Division of Polymer Chemistry (POLY)

Graphical Abstracts

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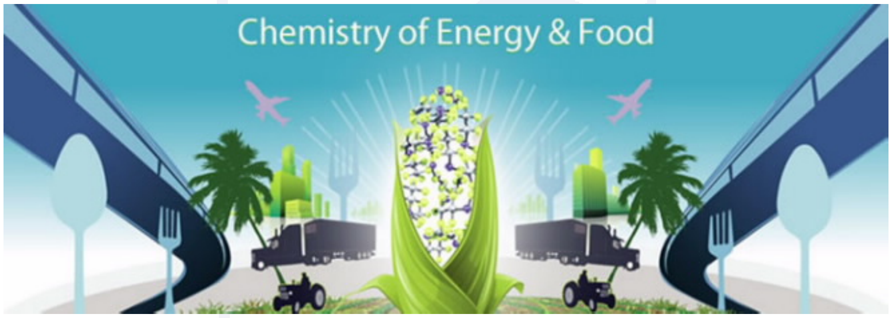
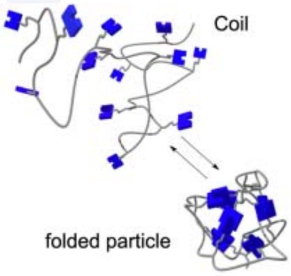
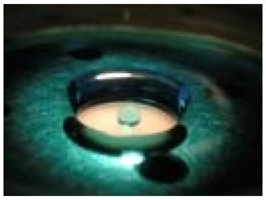
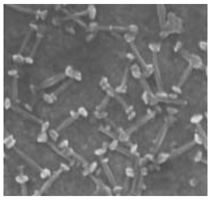
Submitted for the 245th ACS National Meeting & Exposition



April 7-11, 2013 | New Orleans, Louisiana







Division of Polymer Chemistry (POLY)

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Legend

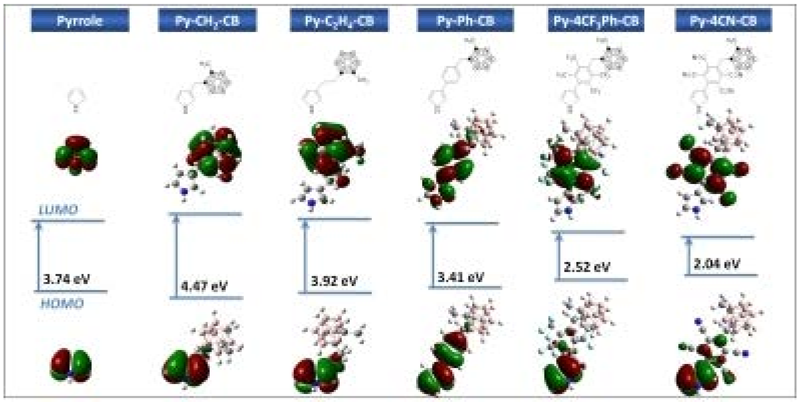
A = AM; P = PM; E = EVE

*th[¸ ƛă űƘŜ ǈrimary organizer of űƘŜ cosponsored symposium

1 - Band-gap engineering of carborane-containing conducting polymers: A computational study

Ethan Harak[1], *petia.bobadova@rockhurst.edu, Bridgette Pretz*[1], *Joseph Varberg*[1], *M. Graca H. Vicente*[2], *Petia Bobadova-Parvanova*[1]. *(1) Department of Chemistry, Rockhurst University, Kansas City, MO 64110, United States, (2) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

Recent experiments have demonstrated that carboranyl substitution dramatically increases thermal stability of conducting polymers. In this study, a series of carboranyl-substituted polypyrroles was modeled computationally and the effect of different combinations of substituents, spacers, and linkages on the HOMO-LUMO gap was examined. Thus, the band gap was finely tuned for maximum conductivity. A comparison with a series of polythiophenes was also made. The results allowed the design of new polymers with enhanced conductive abilities.

