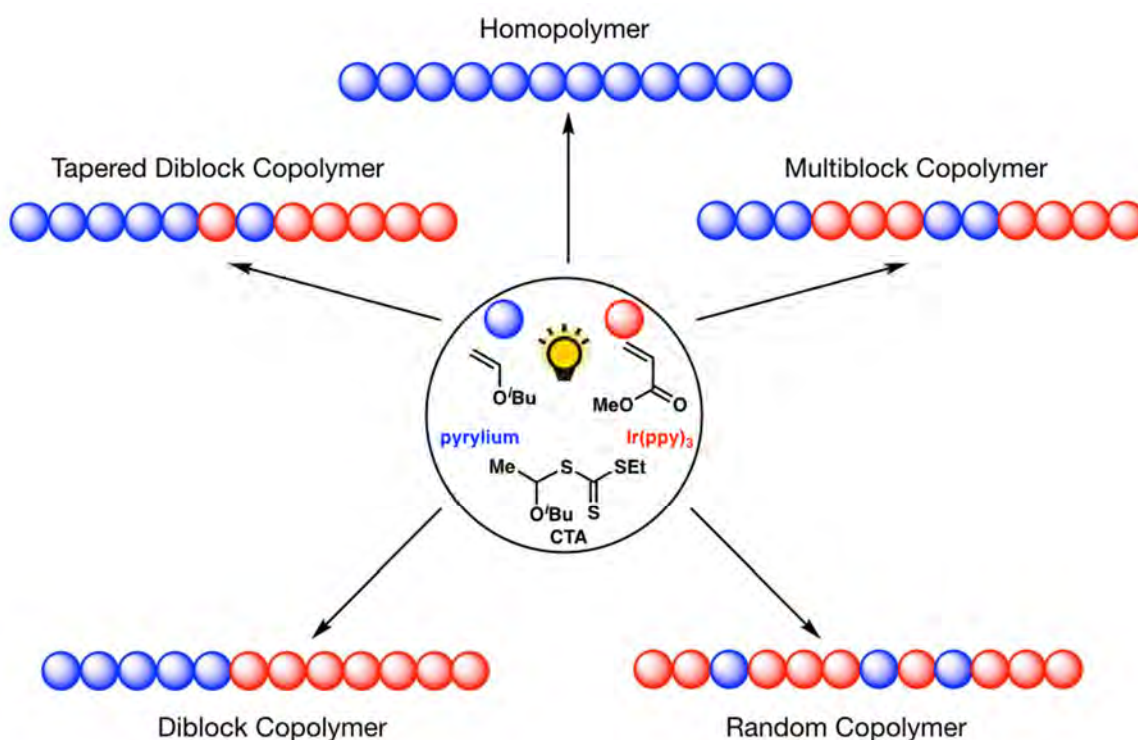
Oxygen is a persistent hindrance in free radical polymerizations. Phthalocyanines (Pc) have been shown to be an effective molecule to circumvent the presence of oxygen by the excitation of molecular oxygen ($^3\Sigma_g^-$) to its singlet state ($^1\Delta_g$) via triplet-triplet energy transfer with Pc rendering its reaction with initiating and propagating radicals no longer energetically favorable. Red-light irradiation of Pc depletes the concentration of oxygen to a threshold level in which monomer reaction with radicals is competitive. We have shown that not only does the red-light irradiation of the Pc Q band lead to $^3\Sigma_g^-$ to $^1\Delta_g$ conversion but also that the UV-irradiation of the metal-complexed Pc B (Soret) band results in polymerization. For the first time, a single molecule has been utilized as both a photosensitizer and a photoinitiator. Irradiation of the Q band at 635 nm and subsequent irradiation at 365 nm of the B band leads to shortened or nonexistent induction times, as well as faster rates of polymerization and final conversions comparable to commercial photoinitiators. By coupling UV-Vis and FT-NIR spectroscopy, we were able to determine the kinetic behavior of the polymerization of di(ethylene glycol) ethyl ether acrylate (DEGEEA) in real-time, including the conversion, rates of polymerization, and quantum yields of photodegradation. Different metal complexes were studied to determine effects on their ability to exhibit this dual-functionality, and a mechanism for this phenomenon is proposed.



POLY 574: Accessing various polymer architectures with the simple flip of a switch

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The development of photocontrolled radical polymerizations has enabled unprecedented control over polymer chain-growth. In order to render these light-regulated processes suitable for monomers that do not undergo radical polymerizations, such as vinyl ethers, a cationic variant was recently developed. The design and mechanistic study of this novel photocontrolled cationic polymerization and its applications toward the preparation of complex polymeric materials will be examined. Then, the discussion will focus on the merging of radical and cationic photocontrolled polymerizations—using a combination of two photoredox catalysts—as a means to streamline access to a diverse array of copolymer architectures using light as a simple external stimulus.

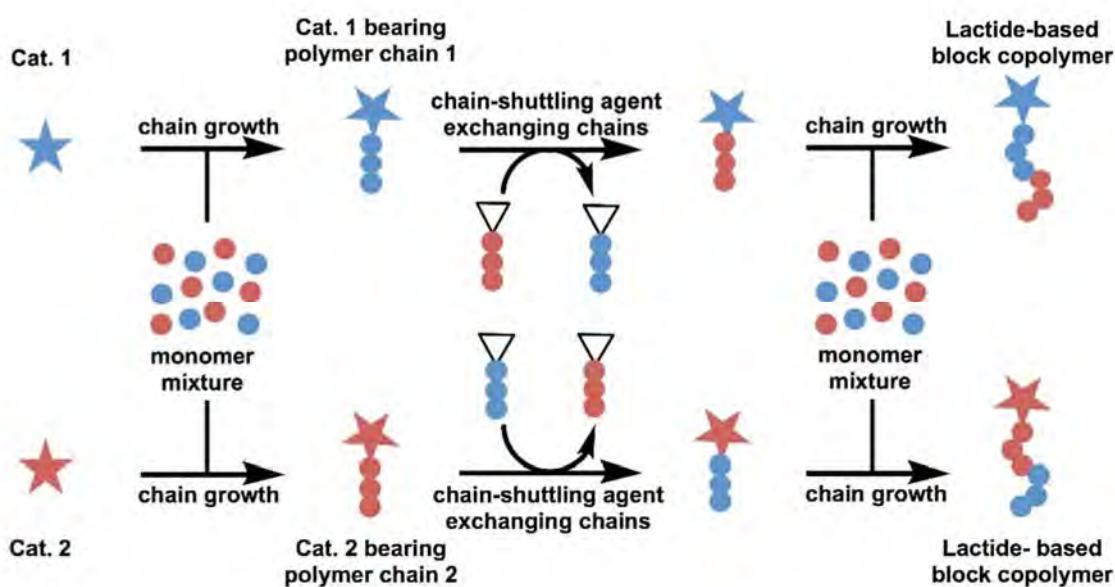


Synthesis of Copolymers through Interconvertible Cationic and Radical Polymerizations Regulated by Light

POLY 575: Development of a chain-shuttling ring-opening polymerization

Melanie Chiu, latimerlabrat@gmail.com. Chemistry, SUNY Stony Brook University, East Setauket, New York, United States

Lactide-based copolymers with controllable degradation profiles and mechanical properties are essential for environmental and biomedical applications. To access new lactide-based copolymers with a high degree of control over copolymer microstructure, a chain-shuttling ring-opening polymerization method has been developed, comprised of two catalysts with complementary monomer selectivities and a chain-shuttling agent that transfers polymer chains between catalyst centers. Kinetic and mechanistic studies on this system, as well as characterization of the resultant copolymers are described. Strategies for implementing external control over the catalyst system and implications for dynamic control over copolymer microstructure are considered.



POLY 576: Organocatalyzed ring-opening atom transfer radical polymerization of vinylcyclopropanes driven by visible light

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Radical ring-opening polymerization (RROP) of cyclic monomers, such as functionalized vinylcyclopropanes (VCPs), produces polymers with low volume shrinkage, or even volume expansion, which has vast application potentials in modeling and filling materials. VCPs generally polymerize through two mechanistic pathways in RROP, affording polymers with mixed linear and cyclobutane units. Historical RROP of VCPs is often performed at elevated temperatures and suffers from several limitations. For example, the free radical polymerization of VCPs is uncontrolled while the Cu(I)-catalyzed ring-opening atom transfer radical polymerization (ATRP) of VCPs provides excellent control over the chain growth, however, it only reaches low conversion. Organocatalyzed atom transfer radical polymerization (O-ATRP) through photoredox catalysis has obtained increasing attention. By using *N,N*-2-naphthyl dihydrophenazine as the photocatalyst, we achieved the first visible-light-regulated ring-opening ATRP of VCPs under mild conditions. A variety of functionalized vinylcyclopropanes were tolerated to afford polymers in high conversions (typically > 90%), and with predictable molecular weight, low dispersities (1.12 – 1.23), and a high degree of linear composition (> 90%). Properties of these obtained polymers, such as high thermal stability and tunable glass transition temperature (T_g), may inspire future applications in material science.

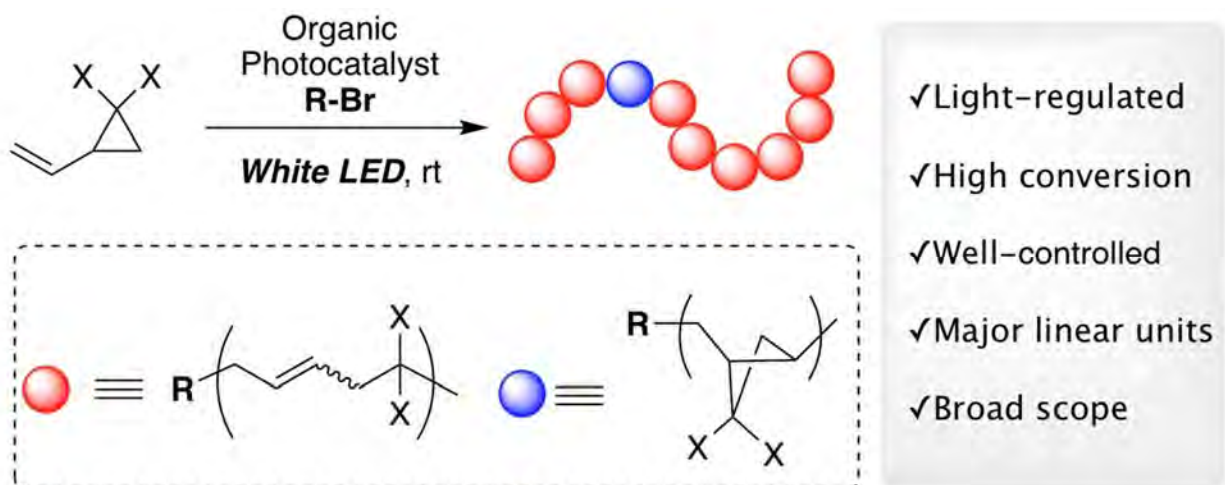
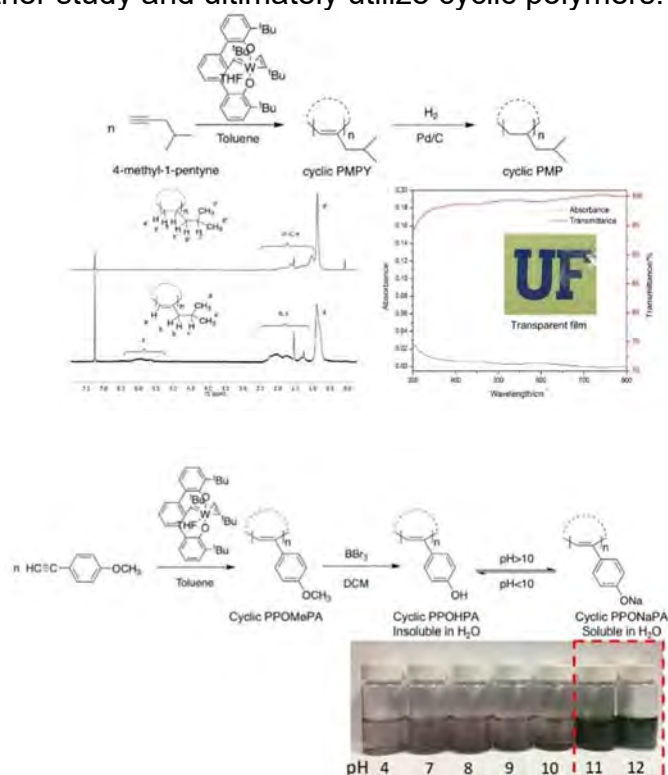


Figure 1. Organocatalyzed Ring-Opening ATRP of VCPs

POLY 577: Catalytic synthesis and post-polymerization modification of cyclic polyalkynes

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Cyclic polymers possess unique properties compared to their linear counterparts, such as smaller hydrodynamic volumes, lower intrinsic viscosities and higher glass transition temperatures, due to the fact that they have reduced sizes, restricted conformational flexibility and lack of chain ends. Several cyclic versions of commercial polymers were synthesized with our reported tungsten catalyst supported by a tetraanionic pincer ligand. Their cyclic topologies were confirmed by size-exclusion chromatography, viscometry and rheology analysis. Cyclic poly(4-methyl-1-pentyne) (PMPY) was synthesized. Upon hydrogenation cyclic poly(4-methyl-1-pentene) (PMP) was afforded. Linear PMP has high optical transparency, relatively high thermal stability and chemical resistance. The cyclic PMP showed high transparency in the 300 nm to 800 nm region of the visible spectrum. A 10 °C increase in glass transition temperature was observed for cyclic PMP versus linear amorphous PMP. Cyclic poly(1-pentene) was also synthesized on a 10-gram scale by polymerization of 1-pentyne and hydrogenation. Also, cyclic poly(p-methoxyphenylacetylene) was made and converted to cyclic poly(p-hydroxyphenylacetylene) via demethylation using boron tribromide. The resulting polymer was found to be soluble in basic aqueous solution and its solubility was pH responsive. The successful synthesis of these cyclic polymers provides a new opportunity to further study and ultimately utilize cyclic polymers.

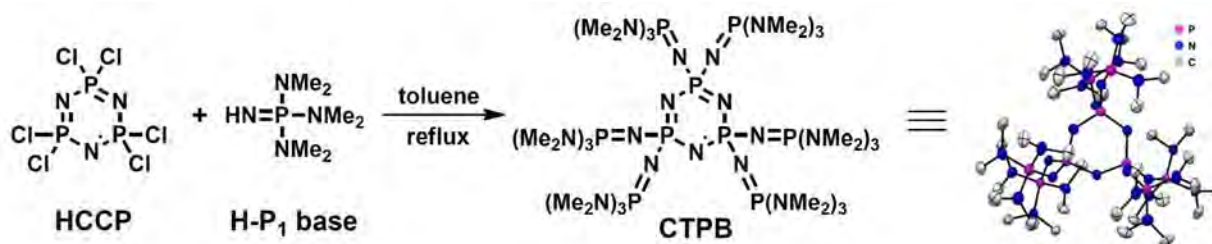


POLY 578: Synthesis of sustainable poly(γ -butylactone) and copolymers by cyclic trimeric phosphazene base catalyzed ROP

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Synthesis of sustainable polyesters via metal-free catalyzed ROP of cyclic esters is of great importance for their biomedical applications, and is therefore becoming the most appealing research topic in polymer synthesis. As a category of organic superbases, phosphazene exhibits high catalytic activity in ROP of cyclic esters. The catalytic performances of phosphazene catalysts highly depend on their structure and basicity. Herein, a new superbase, cyclic trimeric phosphazene base (CTPB), was prepared with high yield and purity (Scheme 1). In the presence of alcohol, the CTPB can serve as highly efficient organocatalyst for ROP of “non-strain” five-membered γ -butyrolactone to offer well-defined poly(γ -butyrolactone) with high conversions. The produced polymers have high molecular weights and low molecular distributions (1.27-1.50). NMR analysis of initiation process and the structural analysis of resulted polymers by MALDI-TOF suggest an activating initiator mechanism.

On the other hand, the preparation of block copolymers containing poly(γ -butyrolactone) block remains as a synthetic challenge owing to the unfavorable thermodynamics towards the ROP of “non-strain” five-membered ring. Using CTPB superbase as catalyst, we realized the successful one-pot preparation of poly(γ -butyrolactone)-*b*-poly(L-lactide) by sequential ROP of γ BL and L-LA for the first time. The thermal stabilities, crystallization and melting behaviors of the obtained diblock copolyesters were also investigated.

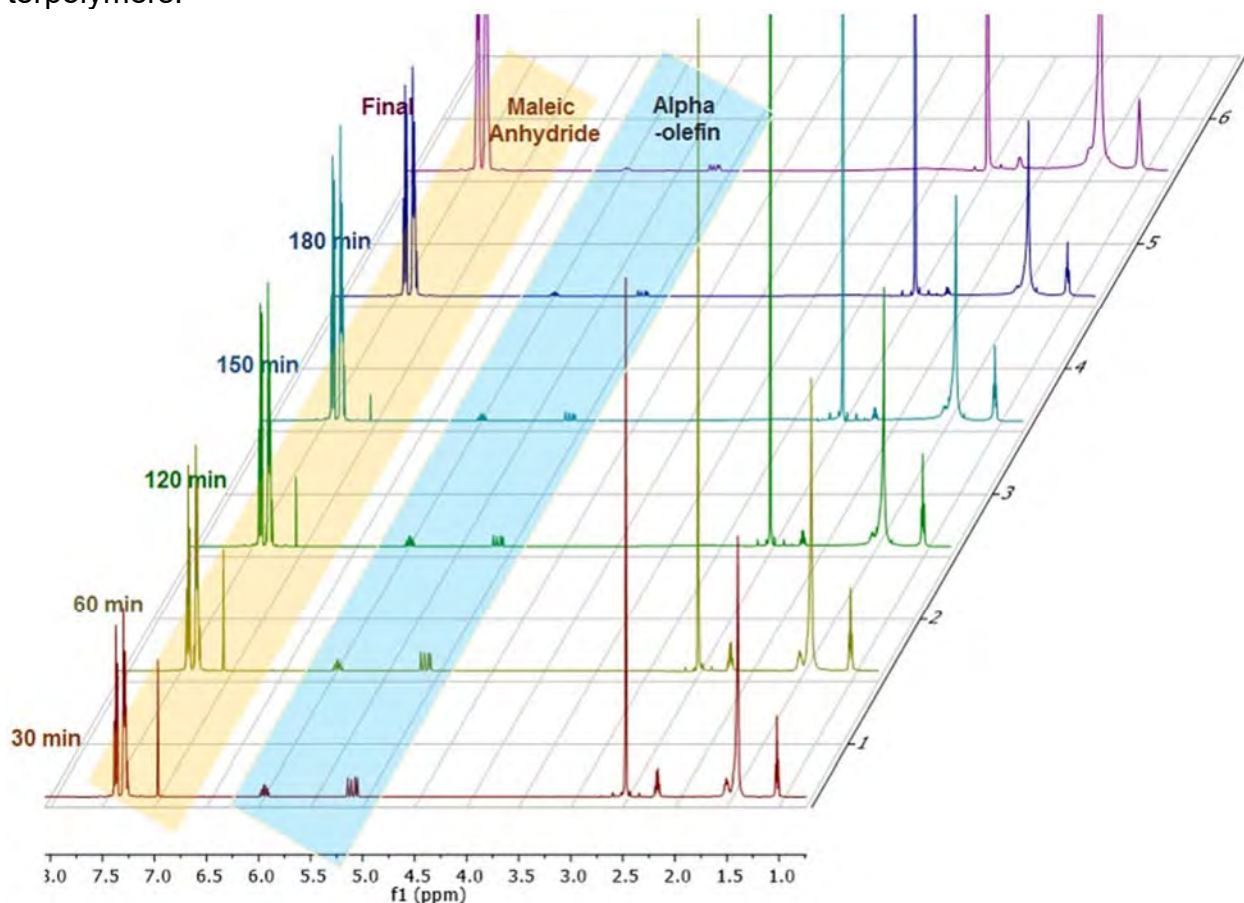


POLY 579: Effects of two different α -Olefins and the composition ratio of their combination on maleic anhydride and α -olefins terpolymerization

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Both α -olefins and maleic anhydride are considered non-reactive as monomers for conventional free radical polymerization. α -Olefins favor hydrogen abstraction over radical addition, creating thermodynamically stable allylic radicals. Maleic anhydride is classified as a 1,2-disubstituted monomer and owes its non-reactivity to its significant steric hindrance. However, these two chemistries are known to readily co-polymerize via electrostatic charge transfer complex formation; resulting in unique alternating monomer sequences in the copolymer backbone of molecular weights in the range of 2000 to 20,000 g/mol.

Much of the recent researches into α -olefins and maleic anhydride copolymers have focused on their diverse properties and applications, with little focus on the polymer formation mechanisms or kinetics. In this paper we report the effects of two different α -olefins and the composition ratio of their combination on terpolymerization with maleic anhydride, especially focusing on conversion and molecular weight of the resulting terpolymers.

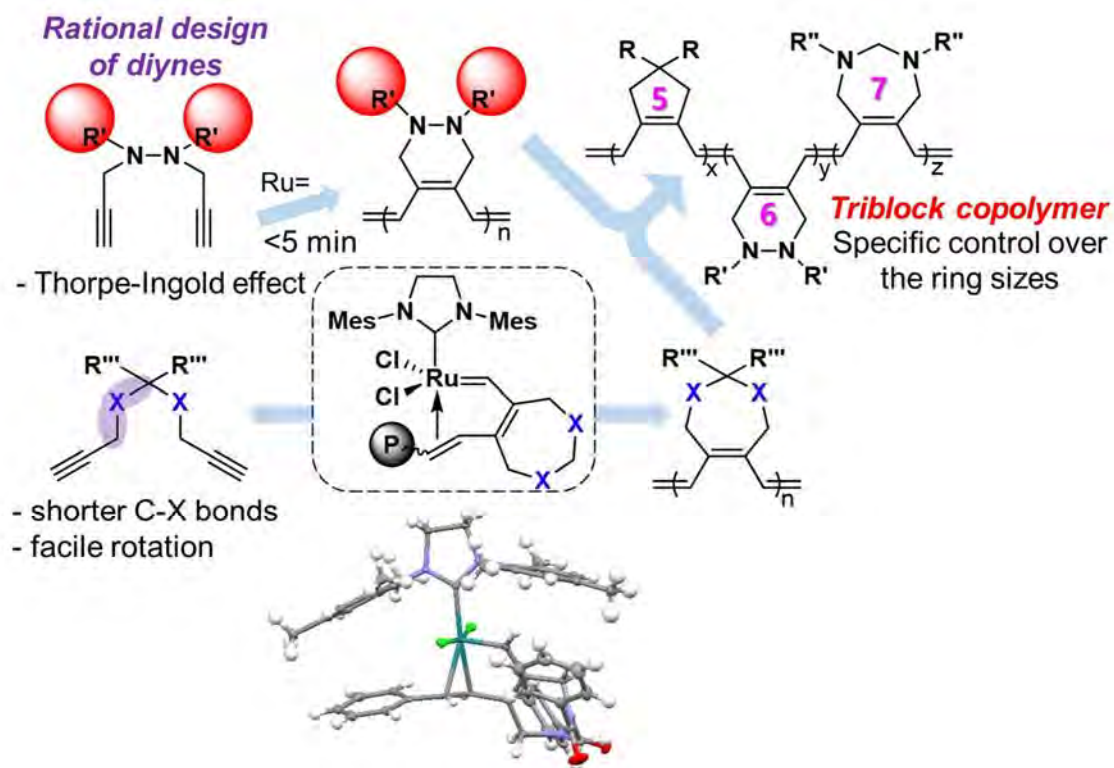


¹H NMR Analysis for Decene-Hexadecene-Maleic Anhydride Terpolymerization

POLY 580: Six- and seven-membered ring-forming cyclopolymerization of various diyne derivatives using Grubbs catalysts: Rational design of monomers and direct observation of propagating carbene

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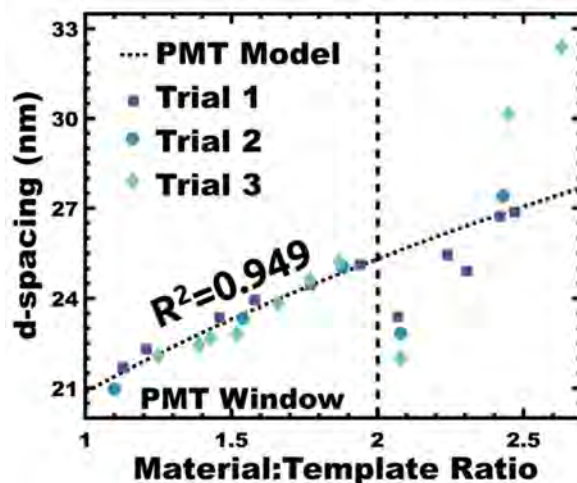
Living/controlled cyclopolymerization (CP) of 1,7-octa- and 1,8-nonadiyne derivatives was achieved by novel design of diyne monomers. Especially, the CP of 1,8-nonadiynes forming challenging medium-sized seven-membered rings was the first example. The key to the successful CP was the introduction of appropriate heteroatoms: i) hydrazide groups, which have two protecting groups, resulting in increased Thorpe-Ingold effect and ii) aminal and acetal groups, which have short C-N and C-O bonds, and low rotational barriers. During our mechanistic investigation into the CP of 1,8-nonadiyne derivatives, we observed a same Ru propagating carbene from two respective polymerizations using 2nd generation Hoveyda-Grubbs catalyst and 3rd generation Grubbs catalyst (GIII) by ¹H NMR spectroscopy. This Ru propagating carbene was isolated and turned out to be a bottom-bound isomer of olefin-bound Ru carbene by X-ray crystallography. Finally, we achieved a controlled CP of the aminal monomers using a fast-initiating GIII with the aid of stable olefin-bound Ru propagating carbene. This allowed the synthesis of not only the diblock copolymer containing five- and seven-membered rings, but also the triblock copolymer containing five-, six-, and seven-membered rings.



POLY 581: Precision nanomaterials from kinetic-controlled block copolymers

Morgan Stefik, stefik@mailbox.sc.edu. Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

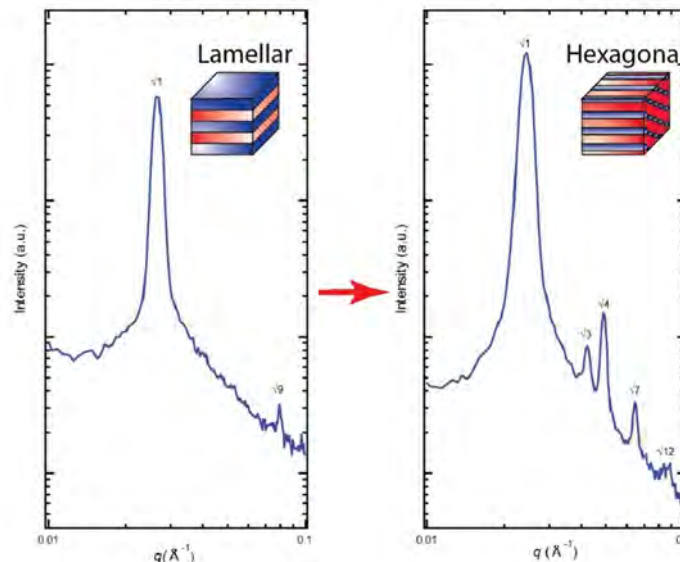
Few aspects are as prevalent and important to energy conversion and storage as the dimension control of porous nanomaterial architectures. Numerous methods based on block copolymers have led to porous materials over the past decades, however the study of nanostructure-dependent behavior has been limited by access to well-defined nanomaterials with independent control over the pore and wall dimensions. This historic limitation is partially due to an overreliance upon dynamic self-assembly processes that are subject to the “tyranny of the equilibrium.” We have developed a new nanofabrication tool kit that is rather based upon templates of kinetically-controlled block copolymer micelles.¹⁻³ Kinetic control of block copolymers is historically difficult to reproduce, a challenge that we have resolved with switchable micelle entrapment to yield reproducible and homogeneous nanomaterial series that follow model predictions. This approach enables seamless access from meso-to-macroporous materials with unprecedented ~ 2 Å precision of independent tuning, commensurate with the underlying atomic dimensions. This precision and independent control of architectures also opens new opportunities for nano-optimized devices.



POLY 582: Nanostructural transitions driven via in situ polymer grafting in diblock copolymer/monomer blends

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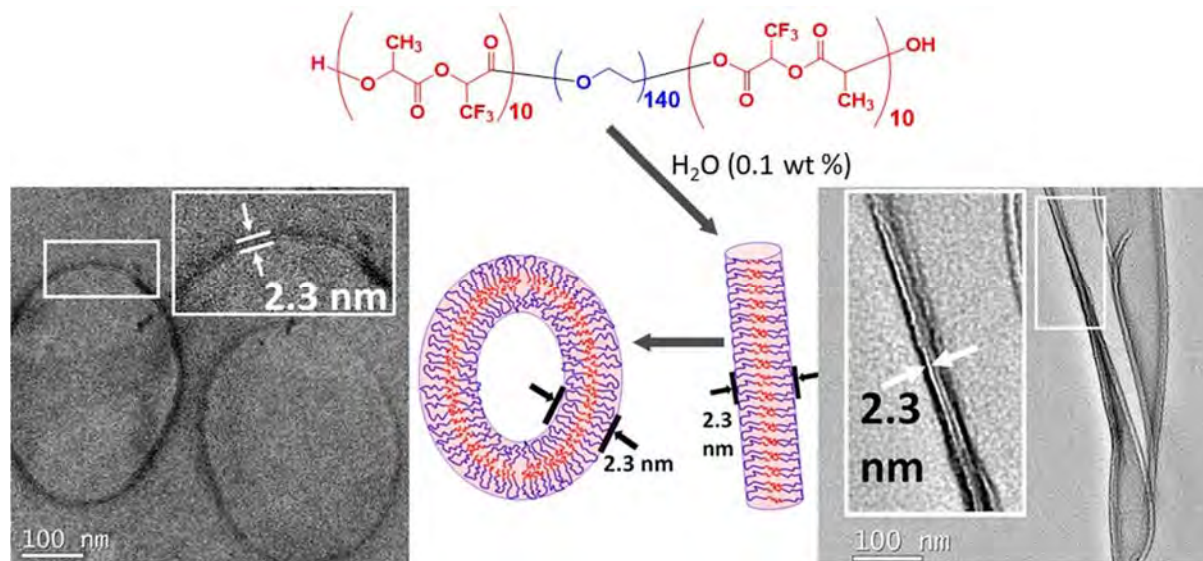
Colloidal and bulk nanostructured materials fabricated via polymerization-induced structural transitions have been used in a host of applications ranging from biomedical to energy technologies. In the previous studies that explore polymerization-induced structural transitions, the starting reagents, such as macro chain-transfer agent (macro-CTA), monomer, and solvent, are initially well solubilized, creating a homogenous mixture. During the macro-CTA chain-extension process, the growing polymer becomes incompatible with the initial polymer segment and/or the solvent, leading to the formation of nanoscale domains. Our group has recently achieved order-order structural transitions by polymer grafting from block polymers that exhibit nanostructured morphologies before polymerization. In our approach, we are able to induce a lamellar-to-hexagonally-packed cylinder transition via the polymerization of styrene, which initially acts as a neutral solvent for the lamellar-forming diblock copolymer, poly(styrene)-block-poly(1,2 butadiene) (PS-1,2PBD). Furthermore, in situ small-angle X-ray scattering (SAXS) experiments during the polymerization process reveal a complex phase path in which the double gyroid phase is an intermediate morphology between the lamellar and hexagonally-packed cylinder phases. The lamellar-to-hexagonally-packed cylinder order-order transition occurs via a PS grafting mechanism in which PS chains are grafted to the 1,2PBD block. The PS grafting leads to an increase in the overall molecular weight and in the PS volume fraction of the PS-1,2PBD copolymer, driving the morphology transitions. The work presented here highlights how the chemical process of converting standard linear diblock copolymers to grafted-block polymers drives interesting and controllable morphology transitions.



POLY 583: Facile synthesis of fluorine-substituted polylactides and self-assembly of their amphiphilic block copolymers in solution

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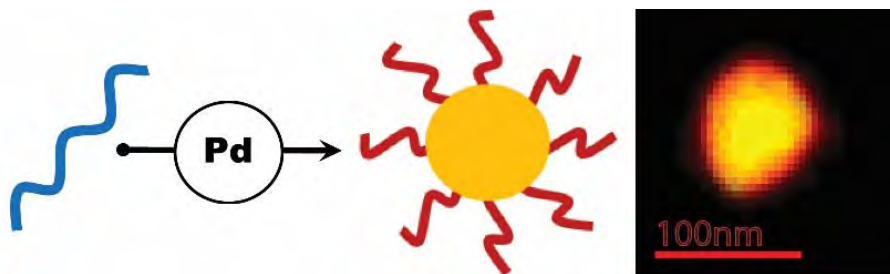
We report successful synthesis of 3-trifluoromethyl-6-methyl-1,4-dioxane-2,5-dione and ring opening polymerization of the new fluoro-lactide monomer to prepare polylactides composed of trifluoromethyl and methyl pendent groups on each repeat unit (FPLA). Molecular weights of the prepared polymers correlated well with the initial molar ratio of monomer to initiator, and were found to range from 6.6 to 22.5 kDa as determined by ¹H NMR spectroscopy. ¹H, ¹³C, and ¹⁹F NMR spectroscopy were consistent with the structures of the lactide monomer isomers, and ¹H NMR analysis was consistent with polymer backbones of alternating trifluoromethyl- and methyl-substituted lactate constituents. Additionally, we prepared amphiphilic block copolymers of FPLA and PEG (FPLA-*b*-PEG diblocks and FPLA-PEG-FPLA triblocks) by using methoxy PEG (mPEG) or PEG as alcohol initiators. We observed the formation of vesicles or worm-like micelles from the particles of FPLA-PEG-FPLA in dilute aqueous solution by TEM, suggesting potential applications for drug delivery.



POLY 584: Pd-catalyzed post-polymerization modification of block copolymers for nanoparticle synthesis

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The Pd-catalyzed Suzuki-Miyaura cross-coupling reaction has been recently demonstrated as an effective method of post-polymerization modification for installing a diverse array of polymer pendant groups. In the present work, this technique is being explored as a method for forming micelle-like polymer nanoparticles through the functionalization of block copolymers. Rational selection of cross-coupling agents and reaction conditions allows tuning of particle morphology, dimensions, and properties. Demonstrated control over particle stability points to the viability of this synthetic technique for drug delivery or other payload-release applications.

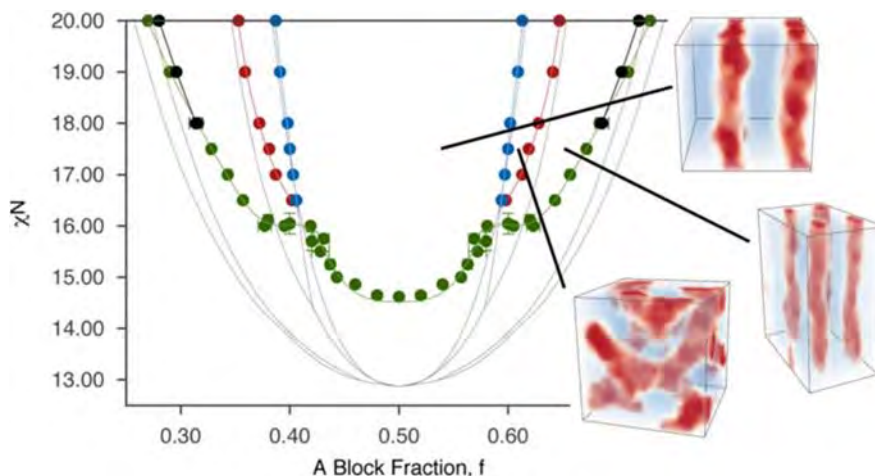


POLY 585: Progress in fully fluctuating field theoretic simulations of polymers

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A field theoretic approach for simulating assemblies of interacting polymers is discussed. By applying a Hubbard-Stratonovich transformation to a molecularly informed coarse-grained polymer model, auxiliary fluctuating fields are introduced to decouple segmental interactions, and particle degrees of freedom are integrated out. The resulting theory has several advantages for simulating dense, long-chain polymeric systems, including efficient equilibration and direct access to mesoscale phenomena without simulating the atomic/molecular scale. The theory is commonly employed in a mean-field approximation (SCFT), which is exact for asymptotically long polymer chains in the melt state. However, for intermediate-molecular-weight melts, for solvated or charged polymers, or for systems close to critical phase transitions, the mean-field approximation is qualitatively inadequate. We discuss a stochastic computational method based on complex Langevin sampling to directly simulate the fully fluctuating field theory without critical inefficiencies of the sign problem.

Applications of the field-theoretic simulation method to the study of fluctuation corrections of block copolymer phase diagrams will be presented, including the formation of novel fluctuation-stabilized morphologies in highly asymmetric branched polymers. Subsequently the application to complex coacervates and self coacervates of polyelectrolyte solutions will be presented, with a focus on phase coexistence conditions, the scaling of the critical point, and the nature of the dilute supernatant phase. Finally, a recently developed extension to the FTS method for simulating soft materials involving polar or polarizable segments, potentially coexisting with charges and/or subject to applied electric fields, will be presented. This new framework is suitable for simulating a vast range of soft-matter systems, including polyelectrolytes, polymerized ionic liquids, ionomers and block copolymers, with phenomena including van der Waals interactions, charge localization and phase-separation-driven dielectric contrast all emerging consistently from the molecular specification.