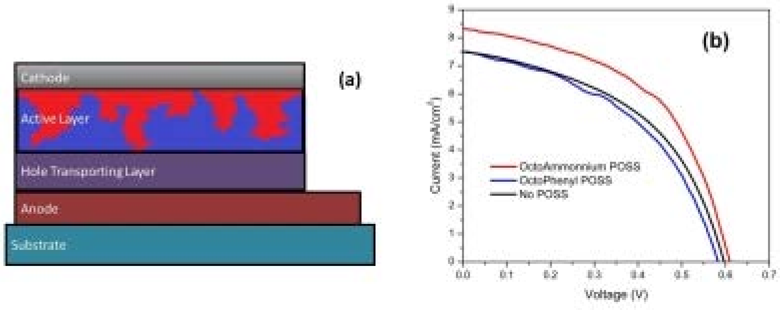


Sunday, April 7, 2013 08:30 AM
Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

2 - Improved efficiency organic photovoltaic cells by exertion of control over processing parameters and incorporation of polyhedral oligomeric silsesquioxane (POSS)

Kelly R McLeod, *kelly.mcleod@eagles.usm.edu, Mithun Bhattacharya, Qi Wu, Sarah E Morgan. School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39401, United States*

A systematic study of the effects of alteration of processing parameters in combination with incorporation of POSS molecules on the properties and structure of bulk heterojunction organic photovoltaic cells made from P3HT:PCBM blends was undertaken. On implementing the correct processing protocol, incorporation of POSS molecules with specific structures resulted in considerable enhancement in cell efficiencies. Figure 1A is a cross section of a bulk heterojunction photovoltaic cell; Figure 1B shows changes in efficiency with POSS incorporation.



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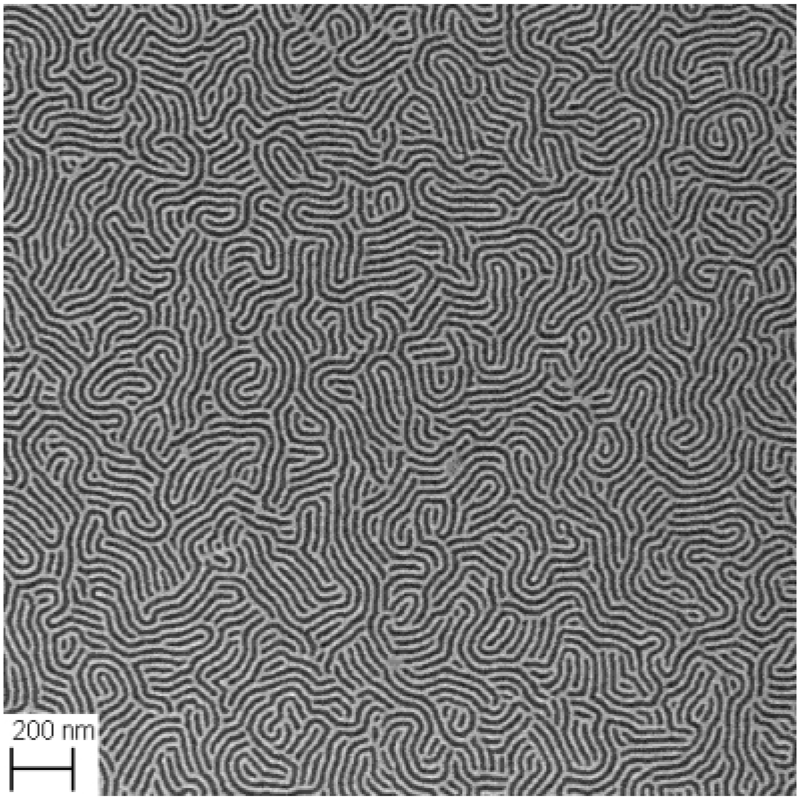
Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

3 - Block copolymer nanostructures for roll to roll manufacturing of photovoltaic devices