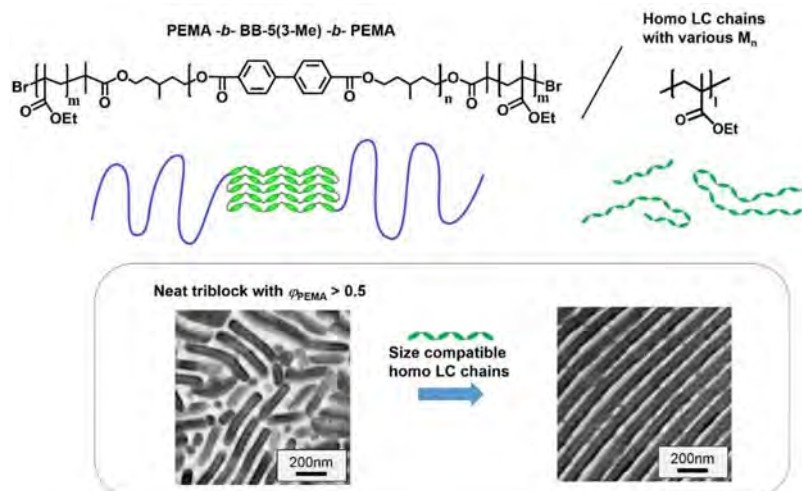


POLY 586: Re-ordering for disordered structure of an amorphous – b – main-chain liquid crystal – b – amorphous copolymer into ordered lamellar structure by adding homo liquid crystalline chains

Mikihiro Hayashi¹, hayashi.mikihiro@nitech.ac.jp, Junpei Kuribayashi², Masatoshi Tokita². (1) Nagoya institute of technology, Nagoya, Aichi, Japan (2) Tokyo Institute of Technology, Tokyo, Japan

Block copolymers construct a variety of nanometer scale morphologies depending on the molecular parameters. So far, our group have reported that triblock copolymers consisting of amorphous end blocks and a main-chain liquid crystalline (LC) middle block showed unique characteristic in forming lamellae. In the series of reports, the LC middle block used was BB-5(3-Me), which comprised 4,4'-biphenyl dicarboxylic acid and 3-methyl-1,5-pentanediol, while the amorphous end block used was poly(ethyl methacrylate) (PEMA). Within the lamellar microdomains, the LC segments were found to extend in the direction perpendicular to the lamellar interface with folding these chain. When the molecular weight of PEMA is increased, LC segments spontaneously adjust the number of chain foldings in order to counterbalance the enlargement of amorphous interfacial area. These features result in the structural characteristic that the lamellar structures were formed at a relatively wide and asymmetric volume fraction of amorphous block (ϕ_{am}), $0.2 \leq \phi_{am} \leq 0.5$. On the other hand, when $\phi_{am} > 0.5$, the structure was disordered since the enlargement of amorphous segments exceed the capability of LC segments for adjusting the chain foldings, which limits the available domain spacing range.

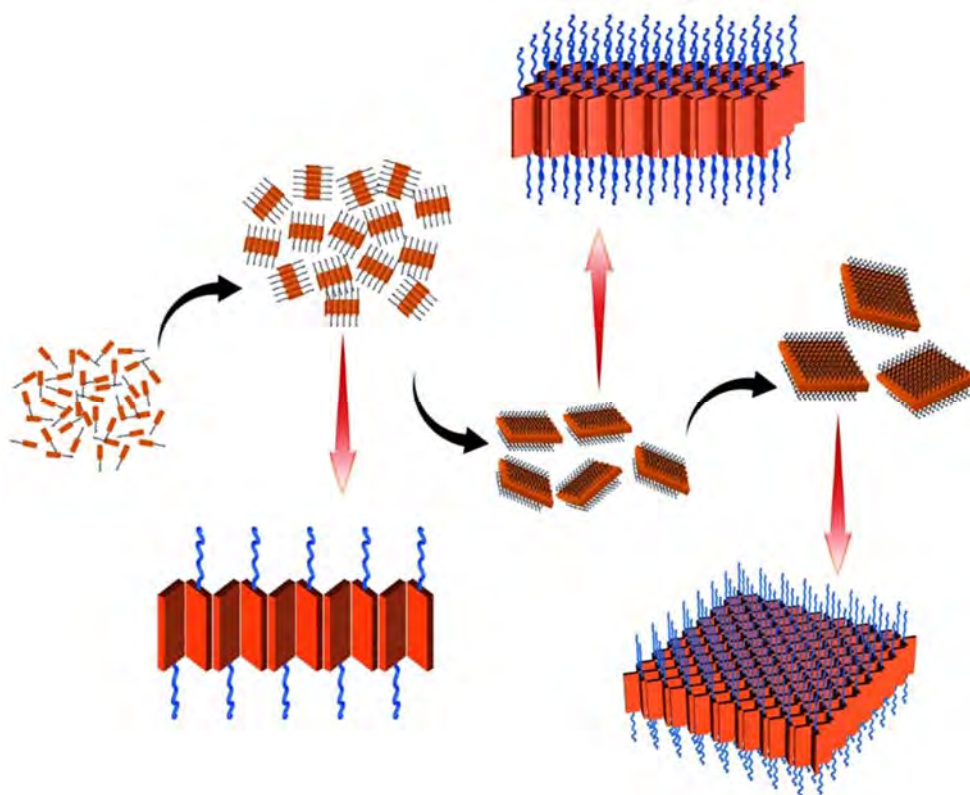
To deal with the problem above, we here demonstrate re-ordering for disordered morphology of the LC triblock copolymers with large ϕ_{am} (> 0.5) into long-range ordered lamellar structures by adding LC homopolymers. The neat triblock copolymer with $\phi_{am} \sim 0.53$ or ~ 0.58 forms disordered morphology, while the blends with LC homopolymers having whole ϕ_{am} of 0.38 shows the long-range lamellar structure according to SAXS and TEM. Such success of transition from disordered to ordered structure is dependent on the size of LC homopolymers. The present finding can lead the widening of amorphous volume fraction range for forming lamellar structures, which is beneficial to create useful nano-materials.



POLY 587: Research on controlled self-assembly of controlled fluorescent block copolymers driven by π - π interactions

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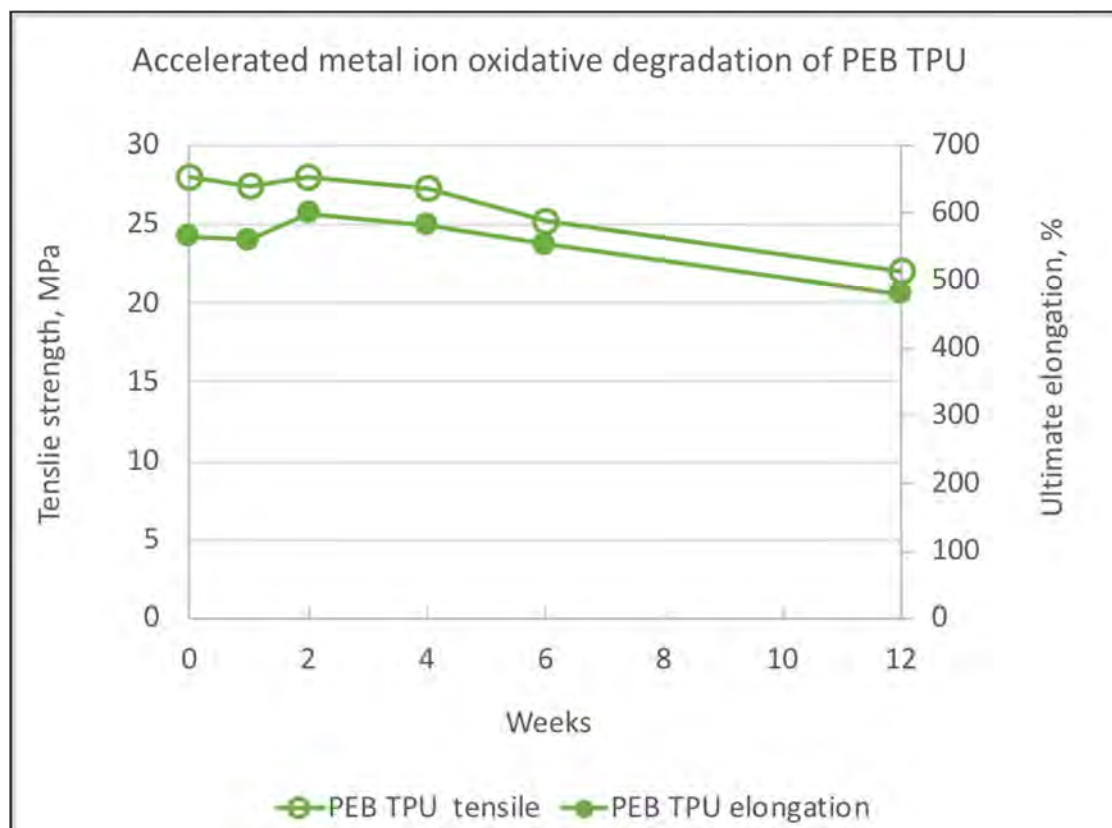
In recent years, block copolymers have attracted much attention for they can be used as building blocks to fabricate 1/2D nano-/micro- architecture driven by crystallization, electrostatic interaction and crosslinking. We combine conjugated fluorescent block poly (phenylene vinylene) (PPV) and poly (2-vinyl pyridine) (P2VP) to build rod-coil type diblock copolymer PPV-P2VP with strong fluorescence and self-assembly property. Nano-/micro- supramolecular fluorescent architectures of the copolymers were obtained by dissolving- cooling-aging process. The obtained structures could be transformed from one-dimensional (ribbons) to two-dimensional (square micelles) by changing the alkyl side chains of PPV blocks, and the scale of the structures could be controlled by changing the block length ratio of PPV and P2VP in the copolymer. The self-assembled morphology of the low block ratio exhibits a significant concentration dependence, and the concentration dependence disappears as the block ratio increases. The morphological characterization and kinetic studies of the formed nano-/micro- architectures show that the conjugated forces play an important role in self assembling process.



POLY 588: Synthesis, characterization and biostability of poly(ethylene-co-butylene) polyurethanes

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Polyether based thermoplastic polyurethanes (TPUs) have been widely used in biomedical applications due to a broad range of physical properties. However, these polymers are highly susceptible to oxidative degradation leading to a deterioration of mechanical properties. Recently introduced polyisobutylene (PIB) based TPUs exhibit excellent oxidative and hydrolytic stability, however, the precursor PIB diol is not available commercially. Generally, TPUs based on nonpolar soft segments possess lower tensile strength and toughness due to premature phase separation, especially in bulk synthesis, leading to compositional heterogeneity. We have investigated the preparation of poly(ethylene-butylene) (PEB) based TPUs by a two-step solution-based synthesis. The tensile strength of the prepared TPUs were still inferior compared to polyether based TPUs, however, addition of a small amount of polyether diol dramatically increased the tensile strength and ultimate elongation. All polyurethanes were completely amorphous with a $T_g = -42\text{ }^\circ\text{C}$, a bit higher than the T_g of PEB ($\sim -50\text{ }^\circ\text{C}$), indicating some phase mixing. Accelerated metal ion oxidative degradation studies were carried out in 20% H_2O_2 solution containing 0.1 M CoCl_2 at $50\text{ }^\circ\text{C}$ for 12 weeks. After 12 weeks the TPU retained 90% of its weight, 79% of tensile strength and 85% of ultimate elongation, indicating superior stability, similar to PIB based TPUs.



POLY 589: Kraton Polymers, 50 years of experience with styrenic block copolymers

Marianne Stol, Marianne.Stol@Kraton.com. Kraton Polymers, Amsterdam, Netherlands

The emergence of anionic, living polymerization in the 1950s enabled the synthesis of polymers with controlled structures. A key consequence of controlled molecular architecture was the distinct phase separation and self-assembling morphologies of polymers containing discrete blocks of styrene and isoprene or butadiene. The self-reinforcing nature of such styrenic block copolymers was recognized for its broad commercial potential as a new class of polymers; styrenic thermoplastic elastomers (TPE-S). More than fifty years after the commercial introduction of styrenic block copolymers, the annual global consumption is significant and includes scores of different polymer structures tailored to meet the specific needs in numerous markets and applications. Applications as diverse as the roads we drive on, the cars in which we drive, the shoes we wear and the personal hygiene utensils we use are all enhanced by the properties of styrenic block copolymer thermoplastic elastomers. New styrenic block copolymers continue to be developed and commercialized as a result of the robust chemistry leading to novel performance features. This presentation will show the versatility of styrene, butadiene and isoprene, combined in block copolymer architectures. This versatility leads to an array of different applications, all based on the self assembly of these materials. Some of these applications will be highlighted.

The logo for Kraton, featuring the word "KRATON" in a bold, blue, sans-serif font. A small green triangle is positioned above the letter 'A'.

POLY 590: Development of polymer science in academia

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Hermann Staudinger, first at ETH Zurich and then at Freiburg, is responsible for founding modern polymer science by proving that polymers are long chain molecules composed of repeating units and not loose colloidal associations as had been previously thought. The synthetic polymer field received great impetus from the success of the industrial scale production of polystyrene under the direction of Herman Mark at I.G Farben in the 1920's. In the 1930s, high pressure or low density polyethylene was developed by ICI and Nylon and neoprene rubber by Carothers at DuPont. World War II saw the development of a large industrial program to develop Styrene Butadiene Rubber (SBR), a substitute for natural rubber. This program received vital contributions from many, but the work of Sparks at what was then Esso Research stands out. Although there remained considerable resistance to the study of synthetic polymers even after Staudinger, a number of academic chemists and physicists entered the field. Many enjoyed illustrious careers and made major contributions. Here the name of P.J. Flory stands out in polymer physics, while K. Ziegler and J. Natta stand out in polymer chemistry. There had been an Institute for Rubber Chemistry at Akron since the 1930's and this was followed in the 1940's by the Polymer Research Institute at Brooklyn Poly Tech headed by Herman Mark. Other academic and government centers were founded in the United States. Polymer research became important in many Japanese Universities and in Europe. Fundamental polymer research in industry was established in the 1920s and 30s at I.G. Farben and at DuPont. Other important industrial centers were then established worldwide. Here we will focus on the UMASS PSE Department and its 50 plus year approach to providing a comprehensive education in polymer physics, polymer chemistry and polymer engineering.

PSE
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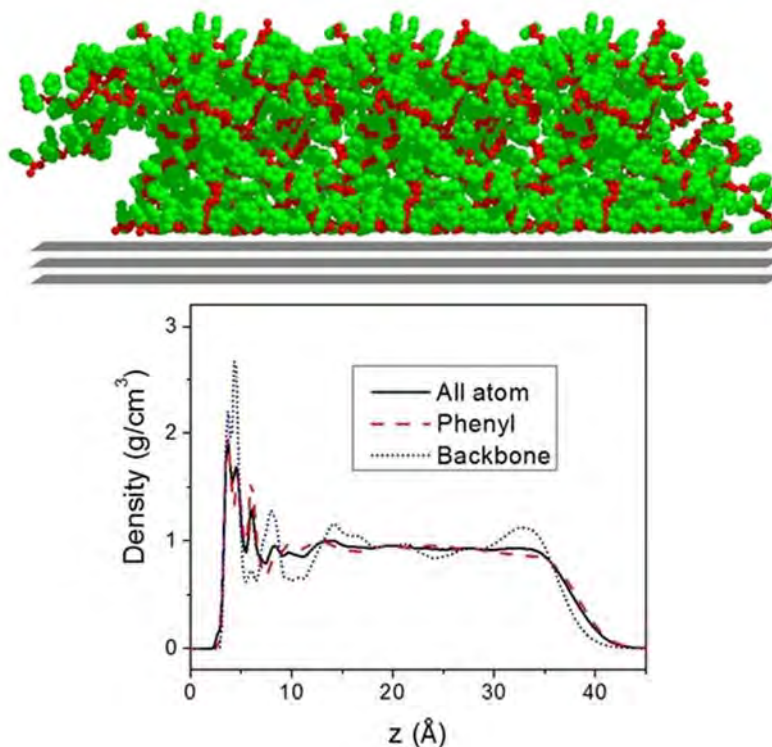


POLY 591: Paul Flory's legacy in polymer science

Do Y. Yoon, doyoon@stanford.edu. Dept of Chemical Engineering, Stanford University, Stanford, California, United States

Paul Flory made many seminal contributions to polymer science for half a century since he first started working on polymers in the Wallace Carother's group at duPont in 1934, as well documented in the three-volume books, entitled "Selected Works of Paul J. Flory I-III," published in 1985 on the occasion to celebrate his 75th birthday. In August, 1985, he presented his last public lecture at the IUPAC Macromolecular Symposium in The Hague, entitled "Development of Concepts in Polymer Science, A Half Century in Retrospect." The paper from this lecture describes practically all the key contributions Paul Flory made, i.e., *Paul Flory's Legacy in Polymer Science*, in his own words to advance our understanding of chemical reactivity, molecular size distributions, molecular configurations, thermodynamics of polymer solutions, the effect of excluded volume, and morphology of macromolecular chains at high concentrations and in bulk polymers.

Since my personal collaborations with Paul Flory were mainly on the topic of morphology of macromolecular chains in bulk polymers, this talk will emphasize his seminal contributions to this field while other topics will be covered very briefly. In addition, recent advances (beyond Paul Flory's legacy) in understanding the molecular conformations of bulk polymers in the polymer-air and polymer-solid interfaces will be discussed, which have important consequences on the glass transition temperatures of polymers in thin films.

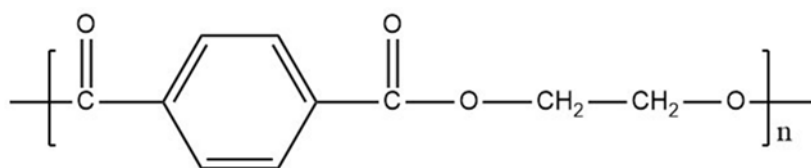


Polystyrene melt films on graphite substrates

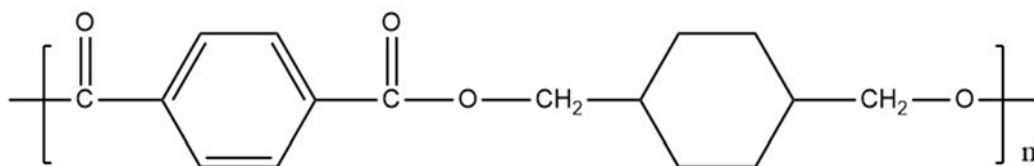
POLY 592: Polyesters-from discovery to indispensable modern materials

Sam R. Turner, *srtur@vt.edu*. *Macromolecules Innovation Institute and Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

Modern thermoplastic polyesters are mainstay polymeric materials that help propel today's growing economies. Important applications include food packaging for insuring our food supply, fibers, molded and extruded plastic objects, high performance films for flexible electronic devices, and advanced composites, *inter alia*. Even though polyesters were not the first commercial synthetic polymers, Carothers' pioneering research at DuPont on aliphatic polyesters in the 1930's is cited as the first intentional polymerizations from monomers to prepare synthetic polymers. However, it was not until the early 1940's that Whinfield and Dickson in the UK at Calico Printers Association (CPA), used terephthalic acid in place of Carothers' aliphatic diacids and obtained poly(ethylene terephthalate) (PET) which has a melting point of ca.270 °C. Thus, PET overcame the low melting points of the aliphatic polyesters and enabled the production of useful synthetic fibers. ICI licensed PET from CPA and DuPont obtained patent rights and proceeded to commercialize PET fiber in the USA. Other companies began to search for new monomers to produce polyesters outside the DuPont patents to enter into the fast growing polyester fiber market. Eastman Kodak Company developed a process for the reduction of dimethyl terephthalate (DMT) to 1,4-cyclohexanedimethanol (CHDM) and commercialized poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) as a competitive polyester fiber. This product demonstrates a basic difference in the R&D process between polyesters and polyolefins. In contrast to polyolefins, where new catalysts can lead to major backbone and property variations, polyesters require new monomers to yield new properties and products. Today new polyesters and copolyesters are entering the marketplace based on incorporation of new diols and diacids. Therefore the history of polyester advances is inextricably linked with the development of new monomers. Some recent examples will be discussed.



PET



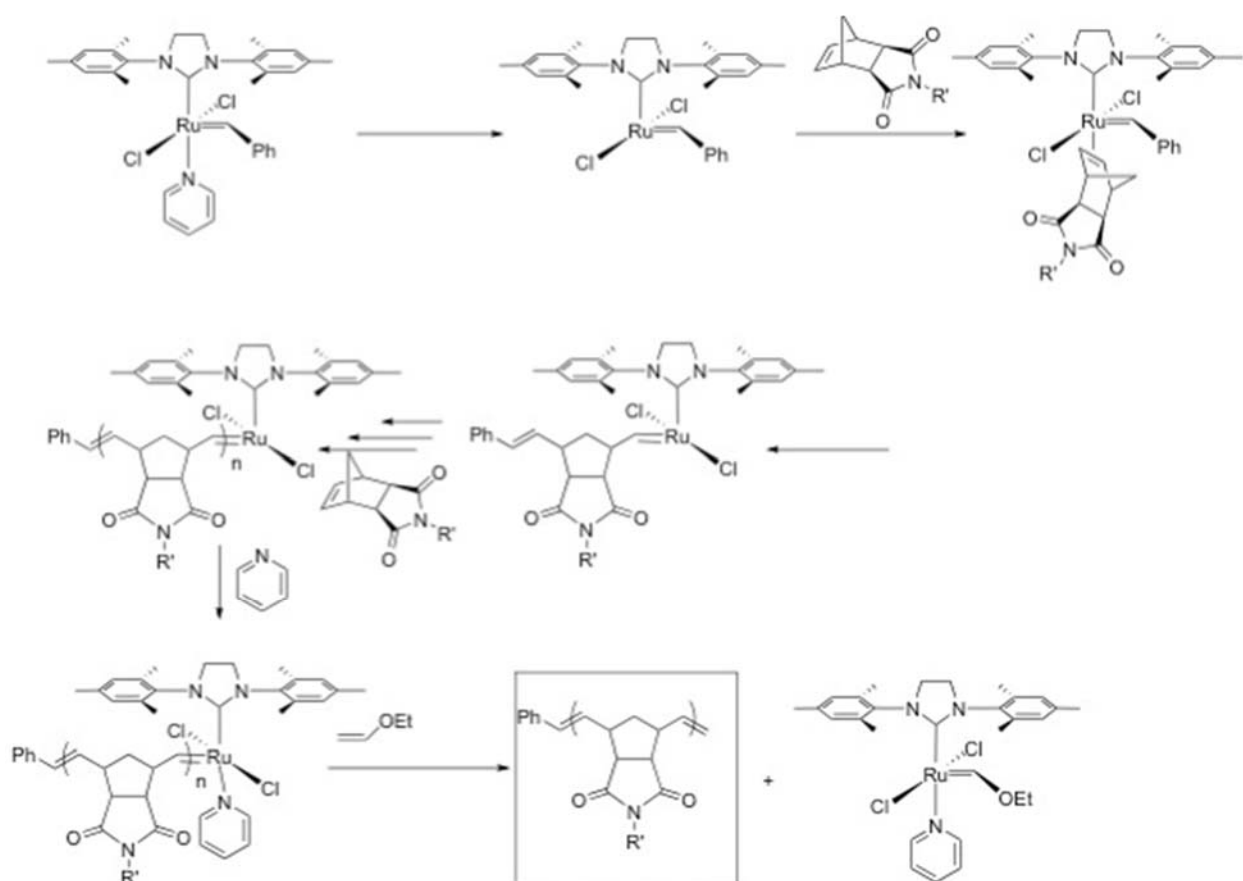
PCT

PET and PCT polyesters

POLY 593: Developments in living polymerization

Robert H. Grubbs, *rhg@caltech.edu*. Cal Tech 164-30, Pasadena, California, United States

Over the past 4+ decades, major advances have been made in the development of living polymerization reactions. Olefin metathesis was found to be living when initiated with well defined complexes and the method has grown into a method for the construction of polymers with predefined structures. The initial discoveries were with titanium based systems and now has expanded to the whole family of metathesis active complexes.



POLY 594: Polymer chemistry history: The development of modern photoresists

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Modern semiconductors are “printed” under water using 193nm light using a technology called Immersion Lithography. My presentation will focus on key innovations in photoresist materials and imaging mechanisms that led the industry to this point and have created such ubiquitous technology and impact. Polymer chemistry has been a key component that enabled continual advancement in semiconductors.



POLY 595: Pressure sensitive adhesives and tapes: From intuition to science

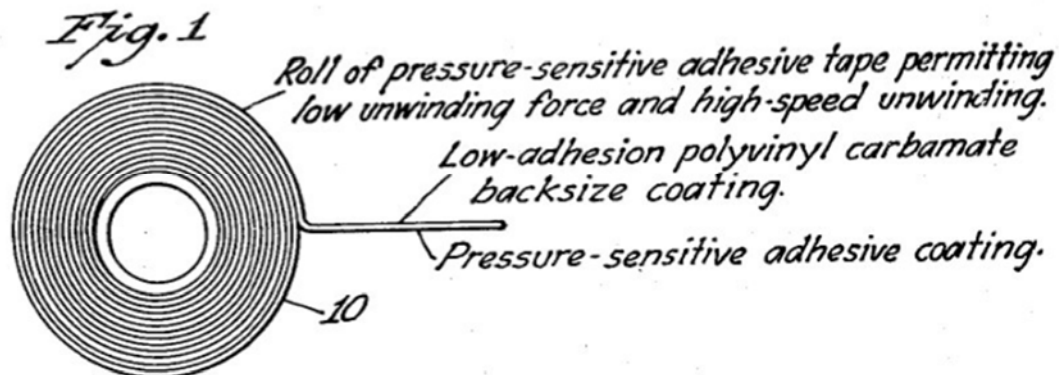
David Yarusso, daveyarusso@gmail.com. Yarusso Consulting, LLC, Shoreview, Minnesota, United States

We will look at some of the key milestones in the development of pressure sensitive adhesives and tapes and products made from them, beginning with crude formulations for medical plasters and tapes in the mid-1800s, progressing to the first industrial masking tapes in the 1920s, and then the explosion of products based on synthetic polymers including acrylates, block copolymers, and silicones. What began as intuition driven formulation using natural products is now a true area of materials science. In the 1950s, Carl Dahlquist was the first to identify the key mechanical properties necessary in all pressure sensitive adhesives and we now understand enough about these materials to design adhesives using fundamental polymer science principles. A full quantitative understanding of the interplay between surface interactions and mechanical properties in determining adhesive performance is still an area of active investigation, however. Some of the most important research results in the science of pressure sensitive adhesion will be reviewed.

Nov. 28, 1950

C. A. DAHLQUIST ET AL
LINERS AND ADHESIVE TAPES HAVING LOW ADHESION
POLYVINYL CARBAMATE COATINGS
Filed Sept. 7, 1946

2,532,011



POLY 596: Translating polymer science and engineering into practice: Air Force Materials Science and Technology

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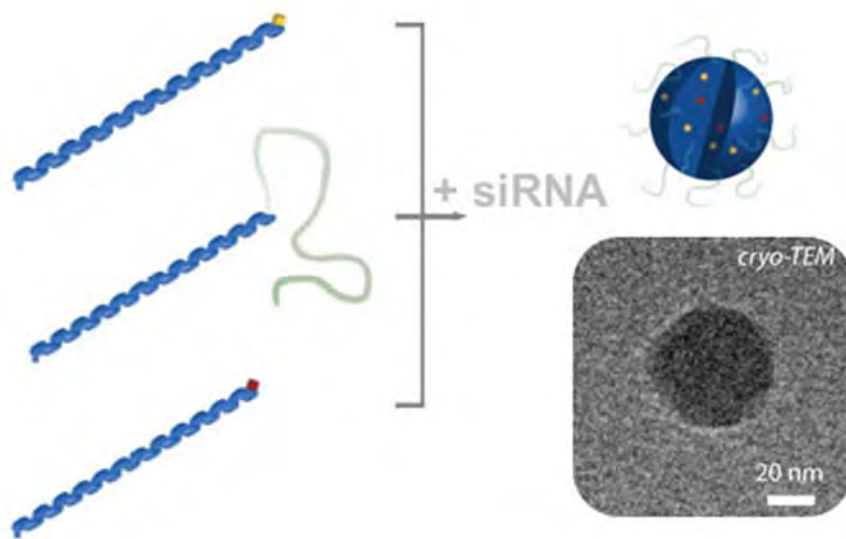
The DOD research laboratories are mission-driven entities combining competency-based scientists and engineers (practitioners) immersed in a application rich (capability) environment. The job of these practitioners is two-fold including a) to mine the best of the best from outside the defense department and to b) invent the future in thrusts where there is no commercial/economic pull. One such laboratory is the Air Force Research Laboratory, performing work across 40 core technical competencies. Efforts centered in the materials and manufacturing areas are nurtured in AFRL's Materials and Manufacturing Directorate. This talk will discuss what it is like to 'have a career' in such a place and on recent focus areas centered in polymer science and engineering. Current areas of focus include additive manufacturing, novel photonic and electronic materials, polymer matrix composites, and thin film coatings.



POLY 597: Designer polypeptides for cancer therapeutics and controlled mRNA delivery

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Synthetic polypeptides provide the basis for new biomacromolecules that can be modified to achieve a broad range of biologically relevant function. We have designed poly(propargyl-L-glutamate) (PPLG) synthetic polypeptides to which different molecules can be “clicked” to achieve dense brush polypeptide backbone structures. A unique aspect of these new amine-functionalized polypeptides is the ability to buffer, and in some cases, change solubility with degree of ionization, over biologically relevant pHs. These polymers are PPLG homopolymers and poly(ethylene glycol (PEG)-b-PPLG) block copolymers substituted with various amine moieties that range in pKa and hydrophobicity. These systems can be further functionalized to target specific cells, and make unique nanoscale drug carriers for systemic delivery in applications such as targeted cancer chemotherapy. A new set of oligopeptide amphiphiles designed to complex siRNA have been shown to be effective in the silencing of oncogenes and “helper” genes to oncogenic behavior in ovarian and non-small cell lung cancer. Recent investigations include a family of amine sidechain functional systems that can be optimized to co-deliver mRNA with its cap protein, eIF4E, to achieve multi-fold enhancements in mRNA translation and extended release periods in animals; similar approaches apply for the delivery of siRNA with the Ago2 protein. The impact of side chain structure on delivery and RNA translation is significant, and indicates the power of polymer chemistry, and the ability to manipulate these sequences to achieve high levels of efficacy

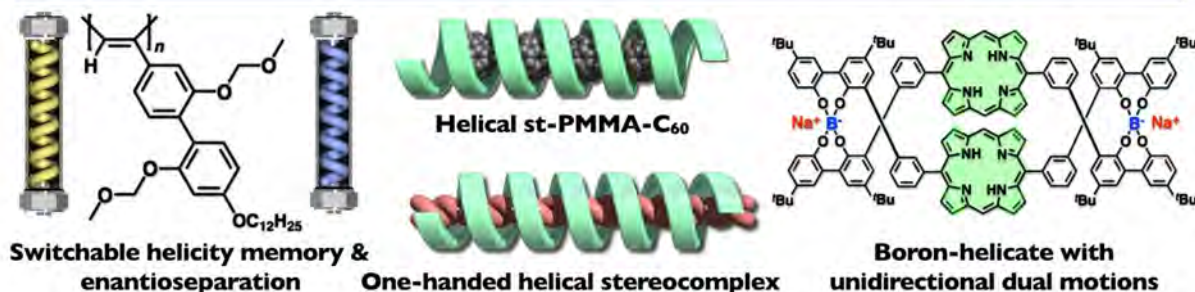
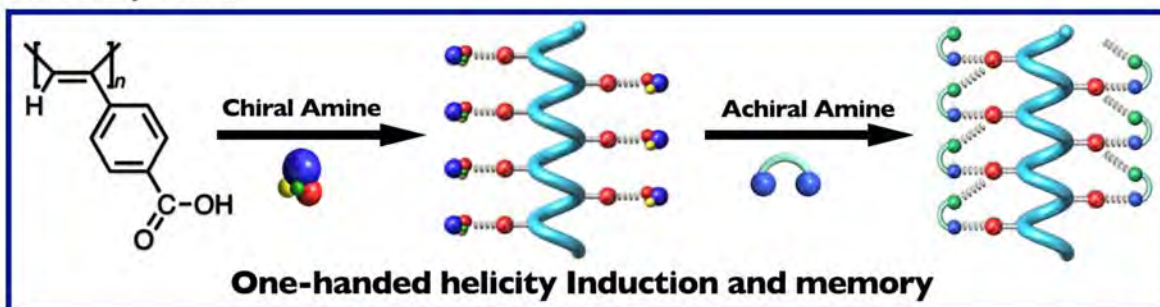
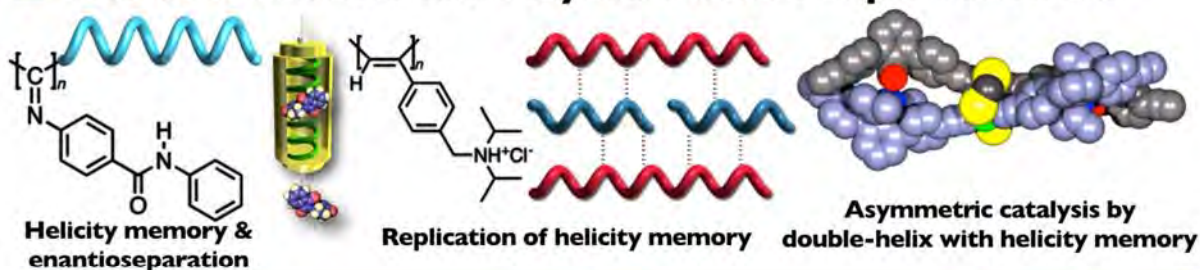


POLY 598: Biomimetic helical foldamers and polymers: Synthesis, structures and functions

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The helix is a central structural motif for biological polymers playing a key role in their sophisticated functions. We show unique macromolecules that fold into a preferred-handed helical conformation induced by chiral stimuli followed by memory of the helical chirality, which provides useful chiral materials for separating enantiomers in a switchable way. The helicity induction and memory strategy has a remarkable advantage from a practical viewpoint such that a preferred-handed helicity can be induced in commodity plastics, such as syndiotactic poly(methyl methacrylate) (st-PMMA). A series of double helices composed of different components and sequences that exhibit specific functions, such as chiral recognition, enantioselective asymmetric catalysis and anisotropic spring-like motion are also described.

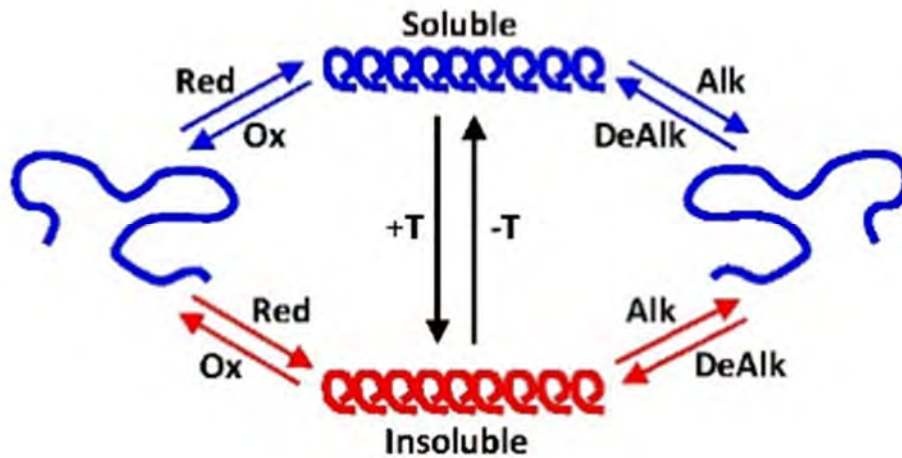
Helical Foldamers and Polymers with Unique Functions



POLY 599: Multifunctional and stimuli responsive polypeptides

Timothy J. Deming, demingt@seas.ucla.edu. Bioengineering Dept, Univ of California, Los Angeles, California, United States

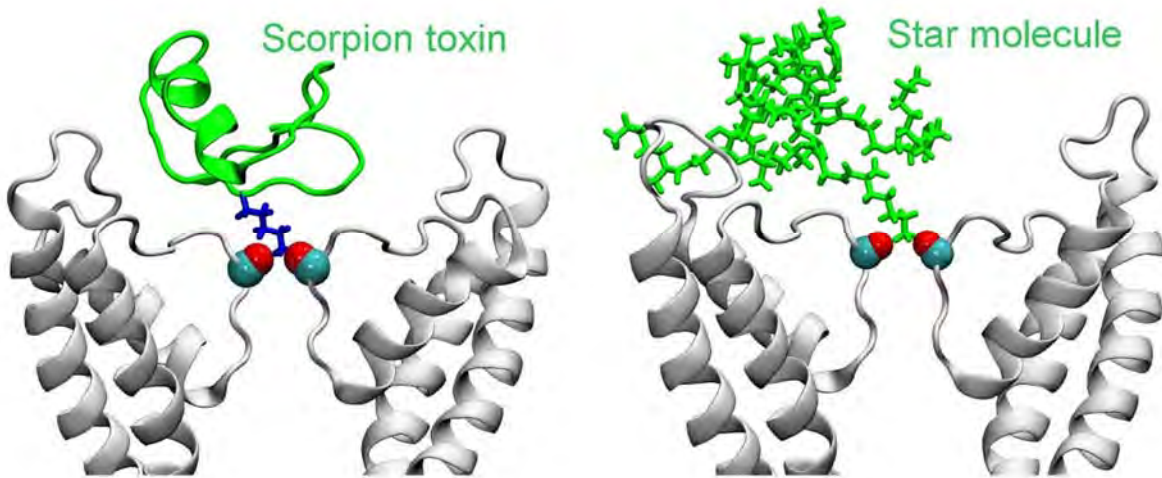
Our lab has pursued development of synthetic methods to allow incorporation of unprecedented levels of functionality into polypeptide materials. We report on the design and properties of stimuli responsive polypeptide motifs that are able to respond differently to different individual stimuli, such as redox, temperature, or enzymes. These materials allow multimodal switching of polypeptide properties to obtain desirable features, such as coupled responses to multiple external inputs. The reversible, multi-responsive nature of these polypeptides makes them particularly attractive as components in molecular devices or nanoscale assemblies capable of sequential, or triggered, responses to different stimuli, akin to switches capable of performing Boolean-like operations. The incorporation of these motifs into self-assembled materials such as hydrogels will be described.