Leon M Dean[1]*, leondean@utexas.edu, Christopher M Bates*[2]*, Julia D Cushen*[1]*, Takehiro Seshimo*[2]*, Michael J Maher*[2]*, William J Durand*[1]*, Gregory Blachut*[1]*, Christopher J Ellison*[1]*, C Grant Willson*[1,2]*. (1) Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States, (2) Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States*

Maximum efficiency in photovoltaic devices demands structures <10 nm in size, on the length scale of exciton diffusion. High c block copolymers can self-assemble into such structures, but they do so slowly and require solvent treatment. New polymer materials and processes that, for the first time, enable the self-assembly of high c block copolymers by thermal annealing will be reported. In some cases, alignment can be achieved in tens of seconds, making the process compatible with roll to roll manufacturing.



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Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
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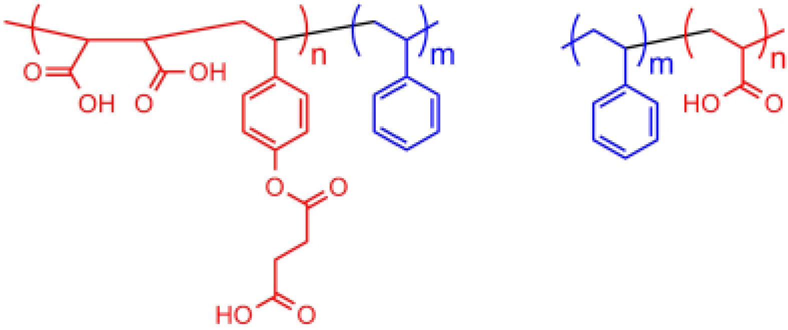
4 - Synthetic design of block copolymer amphiphiles for nanomaterial dispersion

Anton D Chavez[1,2], *pcostanz@calpoly.edu, Greg O'Bryan*[2], *Philip J Costanzo*[1]. *(1) Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407-0402, United States, (2) Materials Chemistry, Sandia National Laboratories, Livermore, CA 94551, United States*

Amphiphilic block copolymers were prepared with a variety of controlled radical polymerization techniques, including RAFT and ATRP. Length of the hydrophobic and hydrophilic block were adjusted to determine optimum dispersion of various hydrophobic nanomaterials. The prepared water-borne dispersions were subsequently utilized for a wide variety of applications.



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Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
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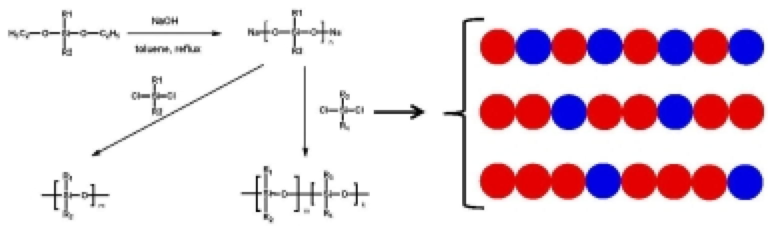
5 - Novel strategies for chemical synthesis of functional silicones

Moshe Dolejsi, *moshe.dolejsi@gmail.com*, *Kirill Efimenko*, *Jan Genzer*. *Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States*

Synthetic pathways leading to formation of functional polymers with stimuli responsive properties has recently attracted a significant research interest. We present novel synthetic strategies allowing preparation of functional homo/block silicones copolymers using disodiumoxysiloxanes as precursors for the reaction. The reactions are carried out at mild experimental conditions and allow precise control over functional silicone unit distribution along the backbone of the parent polymer. Possible mechanisms of polymer formation and its effect on a final polymer composition and polydispersity are discussed.