POLY 600: Dendrimer peptidomimics and polymers for drug and vaccine delivery

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Peptidomimetics are an important class of therapeutic compounds that functions as a peptide therapeutic but with stability towards proteolysis by peptidase and predetermined structural constraints to avoid non-selective binding. In this work we used peptidomimetic compounds to bind to certain regions of ion channels that showed inhibition of selective ion channels with significantly greater potency than commercially available drugs. The peptidomimetics were de novo designed using the MD computational method, synthesized and tested experimentally in animal ion channels. We present a novel antigen delivery system utilizing self-adjuvanting dendrimer. For dendrimer construction, we applied acrylate based polymer, which is known to be easy to synthesize and have little or no toxicity. Self-assembly of these dendritic structures into nanoparticles allowed proper presentation of antigen (e. g. required α -helix conformation) to immune system and elucidated a strong immune response in mouse model.



Mimicking the action of scorpion venom peptides using the four peptidomimetic

POLY 601: Marshalling methods to make soft materials: Design and synthesis of polymer-based materials

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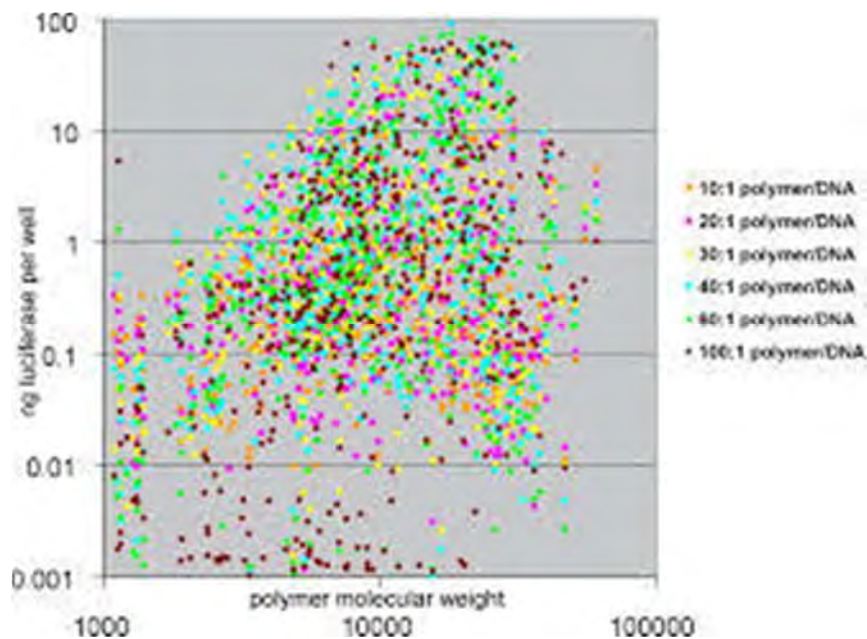
The drive to design functional soft materials is often accompanied by significant synthetic challenges. It is much easier to propose a concept than to actualize it; this is even truer with the vast design space of polymer-based materials. We have investigated several classes of polymers, each with their own synthetic challenges, in efforts to relate structure from the monomer level to structure at the meso-scale to function at larger length scales. For example, we have designed a range of synthetic systems that are designed to assemble in water into smaller micellar aggregates at low temperatures and larger vesicles at higher temperatures. Controlling structure at the block level enables control over the rate and nature of structural evolution during the response and has facilitated the design of responsive hydrogels. The design of these and other systems, potentially including degradable polyacetal block copolymers, metal-functionalized polymers and conjugated polymers for photovoltaic applications, and our efforts to better understand the behavior of the resulting materials will be discussed.



POLY 602: Combinatorial library approach to biomaterials

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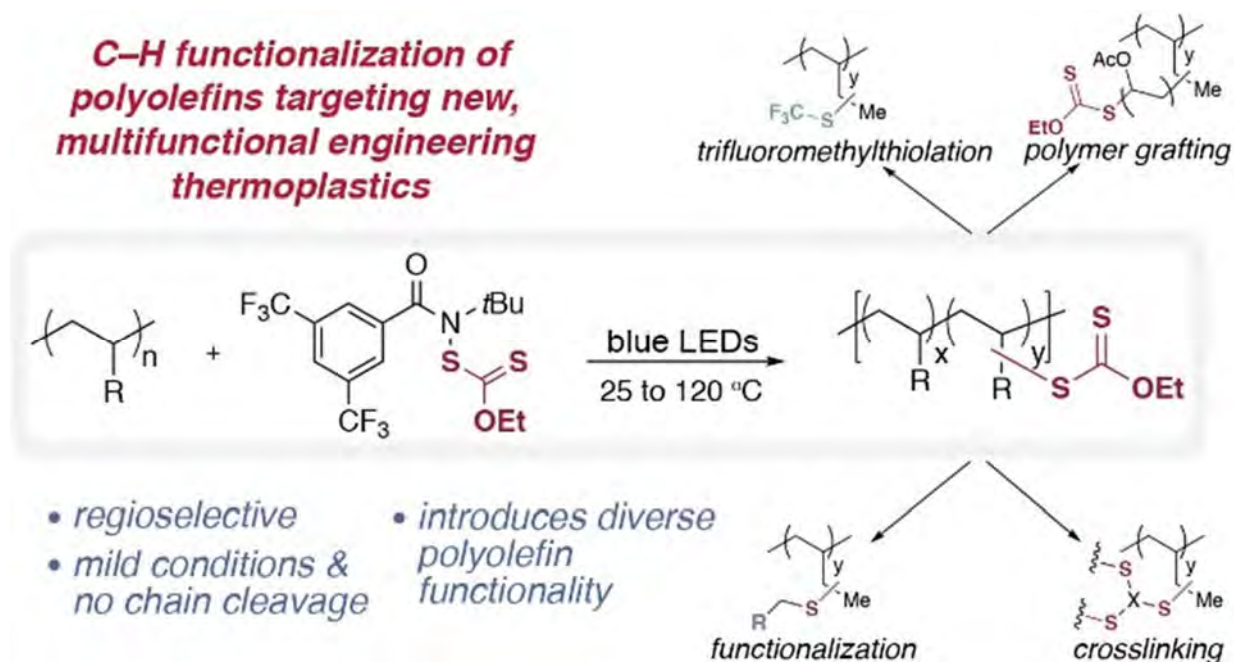
We have used combinatorial approaches to create polymer and lipid libraries to address a number of problems. These include 1. polyBaminoester libraries that have been used for a range of products ranging from gene therapy reagents to hair care products. 2. Lipid libraries to create lipid nanoparticles to deliver siRna and 3. Libraries of Alginate derivatives to create a whole new approach to a super biocompatible artificial pancreas.



POLY 603: Regioselective C–H xanthylation as a platform for polyolefin functionalization

Jill Williamson, jillwill@ad.unc.edu, William Czaplowski, Erik J. Alexanian, Frank A. Leibfarth. Chemistry, UNC Chapel Hill, Chapel Hill, North Carolina, United States

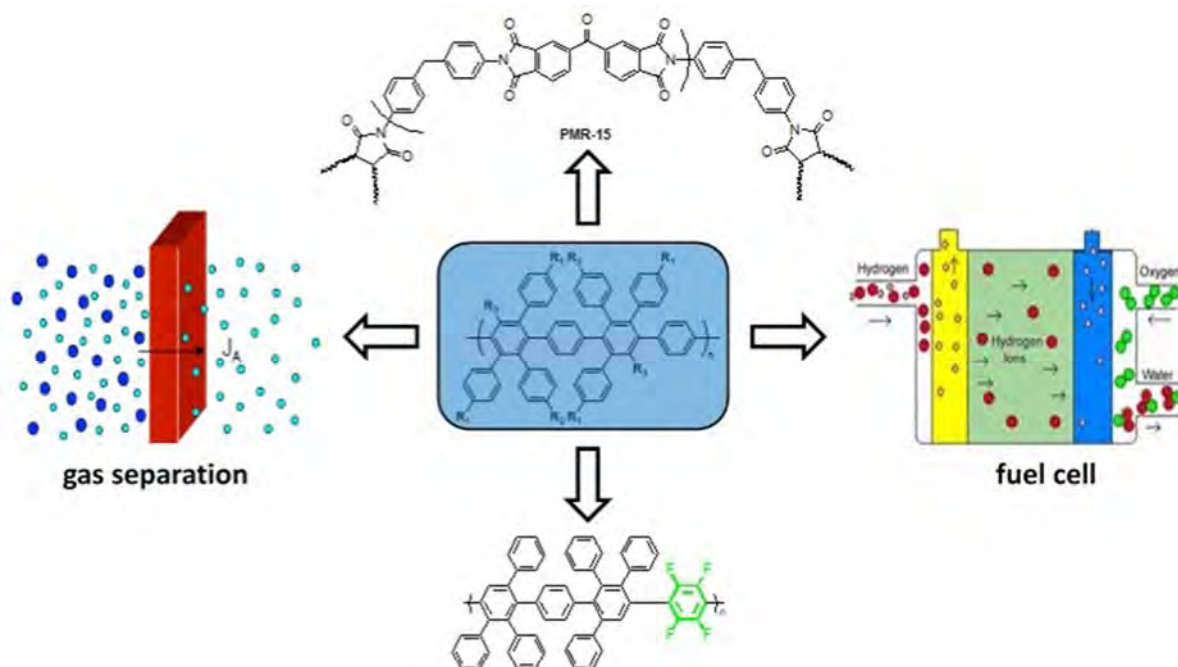
The addition of polar functionality to branched polyolefins has been a long-standing challenge in the field of polymer science due to their potential as next-generation, lightweight engineering thermoplastics. Copolymerization approaches have not succeeded thus far in developing catalysts with the sufficient activity necessary for scalable acquisition of such materials. Post-polymerization modification is an attractive approach due to its utilization of low-cost and widely available starting materials, but current industrial methods lead to a dramatic decrease in molecular weight and desirable mechanical properties of the final material. While few methods have been reported to functionalize branched polyolefins chemoselectively, all rely on precious metal catalysts and remain limited to a particular functional group. Our approach utilizes a metal-free method for radical-mediated, regioselective C–H xanthylation, resulting in the functionalization of branched polyolefins without coincident polymer chain scission. This method enables a tunable degree of polymer functionalization and capitalizes on the versatility of the xanthate functional group to unlock a wide array of C–H transformations previously inaccessible on branched polyolefins. We report a general approach to diversify polyolefin properties through regioselective aliphatic C–H xanthylation amenable to high molecular weight and commercial polyolefins.



POLY 604: Polyarylene synthesis, characterization, and optimization for high performance applications

Stephen M. Budy, *SBudy@email.smu.edu*, David Y. Son. Chemistry, Southern Methodist University, Dallas, Texas, United States

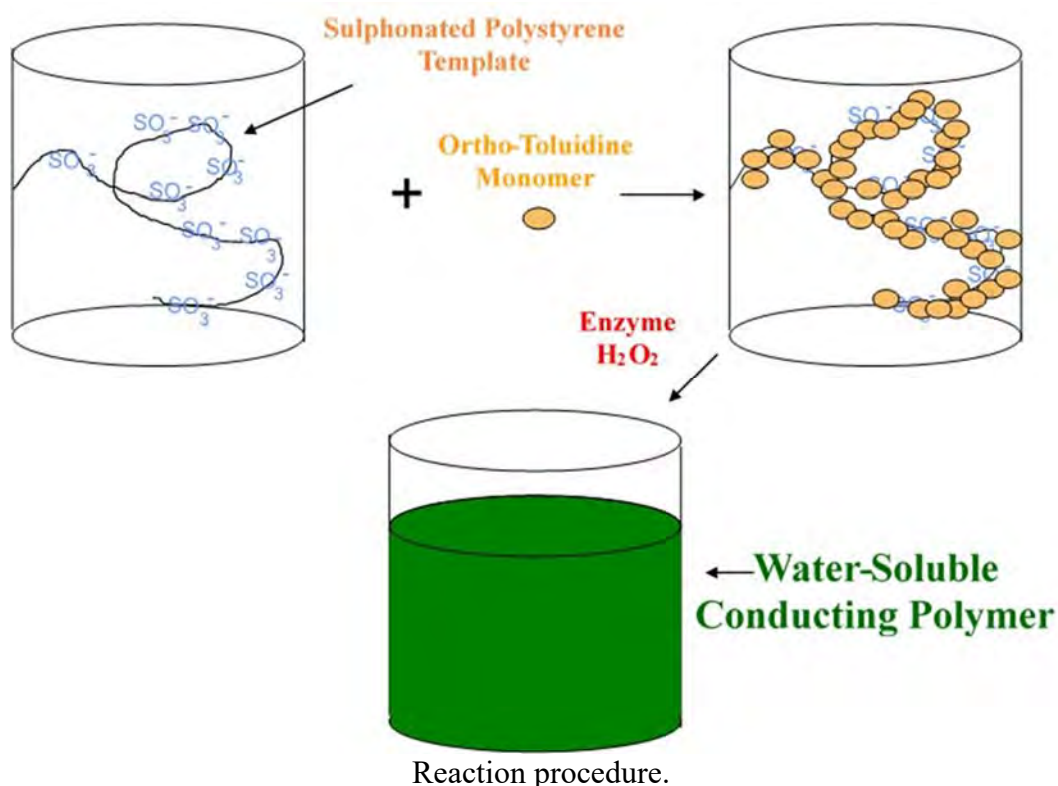
A series of Diels–Alder polyarylene polymers were synthesized via traditional oil bath and microwave-assisted step-growth polymerization. Optimization of the reaction of bistetracyclone with 1,4-diethynylbenzene using a variety of solvents, concentration, and time was achieved. The polyarylene polymers were characterized by ^1H , ^{13}C , and ^{19}F NMR spectroscopy, ATR-FTIR spectroscopy, TGA, DSC, DMA, and GPC. Diphenyl ether (Ph_2O) worked well for oil bath synthesis whereas polar solvents (e.g., tetrahydrofuran and nitrobenzene) worked well for microwave-assisted polymerization. Thermal analysis showed little change in the series of polymers for onset of decomposition ($T_d = 550\text{ }^\circ\text{C}$). Molecular weights were monitored over time affording well over 100 kg/mol and dispersities more difficult to control in the range 2.0 to 20.1. Applications will be discussed including proton exchange membrane fuel cells, gas separation membranes, coatings, semi-fluorinated optics, and polyimide resins.



POLY 605: Synthesis and evaluations of substituted polyaniline with high conjugation and conductivity

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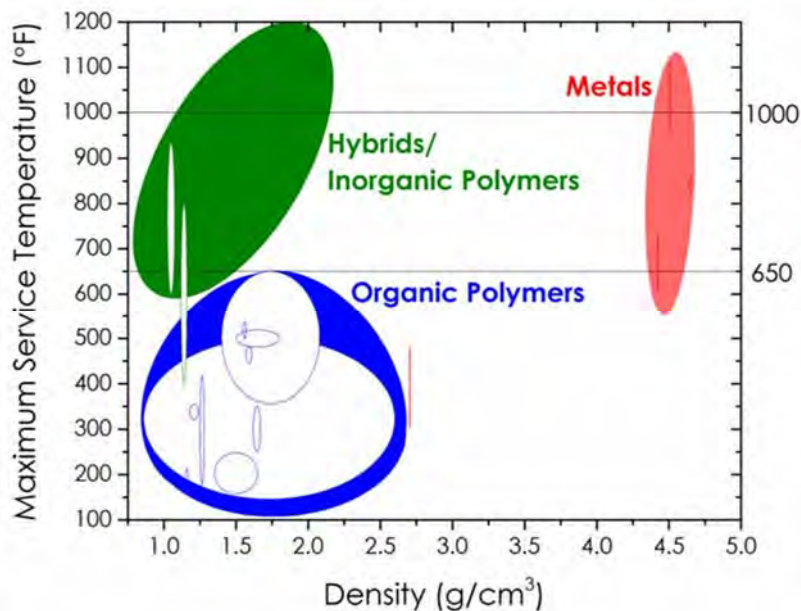
Enzymatic mediated synthesis of water-soluble conducting polymer of substituted aniline complexed with poly(sodium 4-styrenesulfonate) is reported. This polyelectrolyte assisted horseradish peroxidase catalyzed polymerization of, e.g., ortho-toluidine provides a procedure to synthesize water-soluble, highly conductive polymers under acidic conditions. The UV-Vis, FTIR, thin film conductivity, molecular weight assessment and modeling studies of the polymer complex show the existence of a thermally stable and electroactive polymer with large conjugation that was not present in similar conductive polymers (e.g. polyaniline). Furthermore, the use of water-soluble templates provide a unique combination of properties such as high conductivity and processability. Nevertheless, the same process was also implemented for the polymerization of 2,6-xylydine: however, the synthesis of highly ordered polymers with high conductivity, did not occur, suggesting a much more complex stereo-specificity of the enzymatic polymerization. Modeling studies were implemented to delve into the chemistry of these reactions. Finally, the conductive poly(ortho-toluidine) has been tested as chemiresistive sensors for the detection of humidity. Further improvements for electrical conductivity of the poly-ortho-toluidine using carbon nanotubes are being investigated.



POLY 606: Development of high temperature inorganic-organic polymers and hybrids

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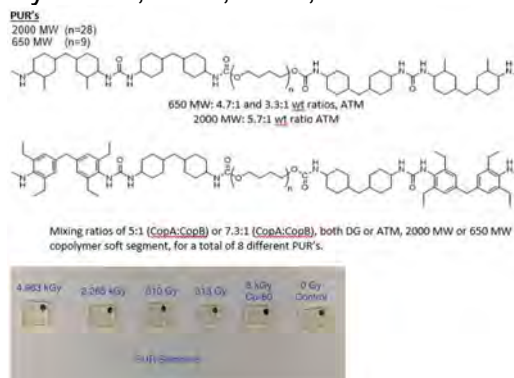
The current state-of-the-art high temperature polymer matrix composites (PMCs) typically cannot withstand temperatures above 300°C (>570°F) in air for extended periods of time. Much of this is due to the limitations of matrix resin, which is reaching its fundamental chemical and physical limit. As a result PMCs are often replaced with either metals or ceramic matrix composites (CMCs) for higher temperature applications, which are typically much heavier than PMCs and can be more expensive. Ideally a low-density material that can address the temperature capability gap between PMCs and CMCs, as shown in the Ashby plot figure, would lead to numerous benefits in reducing the weight of aircraft. The focus of this work is on developing, designing and modifying inorganic polymers and preceramic polymers to be used alone as a matrix resin or with thermosetting resins such as epoxy and benzoxazines to create inorganic-organic hybrids. For the design and synthesis of inorganic polymers, the discussion will be on the development of polymers that contain a high concentration of boron. The development of hybrids through the use of a preceramic polymer, polysilazane, in combination with epoxy and benzoxazines will also be discussed. The cross-link chemistry of these networked systems can be tailored by controlling various processing parameters leading to inorganic/organic hybrids that could be used for higher temperatures as well as bonding organic polymers to ceramics. Techniques to incorporate the preceramic polymer into the crosslinked network of the organic thermoset along with the mechanical properties and thermal stability of these inorganic-organic hybrids will be presented.



POLY 607: Fast neutron irradiation of polymeric materials

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Methods for evaluating dose dependent changes in polymeric materials resulting from neutron irradiation are useful for establishing the exposure history of polymers. While many polymers have been evaluated under varying types of radiation, polyurethanes (PUR's) and polysiloxanes have not been well documented in response to low dose fast neutron radiation. These polymers have many established applications in the medical, electrical, and defense industries where the polymer could be exposed to neutron radiation sources (i.e. medical isotope production, broad space, and weapon-based applications). Our group seeks to identify mechanisms of radiological damage to PUR's and polysiloxanes resulting from exposure to fast neutrons. PUR elastomer surrogates of Halthane-88 were synthesized with varied glycol linkers followed by curing with an aromatic or aliphatic bis(amine) to create the PUR. Polydimethylsiloxane (PDMS) and polydiphenyl-polydimethylsiloxane have also been synthesized for these studies. The samples were irradiated using a 16.5 MeV PETtrace cyclotron facility and in the pneumatic tube irradiation position at the University of Missouri Research Reactor Facility. At the cyclotron facility polymer samples were irradiated in a low dose regime using fast neutrons produced from the reaction $^{18}\text{O}(p,n)^{18}\text{F}$, with the final dose ranging between 70 and 5500 Gy. The neutron dosimetry for the cyclotron irradiation was determined by unfolding the neutron spectrum using the PNNL-STAY'SL program. The differences in the aromaticity and glycol linkers in the PUR surrogates are expected to promote processes of chain scissions or crosslinking within the polymers, which will be reported through analysis by FT-IR, DSC, TMA, and GC-MS.

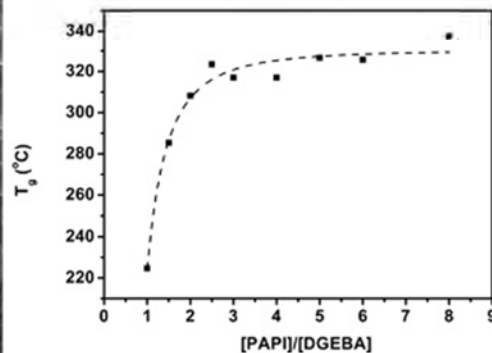
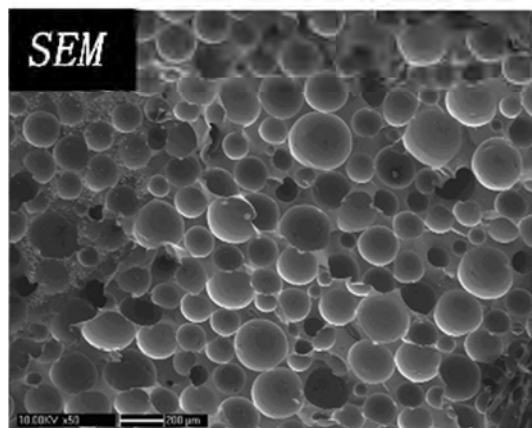
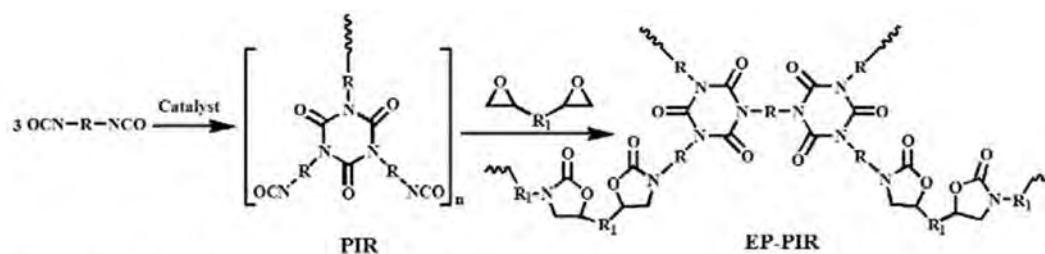


This picture shows one of the polyurethane samples after irradiation at the respective doses. It was synthesized by degassing the two copolymer segments under vacuum (a 2000 MW PTMEG containing isocyanate and an aromatic bisamine) and mixing in a 5:1 weight ratio of copolymer A to copolymer B.

POLY 608: Preparation and properties of highly thermostable polyisocyanurate foams modified with epoxy resin

Keping Chen, *kepingchen@caep.cn*, *chunrong tian*. Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, China

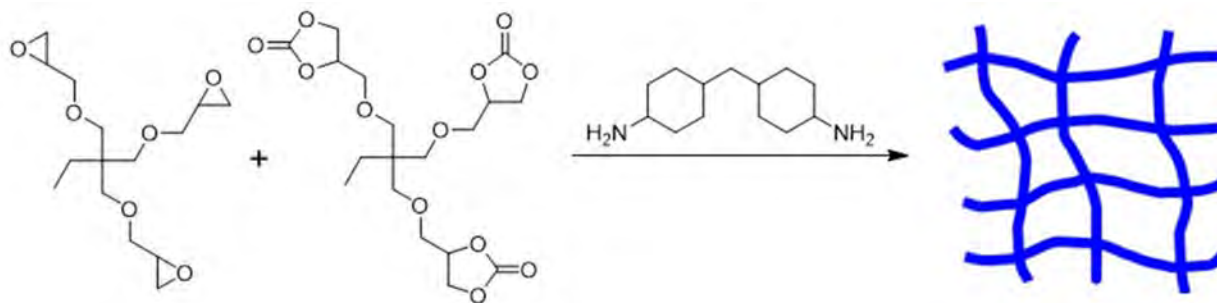
A series of epoxy resin modified polyisocyanurate (EP-PIR) foams with oxazolidone (OX) ring and isocyanurate (IS) ring have been successfully prepared by the reaction of polymethylene polyphenylene isocyanate (PAPI) and diglycidyl ether of bisphenol-A (DGEBA). Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) are performed to investigate the influence of curing temperature on the chemical structure of EP-PIR foams. The glass transition temperatures of EP-PIR foam are in the range of 224-337 °C. The influence of the mole ratio of [PAPI]/[DGEBA] on the mechanical property, thermal stability and flame retardation has also been studied. The results indicated that the excellent thermostability of EP-PIR foams was due to the abundant highly thermostable isocyanurate ring and oxazolidone ring. UL94 results revealed that the foams with [PAPI]/[DGEBA] ratio above 2.5 could reach V-0 classification. With increasing the stoichiometry of [PAPI]/[DGEBA], the limiting oxygen index values increased linearly from 24.5 to 30.0 vol %. Scanning electron microscopy images of burned foams illustrated the flame-retardant mechanism was due to the excellent charring ability. Cone calorimeter tests showed that the peaks of heat release rate were always as low as 266.5 kW/m². Moreover, highly thermostable isocyanurate ring played an important role in the suppression of smoke emission.



POLY 609: Adhesive and mechanical properties of hybrid polyhydroxyurethane-epoxy network polymers

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Polyhydroxyurethanes are an environmentally friendly non-isocyanate based alternative to more traditional polyurethanes. They are formed from the reaction between multifunctional amines and cyclic carbonate (CC) monomers. For practical applications, cyclic carbonate resins can be difficult to formulate as they are often very viscous or crystalline solids and require the use of solvents or reactive diluents to form films or bulk polymer. CC resins can be blended with epoxy resins to produce hybrid network structures wherein the functionality and cross-link density of the network can be tuned depending on the feed ratio of CC and epoxy resins. In this work, trimethoylpropane triglycidyl ether (TMPTGE) was converted to the trifunctional CC (TMPTGECC). TMPTGE and TMPTGECC were combined at various ratios and cured with bis-(p-aminocyclohexyl) methane (PACM). The mechanical behavior of the network polymers was characterized by dynamic mechanical analysis (DMA) and tensile testing with digital image correlation. The adhesive properties of the materials were also characterized with single-lap-joint testing of grit blasted aluminum substrates at room temperature. It was found that with increasing levels of TMPTGECC, M_c increased along with simultaneous increases in Young's modulus, yield stress, and toughness. It was also observed that the peel strength and displacement at complete failure also increased with increasing TMPTGECC content.

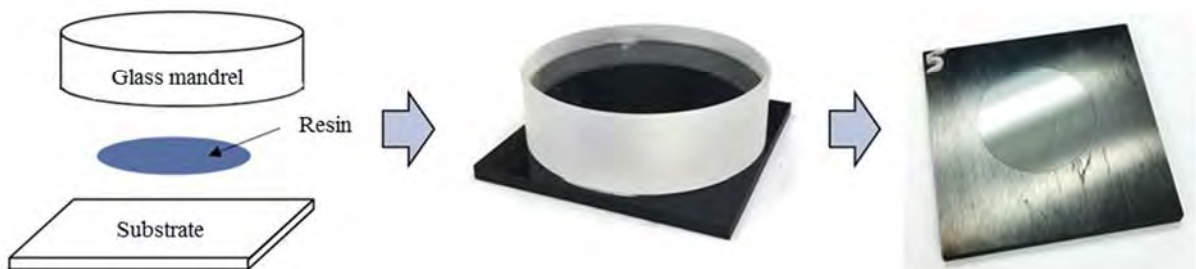


POLY 610: Hygroscopic, thermal, and radiation stability of high precision replicated epoxy composite mirrors

Hyun Kim¹, hyun.i.kim@aero.org, Geena Ferrell², rafael zaldivar³. (1) Surface Science and Engineering, The Aerospace Corp, El Segundo, California, United States (2) Materials Science, The Aerospace Corp, El Segundo, California, United States (3) Material Science, The Aerospace Corp, El Segundo, California, United States

Replicated lightweight composite mirrors are gaining increasing attention for space applications due to potential weight savings, cost reductions, and faster manufacturing times over traditional glass mirrors. However, nanometer-scale dimensional stability remains one of the critical issues for these resin-based high precision optics. Composite mirrors with a surface figure error (SFE) better than 1/20 were manufactured at a coupon level using a UV cured replicated layer (RL). Subsequently, these high precision mirrors were exposed to varying hygrothermal and radiation environments to observe their impacts on SFE. Compared to a typical amine-cured system, UV-cured RL showed much greater dimensional stability, which was corroborated by less moisture absorption. The moisture absorption of the UV-cured epoxy was shown to be inversely proportional to the cure state as determined by FTIR, which could be tailored by a secondary cure processing. The resulting degree of cure was shown to impact the thermal stability as well. RLs that underwent secondary cure steps showed greater dimensional stability up to 145 °C. Additionally, replicated mirrors were exposed to a varying degree of gamma radiation using ⁶⁰Co ranging from 0 to 50 Mrad. Amine-cured RLs showed significant increases in SFE while the UV-cured RLs showed negligible changes up to 50 Mrad. DMA, TGA, and GC-MS showed that the observed SFE changes are correlated with radiation-induced scission and fragmentation of the polymer backbone. Based on the environmental stability observed here, the UV-cured resin system offers a promising solution for future development of space composite optics.

Replicated Composite Mirror Processing

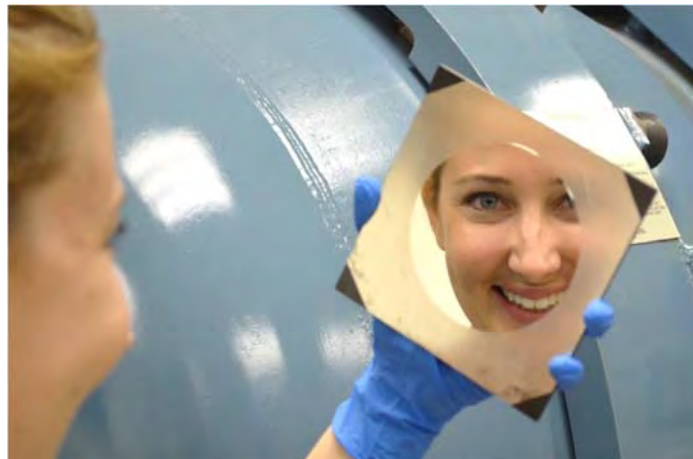


A schematic illustration of composite mirror fabrication. An uncured resin is sandwiched between a glass mandrel and a composite substrate. The resin is allowed to "replicate" the mandrel surface and then cure. Subsequently the replicated mirror is released from the mandrel. The quality and the stability of the replicated mirror is dependent on the replicating resin material selection and processing conditions.

POLY 611: Underlying causes of quality and dimensional stability in high-precision replicated composite optics

Geena Ferrelli, *geena.l.ferrelli@aero.org*, Hyun Kim, Rafael Zaldivar. *The Aerospace Corporation, El Segundo, California, United States*

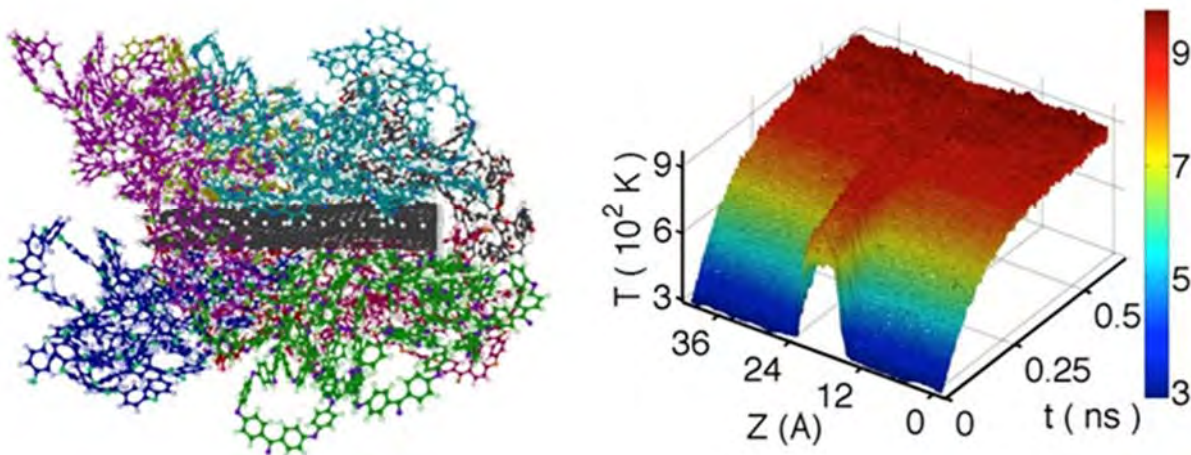
As next-generation space-based telescopes require larger mirrors, replicated composite optics are gaining increased attention due to limitations in the scalability of conventional glass optics. Replication, in this instance, is the process of transferring an optical surface to a thin polymeric film supported by a composite substrate, offering potential weight savings, cost reductions, and faster manufacturing times. For this application, these optical surfaces require both dimensional precision (RMS < 32nm) and dimensional stability in a variety of environments. In previous work, high quality and stability replications have been fabricated with an off-the-shelf UV-cured epoxy resin. The research indicates the behavior is critically dependent on replicating resin material and processing, however, the fundamental properties governing the behavior are not well understood. In this paper, a cycloaliphatic epoxy will be photopolymerized with varying amounts of photoinitiator, modifying the kinetic, mechanical, hygroscopic, and thermal behavior of the replicating resin. Polymer curing behavior such as shrinkage and residual stress will be evaluated and correlated to the quality of replications fabricated with the various resin formulations. Other properties, such as moisture absorption and glass transition temperature, are related to stability. By fabricating replications with a range of mechanical, thermal, and kinetic properties, the dominating causes of quality and stability can be understood.