Sunday, April 7, 2013 09:30 AM
Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
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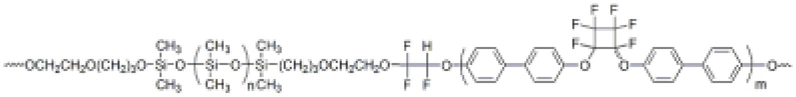
6 - Development of silcone-segmented semifluorinated polymers for high performance applications

Olawale B. Lawal, *c13olawale.lawal@usafa.edu, Sharon C. Kettwich, Scott T. Iacono. Department of Chemistry, United States Air Force Academy, USAF Academy, Colorado 80841, United States*

Semifluorinated perfluorcyclobutyl (PFCB) aryl ether polymers are a class of processable, step growth polymers that are easily tailorable for a multitude of high performance applications. Recently, it has been shown that PFCB aryl ether oligomers possessing reactive aryl trifluorovinyl ethers (TFVE) undergo block copolymerization with polyols/polybisphenols employing an aryloxylation methodology. In this work, PFCB-segmented silicone polymers were prepared in high yield via the step-growth addition polymerization of discreetly sized PFCB prepolymers and carbinol silicones. These hybrid fluorosilicone polymer systems displayed a high degree of thermal stability as determined by the decomposition temperatures found using TGA analysis and were structurally characterized using $^1H/^{19}F$ NMR and GPC analysis. Thermal analysis by DSC proved the polymers were entirely amorphous with tunable glass transition temperatures. Film preparation employing spin casting demonstrated excellent solution processability. Work continues to post-functionalize these polymers for development of proton exchange membranes for fuel cell applications.



AA-BB block copolymer

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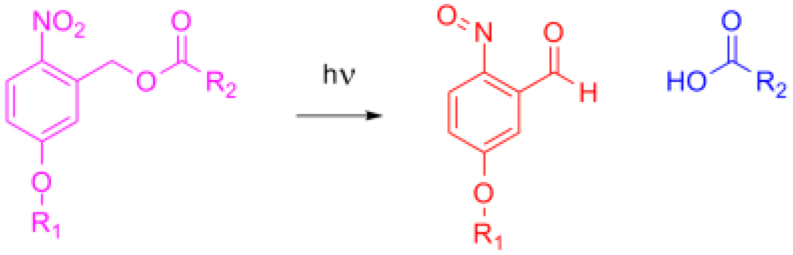
7 - Controlling surface energy and wetability with a light responsive linker system

Christopher C Pattillo, *pcostanz@calpoly.edu, Philip J Costanzo. Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407-0402, United States*

This work focuses on the development of stimuli-responsive surface coatings. By controlling the functionality, the surface energy can be manipulated to be either hydrophilic or hydrophobic, and the resulting change can regulate wet-ability and fluid flow. Here light responsive moieties were tethered to glass surfaces and upon exposure, cleavage was induced to change surface energy and wet-ability.



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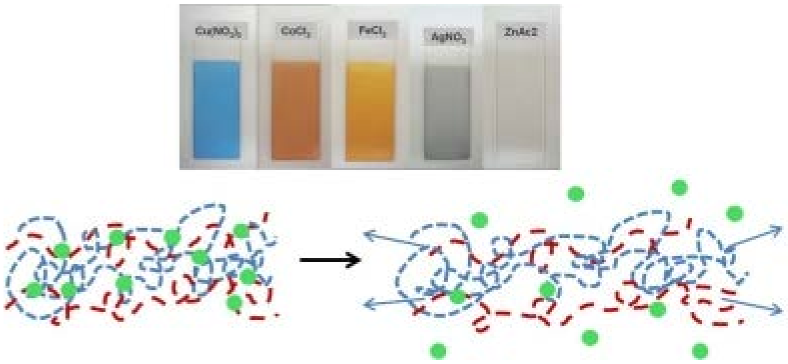
8 - Release of encapsulated CA^{2+} ions from a polyelectrolyte multilayer system via mechanical stretching

***Amanda B Schubert**, br00kie@tamu.edu, Xiayun Huang, Nicole S. Zacharia. Mechanical Engineering, Texas A&M University, College Station, Texas 77840, United States*