POLY 612: PEEK-graphene nanocomposites: Experimental properties and atomistic modeling

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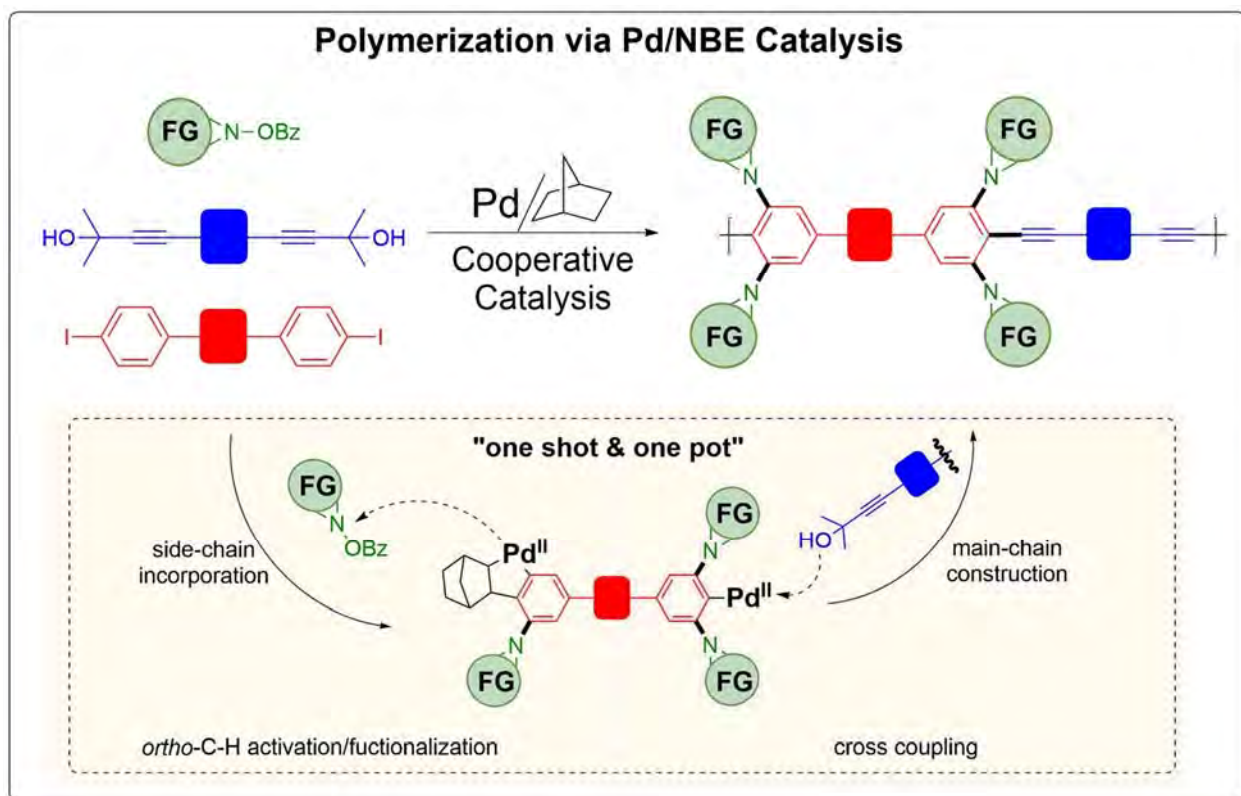
Polyetheretherketone is a widely used engineering polymer that is especially suitable for high-temperature applications and graphene is a two-dimensional allotrope of carbon that has been studied extensively over the past decade because of its exceptional mechanical, electrical, and thermal properties. The addition of graphene into polymers has the potential to improve various properties. Here, PEEK-graphene composites have been studied experimentally and shown to exhibit microwave absorption properties that result in melting and thermal energy transfer from the embedded graphene to the PEEK polymer. This allows these composites to be used as a high temperature adhesive, which can be activated by microwave radiation. In this system, microwave absorption by the graphene results in local composite heating, since the PEEK polymer alone does not absorb microwaves. Molecular dynamics simulations of the system have been used to understand the molecular mechanism of energy transfer. In these simulations, we explore the effect of the number of graphene layers on the transfer of energy to the polymer and specifically look at how the orientation of the PEEK molecules to the graphene plays a role in heat transfer. This work provides insight for designing composites for improved heat conduction and absorptive processes, such as microwave absorption and heating.



POLY 613: Polymerization via Pd/norbornene cooperative catalysis

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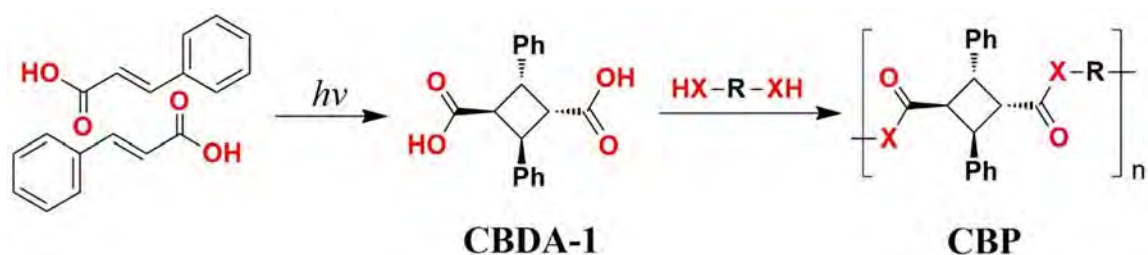
The first example of palladium/norbornene cooperatively catalyzed polymerization is reported. It simplifies synthesis of functional aromatic polymers including conjugated polymers. Specifically, a multicomponent A₂B₂C-type polymerization is developed using Catellani-type *ortho*-amination/*ipso*-alkynylation reaction for preparing various amine-functionalized arylacetylene-containing polymers. Within a single catalytic cycle, the functional amine side-chains are site-selectively installed *in situ* during the polymerization process, which represents a major difference from conventional cross-coupling polymerizations and multicomponent polymerizations.



POLY 614: Construction of cyclobutane-containing polymer (CBP) by using [2+2] photocycloaddition

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Cyclobutane-containing polymers (CBPs) are a type of polymers bearing cyclobutane building blocks. Cyclobutane represents a unique building block in polymers due to the partially conformational freedom of the four-membered ring. It offers a semi-rigid and semi-flexible property, which is different from those well-known flexible aliphatic or rigid aromatic building blocks. CBPs can be obtained by [2+2] photopolymerization of multimers containing two or more carbon-carbon double bonds, or by generating cyclobutane-based monomers (e.g., CBDA-1 shown below) through olefin photodimerization, which further polymerizes to yield CBPs by condensation. In this presentation, we will show that a variety of CBPs, for example poly- α -truxillates, were synthesized by condensation between cyclobutane-containing diacids (CBDAs) and different linkers such as ethylene glycol. The structures of the poly- α -truxillates were characterized by NMR, IR, and HRMS etc. Powder X-ray diffraction patterns of the poly- α -truxillates showed that they are semi-crystalline materials. Despite ring strain of cyclobutane, preliminary tests showed that the PCBs have good thermal, chemical, and photochemical stabilities.



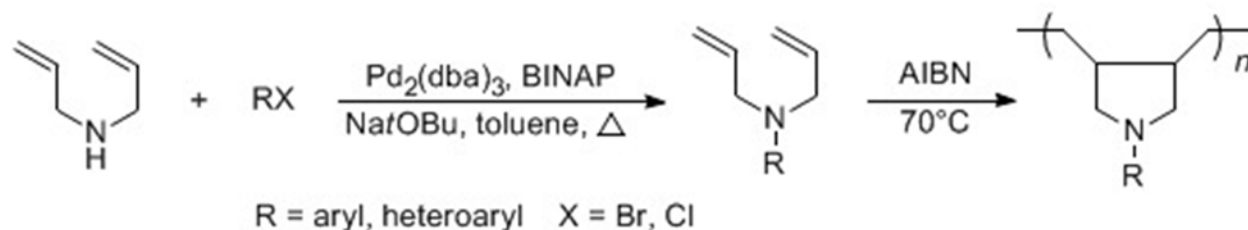
POLY 615: Cyclopolymerization of *N*-aryl substituted diallylamines

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Since cyclopolymerization mechanism of diallyl quaternary ammonium salts in aqueous media was introduced by Butler and coworkers, diallylamine polymers have received considerable attention for possible industrial applications ranging from the use in water treatment to papermaking, textiles, pharmaceuticals, coatings and adhesives. Most of their attempt to polymerize diallylamine derivatives have been carried out in aqueous solution with inorganic acid. In this paper, we report the synthesis of a series of *N*-aryl substituted diallylamine and polymerization of them in neat conditions. We also have synthesized model compounds having five and six member rings and investigated the cyclic structure of poly(*N,N*-diallylamino-2-pyrimidine) based on the NMR spectra.

Diallylamine monomers bearing phenyl, 2-pyridinyl, 4-pyridinyl, 2-pyrimidinyl, and benzyl group were prepared by Buchwald-Hartwig coupling reaction or other suitable synthetic procedures. The bulk polymerization of a series of *N*-substituted diallylamine monomers were carried out using AIBN at 70 degree C. While the aromatic ring directly substituted diallylamine monomers exhibited the ability of polymerization, *N*-benzylallylamine didn't polymerize substantially under this reaction condition. All the polymers are soluble to many organic solvents but insoluble to neutral water.

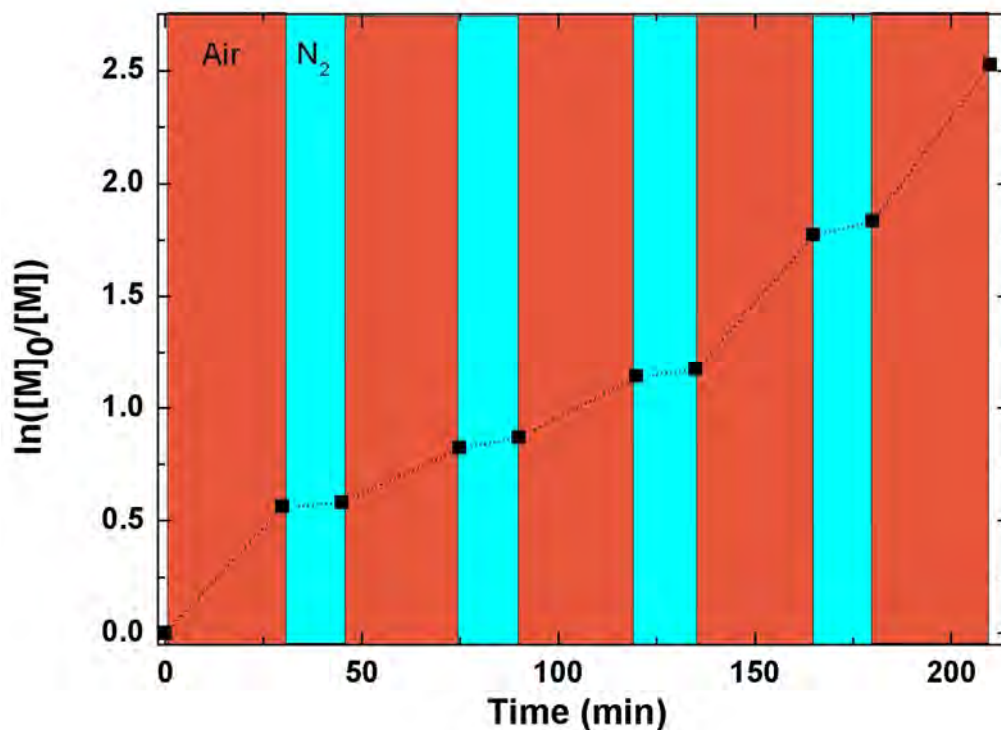
Although the cyclic diallylamine polymer structure was initially believed to be a six membered ring from the thermodynamic stand point, the most of the cases except the monomer possessing substituents at β -carbon have been found to be a five-membered ring because of the kinetic preference. To confirm the structure of the obtained polymers, the model compounds having a five and a six-membered ring were synthesized. Compared with $^1\text{H-NMR}$ spectra of these model compounds, we conclude that poly(*N,N*-diallylamino-2-pyrimidine) has exclusively five member ring cyclic structure with cis and trans configuration.



POLY 616: Borane chemistry in polymer synthesis

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Borane chemistry is fruitful in radical organic chemistry, and it is extending to polymer synthesis now. Triethylborane is an efficient radical initiator at ambient temperature or even below at $-78\text{ }^{\circ}\text{C}$, and it was successfully adopted into controlled radical polymerization at ambient atmosphere and temperature. Oxygen molecule was used to initiate the controlled radical polymerization as well as to regulate the whole process "on"/"off" with air. N-Heterocyclic carbene was further used to stabilize boryl radical, which could involve in lots of radical transformations. Herein, N-Heterocyclic carbene borane efficiently reduced and modified the chain end fidelity of polymers synthesized from RAFT and ATRP.

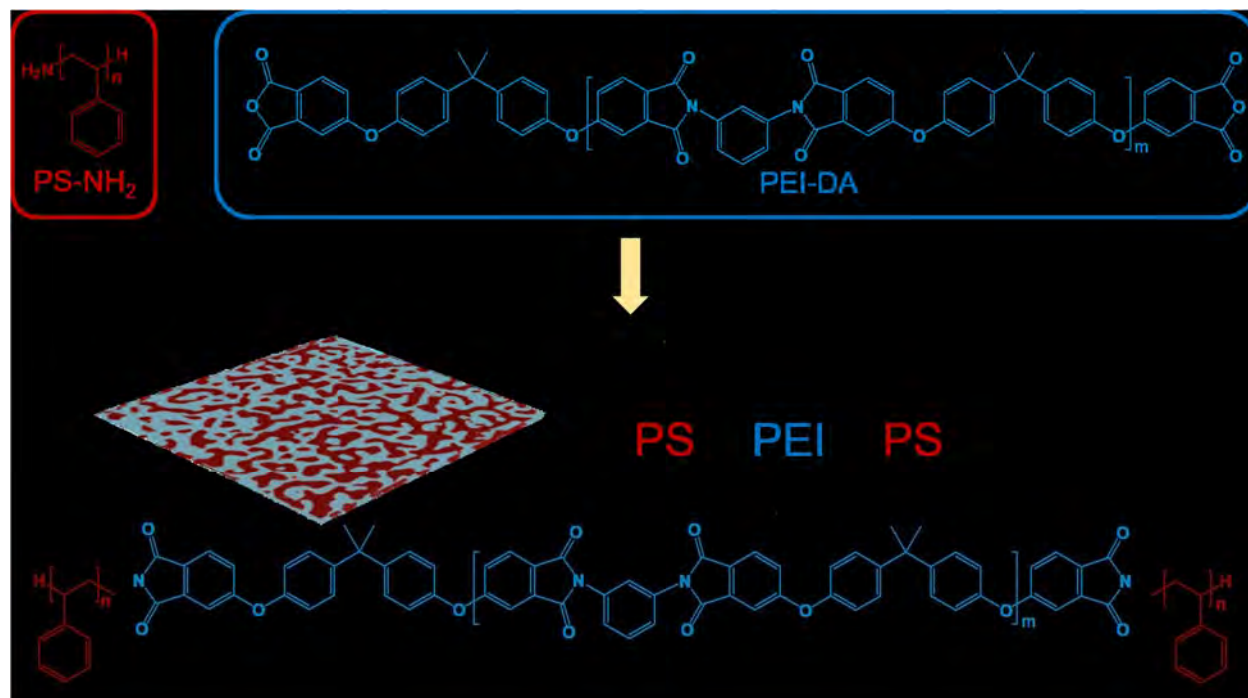


POLY 617: Telechelic polyetherimides and their block copolymers

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Solution-processable telechelic polyetherimides (PEIs) with ureido-pyrimidinone (UPy) end groups were prepared by incorporating monoisocyanato 6-methylisocytosine into amine-terminated PEI oligomers. After functionalization with UPy end groups, PEI with a molecular weight as low as 8 kDa (8k-PEI-UPy) can be solution-cast to form films. Tensile tests revealed that 8k-PEI-UPy had an outstanding Young's modulus higher than those of state-of-the-art high-molecular-weight commercial PEIs.

In addition, based upon the telechelic oligomers, PEI-based block copolymers are synthesized by copolymerizing with other oligomers. Dielectric polyetherimide (PEI) thin films require ultra-small air voids to reduce the dielectric constant and maintain the structural integrity. Conventional synthesis of dielectric PEI uses high-molecular-weight thermally labile polymers to create air voids. The air voids, however, are often in the range of hundreds of nanometers to several micrometers, which limits the use of the PEI in ultrathin films. Herein we present the synthesis and microphase separation of polystyrene-*b*-polyetherimide-*b*-polystyrene triblock copolymers with extremely low molecular weights. Despite the extremely low molecular weights, the triblock copolymers exhibit microphase separation and form PS domains embedded in PEI. The periodic spacings are in the range of 14.1-15.2 nm and the average dimension of the PS domains is less than 8 nm, allowing for the preparation of ultra-small air voids in PEIs.



POLY 618: Nanoscale self-assembly materials of amphiphilic random and block copolymers

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In this paper, we report the design and functions of nanostructured materials via the self-assembly of amphiphilic random and/or block copolymers (Figure 1). Amphiphilic random copolymers bearing hydrophilic poly(ethylene glycol) (PEG) and hydrophobic or functional alkyl pendants afford precision self-assembly of the pendants not only in aqueous and organic media but also in solid state. The copolymers thus serve as novel, versatile scaffolds to create nanoscale self-assembly materials with sub-10 nm domains: compartmentalized polymers in solutions, hydrogels, and microphase separation materials in solid. Typically, amphiphilic random block (A/C-b-B/C) copolymers bearing hydrophobic dodecyl (A) and benzyl (B) units and hydrophilic PEG (C) induced double self-folding in water, followed by intramolecular crosslinking, to form double compartment yet single-chain polymers. Thermoresponsive polymer micelles, polymer catalysts, and selective encapsulation materials were obtained via designing primary structure (pendant structure, composition, functionalization), catalytic sites, and in-core cavities in self-assembly and crosslinked polymers. Amphiphilic random copolymers further induced sub-10 nm microphase separation in solid/film state, much smaller than conventional block copolymers.