Polyelectrolyte multilayer systems are becoming more commonly used in medical applications such as in drug carrier systems. They are fabricated by the directed complexation of oppositely charged polyelectrolytes onto a substrate. In this study we encapsulated Ca^{2+} ions within the nanostructure of a polyelectrolyte system. This was accomplished by utilizing dipped Layer-by-Layer (LbL) technique, with the substrate being Poly(dimethylsiloxane) (PDMS). Alternating layers of branched polyethylene imine (BPEI) complexed with metal ions and polyacrylic acid (PAA) were used to create the films.. This allowed formation of thin cross-linked films with metal ligand coordination complexes within them. A range of metal ions were used, including Cu^{2+}, Co^{2+}, Zn^{2+} and Ca^{2+}. These materials were characterized with UV-vis and profilometry. When wet, the polyelectrolyte multilayer materials act as soft, viscoelastic materials. In the dry state they are glassy. With mechanical stretching of the LbL system, the release of the encapsulated ions is potentiated by breaking of the coordination complexes. The metal ions can also be removed from the multilayers by soaking in EDTA solution. The amount of the Ca^{2+} release is controlled by the degree of stretching and time. This polyelectrolyte multilayer system could enhance several medical applications, including internal fixator's, prosthetic joints and possibly undiscovered applications involving bone remodeling.



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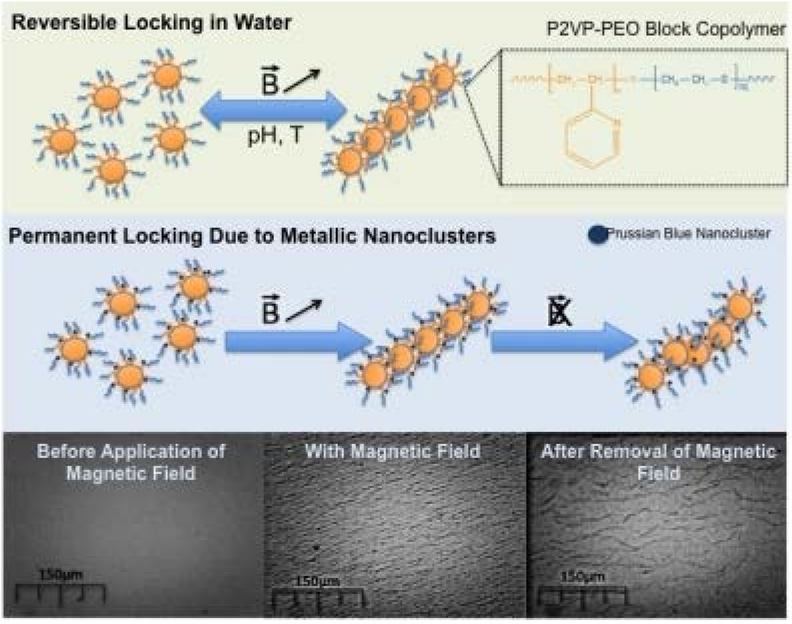
9 - Locking properties of magnetic nanoparticles decorated with stimuli-responsive block-copolymer brushes

Matthew A Kahabka, *kahabkma@clarkson.edu, Sergiy Minko. Department of Chemistry and Bimolecular Science, Clarkson University, Potsdam, New York 13699, United States*

Linear structures and three-dimensional networks of locked magnetic nanoparticles were formed in aqueous solutions and polymeric fluids by grafting mixed block-copolymers (P2VP-PEO) to the surface and decorating the copolymers with metallic nanoclusters. The outer polymeric layer sterically stabilized the system in the absence of a magnetic field. In contrast, sufficiently strong fields facilitated the locking mechanism of the inner segment by the forced proximity of the particles. This assembly method has applications in polymer composites, drug-delivery systems and anticancer therapy.