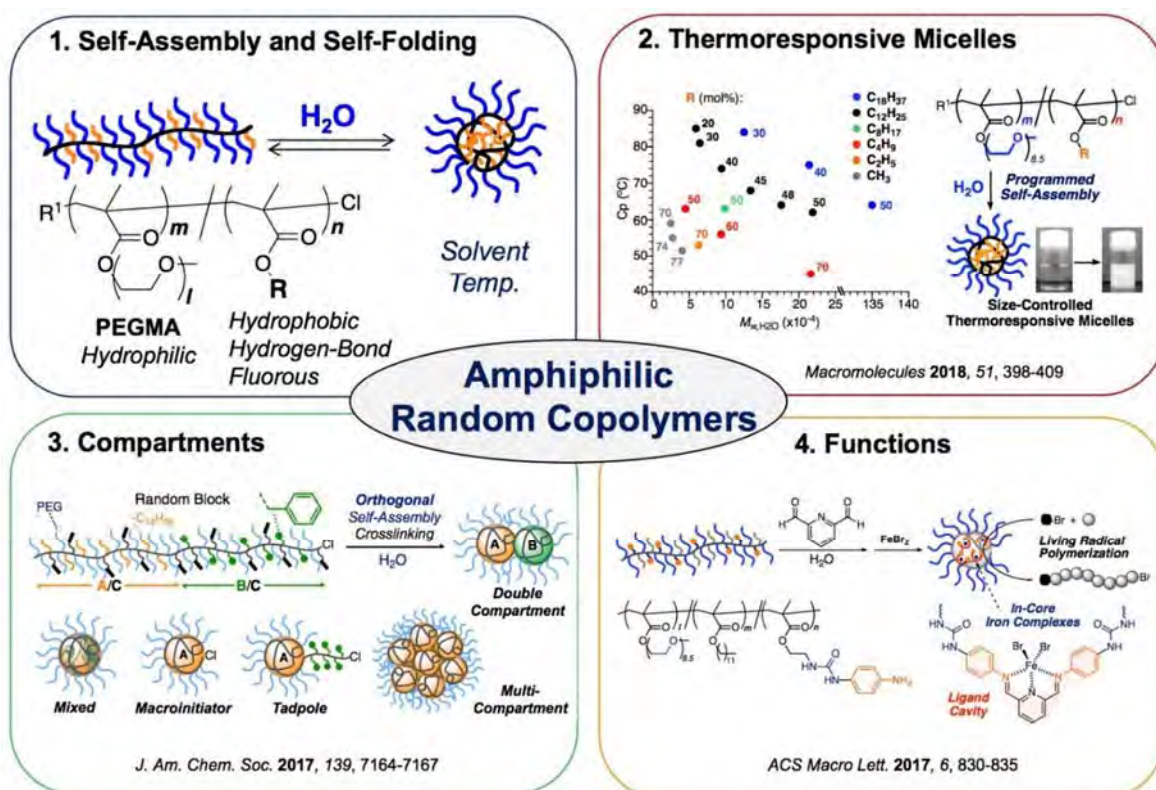


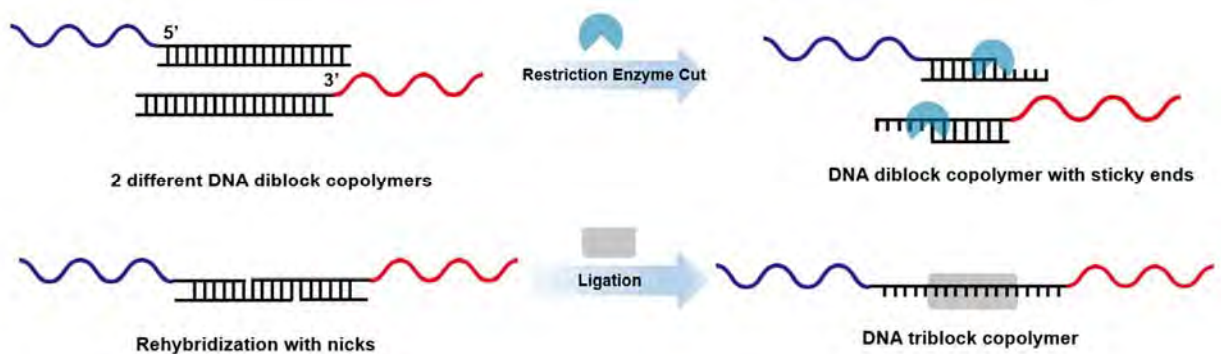
Figure 1. Nanoscale Self-Assembly Materials of Amphiphilic Random and Block Copolymers

POLY 619: Synthesis of DNA triblock copolymer using a combination of restriction and ligation enzymes

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DNA containing block copolymers are expected to find utility in a wide range of biomedical applications, since these materials have the potential to encode highly specific biological information, whereas the positions at which the information is expressed can be tuned by manipulation of the block copolymer microdomain morphology. Synthesis of DNA block copolymers with desired chemical structure and composition remains to be a major challenge, as the DNA segments are different from most conventional synthetic polymers in many aspects including their solubility. Most of the earlier publications typically treat the DNA segment as another hydrophilic polymer, and known chemical synthesis techniques are applied to conjugate the DNA block with the synthetic block. In recent years, it has become clear that many molecular biology techniques commonly used to manipulate DNA can be successfully applied to DNA block copolymer as well.

In this contribution, we report the use of a combination of restriction enzyme and ligation enzyme to generate novel DNA hybrid material with a triblock copolymer structure. In this method, two DNA diblock copolymers are cut with the same restriction enzyme to generate complementary sticky ends. The two cut DNA segments are then reconnected using a ligation enzyme to generate the desired triblock copolymer. The triblocks are unique in the sense that all the segments are connected by covalent bond such that they remain stable even when heated to high temperatures. More importantly, we show that by using the cut and paste technique, the triblock copolymer can also be digested to regenerate the diblocks, thus allowing the material to be recycled for the generation of a different triblock copolymer.

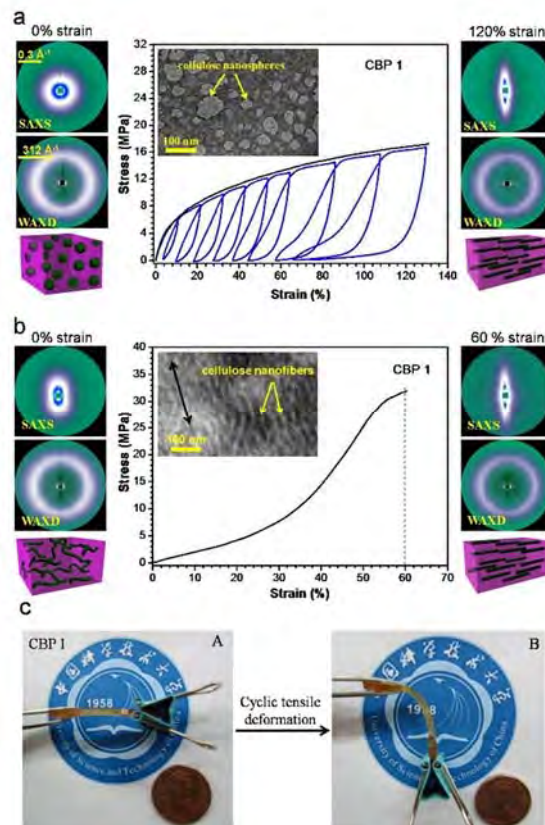


Schematic for DNA Triblock Copolymer Synthesis

POLY 620: Bioinspired design of nanostructured elastomers to mimic mechanical properties of human skin

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To date, the development of materials to mimic the unique mechanical properties of human skin is still a great challenge. Human skin exhibits highly nonlinear elastic properties that are essential to its physiological functions. It is soft at low strain but stiff at high strain, thereby protecting internal organs and tissues from mechanical trauma. Here we report a bioinspired design of nanostructured elastomers combining two abundant plant-based biopolymers, stiff cellulose and elastic polyisoprene (natural rubber), to mimic the mechanical properties of human skin. Importantly, the mechanical properties of these nanostructured elastomers can be tuned by adjusting cellulose content, providing the opportunity to synthesize materials that mimic the mechanical properties of different types of skins. The nanostructured elastomers show highly nonlinear mechanical properties closely mimicking that of human skin. Given the simplicity, efficiency, and tunability, this design may provide a promising strategy for creating artificial skin both for general mechanical and biomedical applications.

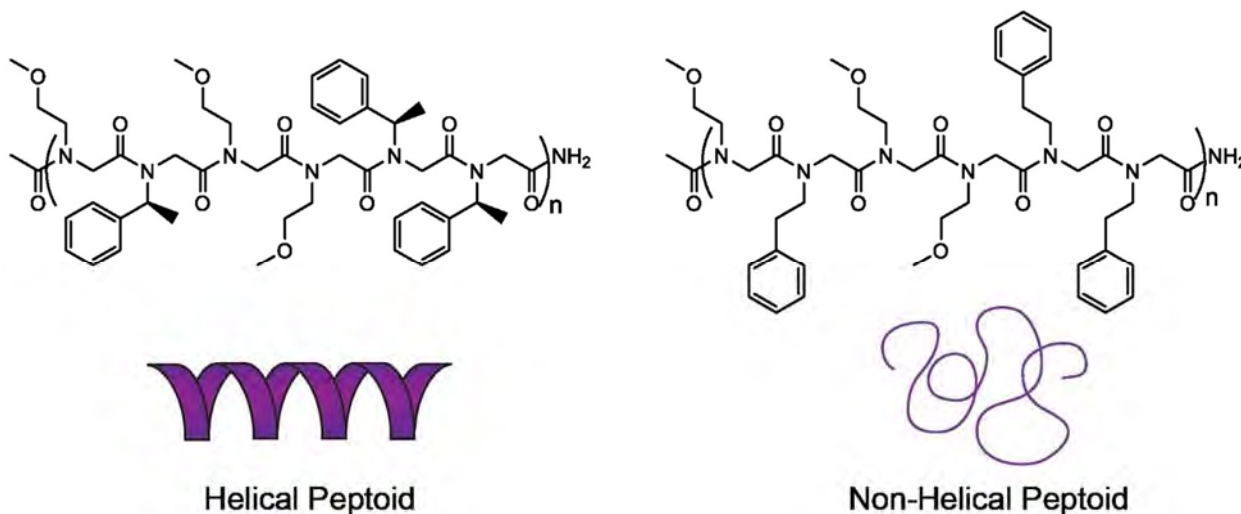


Cyclic tensile deformation to reconfigure the microstructure and reprogram the mechanical properties for CBPs.

POLY 621: Nanostructure control of biomimetic materials

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Biological polymers are functional due to their monomer sequence specificity and chain structure. In particular, the helix is a common structural motif in biomacromolecules, leading to increased chain stiffness and bulk mechanics. Here, structure-property relationships of sequence-defined, helical polypeptoids were examined in bulk block polymer and hydrogel systems. First, the impact of helicity on hexagonally-packed cylinder domain size was investigated using poly(*n*-butyl acrylate)-*b*-polypeptoid block polymers. Small angle X-Ray scattering measurements revealed that location of the helical domain at the block junction led to unfavorable packing interactions of the peptoid blocks, leading to an increase in self-assembled domain size compared to unstructured block polymers. Leveraging this control over chain structure, the effect of peptoid helicity on hydrogel mechanics was also investigated. Structural control of peptoid crosslinkers enabled decoupling of bulk modulus from network connectivity and chemical composition. Such control over the self-assembly of molecules with functional chain shapes will lend insight to the design of advanced materials with non-ideal chains, as well as biomimetic systems with potential applications in tissue engineering.

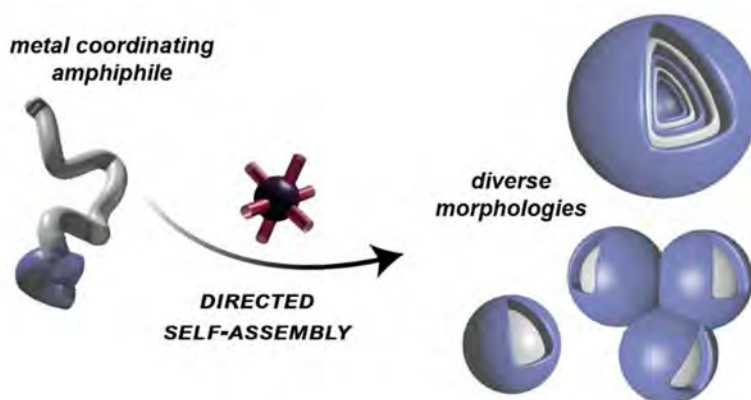


Chemical structure of helical and non-helical peptoids.

POLY 622: Self-assembly of peptide-polymer amphiphiles directed by metal ion coordination

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Inspired by natural amphiphilic marine siderophores that self-assemble into different nanomaterials in the presence and absence of metal ions, we synthesized peptide-polymer amphiphiles containing hydrophobic polymeric tails to drive self-assembly and peptides capable of metal ion coordination. With a simple hexahistidine peptide, different covalent transition metals led to the formation of micelles, vesicles, and aggregated particles. This work highlights the versatility of metal coordination as a tool in the development of dynamic nanomaterials.



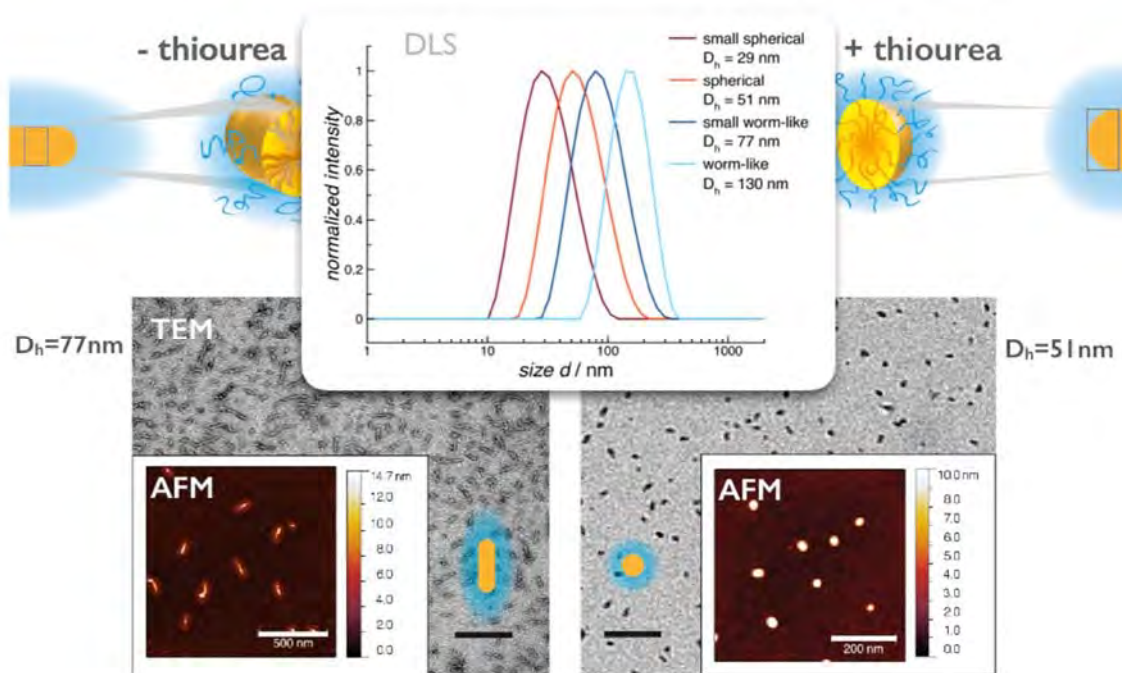
POLY 623: Secondary structure controlled self-assembly of di- and triblock copolypept(o)ides: From solution to template assisted self-assembly

Matthias Barz, barz@uni-mainz.de. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

Polypept(o)ides combine the properties of polypeptoids with polypeptides and thus enable the combination of stealth-like properties of polysarcosine with the functionality and secondary structure formation of polypeptides in one biocompatible class of polymers. We could recently demonstrate that β -sheets in polypeptides segments lead to a one dimensional self-assembly process of polypept(o)ides into worm-like micelles. Most importantly, in the presence of chaotropic agents, e.g. thiourea, the β -sheets are converted into random coils and lead to a self-assembly process controlled exclusively by the volume ratio of hydrophobic to hydrophilic block. Therefore, secondary structures in polypeptides can be used to direct the self-assembly process of block copolymers in solution.

In addition, the morphology of micelles can be further fine tuned by the applied self-assembly conditions, polymer microstructure, homopolymer addition or template structures. We present multiple micelles morphologies, which are normally not accessible by blockcopolymer self-assembly.

Since most micelles are based on reactive polypeptides the structures can be preserved and functionality can be introduced by core cross-linking. Therefore, the presented strategy enables precise control over size, morphology and function of biocompatible polymer micelles.

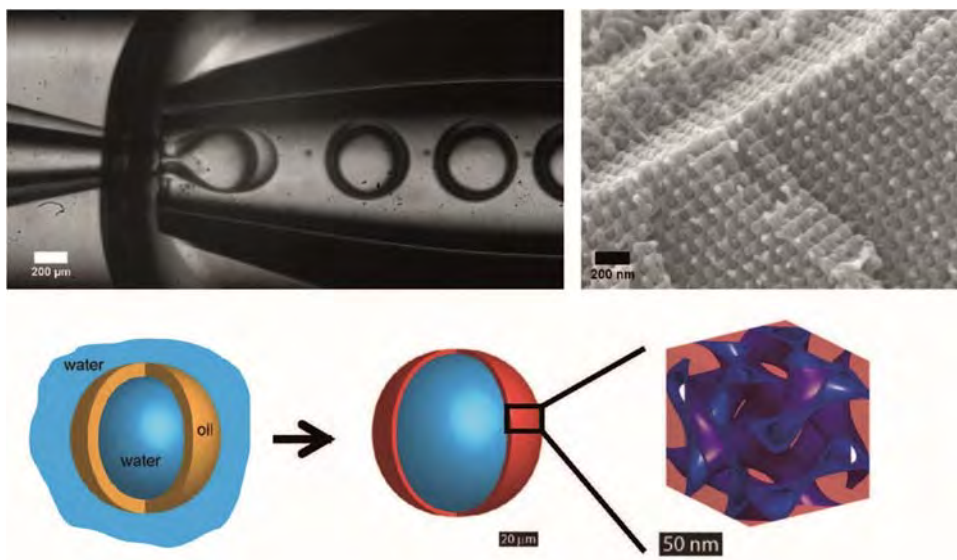


Secondary structure directed solution self-assembly of block copolypept(o)ides

POLY 624: Block copolymer self-assembly in microfluidically produced double emulsion droplets

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Block copolymer self-assembly can be used to create solid ordered nanostructures in thin or bulk films, as well as well-defined nano-objects in solution assembly. In combination with sacrificial porogens, the co-assembly of block copolymers creates ordered nanoporous polymers with homogenous porosity. While the casting of block copolymers on solid substrates yields substrate-bound films, their preparation in emulsion drops can lead to freely dispersed polymeric particles with internal ordered nanostructure. However, the self-assembly of block copolymers in single emulsion drops is typically limited to submicron particles. Complex emulsions enable the formation of large, thin polymeric films freely dispersed in liquids in the form of microcapsules. Here we report the combination of the microfluidic fabrication of double emulsion drops with the nanoscale co-assembly of amphiphilic block copolymers with a sacrificial porogen. The co-assembly of di- and triblock copolymers with removable small molecule additives inside the oil phase of homogeneous water-in-oil-in-water double emulsion droplets is described. The obtained microcapsules with controllable diameters of 100s of microns exhibit thin polymeric shells with ordered nanostructures and well-defined nanopores with pore sizes in the 10s of nanometers. Self-assembled nanoporous morphologies include three-dimensionally ordered, bicontinuous gyroid networks, and one-dimensional hexagonally packed cylinders. The challenges in using amphiphilic block copolymers in water-in-oil-in-water double emulsions are also discussed.



POLY 625: Block copolymer derived nanostructured surfaces: Templating confined surface reactions

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Polymer-inorganic hybrid materials that yield highly crystalline and hierarchically structured composites remain a challenging to realize, yet continue to entice for their applications from new synthetic biomaterials to improved catalysis. Block copolymer assembly, with the ability to produce periodically ordered structures over long ranges, has been used to structure direct a variety of inorganic materials, but relies primarily on spatial confinement. In contrast, proteins that assemble biological hierarchical composites such as nacre and bone utilize self-assembly pathways in which the chemical moiety localization in the protein matrix (determined by the amino acid sequence and chain folding) directs the crystal phase and orientation of inorganic materials. Here we introduce a system based on a reactive block copolymer that can be tailored with a variety of chemical moieties to introduce independent chemical and spatial control on the 10s of nanometer length scale. The versatility of this system is demonstrated with localized thin film functionalization by amino acids and ultrasmall silica nanoparticles, and this platform could produce new approaches to catalyst and sensing technologies. Implications for inorganic growth control over multiple length scales will be discussed.