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10 - PDMS-PCL shape memory polymer (SMP) foams

Olivia J. George[1], *olivia.g@neo.tamu.edu, Dawei Zhang*[2], *Keri M. Petersen*[1], *Melissa A. Grunlan*[1,2]. *(1) Department of Biomedical Engineering, Texas A&M University, College Station, Texas 77843, United States, (2) Materials Science & Engineering Interdisciplinary Program, Texas A&M University, College Station, Texas 77843, United States*

Thermoresponsive shape memory polymers (SMPs) are a class of stimuli-sensitive smart materials that can be deformed to a temporary fixed state, and upon heating, recover their original conformation. Both solid and porous SMPs are of significant interest for creating biomedical devices which self-deploy or self-fit for ease of implantation. We have recently reported hybrid SMPs comprised of organic “switching segments” [poly(e-caprolactone), PCL] and inorganic “soft segments” [polydimethylsiloxane, PDMS] with the general formula AcO-PCL$_n$-*block*-PDMS$_m$-*block*-PCL$_n$-AcO. Herein, porous SMP foams were prepared via a modified solvent-casting/particle leaching method (SCPL) which included photochemically crosslinking the dichloromethane-based macromer solution over a water-fused salt template. By tailoring the PDMS segment length (m = 20, 37, 66 and 130; n = 40), a series of SMP foams were produced with tunable pore size, modulus (i.e. stiffness) and degradation rate. Their utility for treating bone defects will be described.

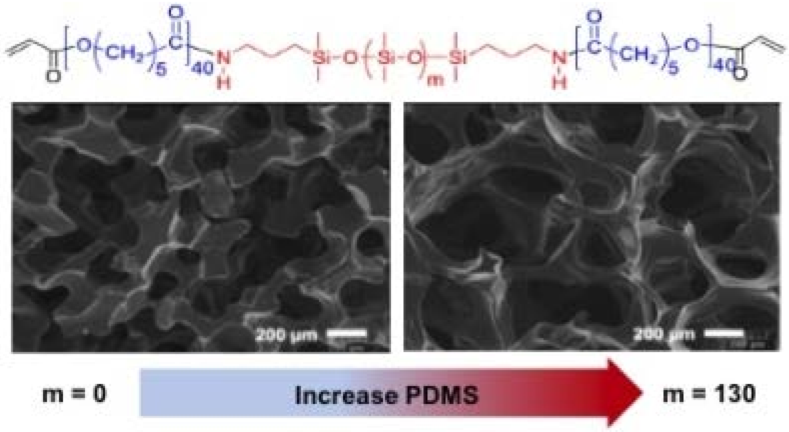

Figure 1. Adjusting “soft segment” [polydimethylsiloxane, PDMS] length to tune scaffold properties

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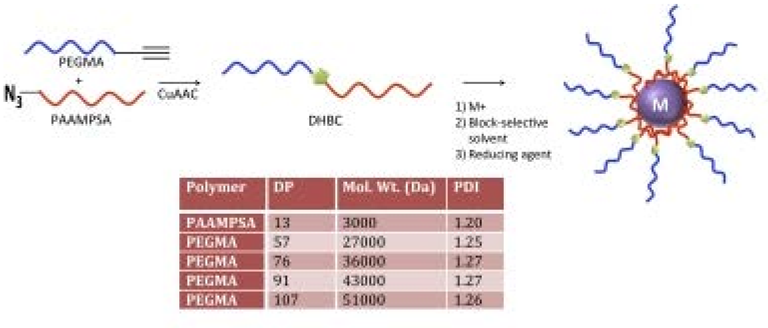
11 - PAAMPSA and PEGMA dihydrophilic block copolymers as model self-assembled nanoreactors

Derek Luong, *dluong@clarku.edu, Xiaorui Chen, Sergio Granados-Focil. Department of Chemistry and Biochemistry, Clark University, WORCESTER, MASSACHUSETTS 01610, United States*

Dihydrophilic block copolymers (DHBC) consisting of two water soluble blocks, are attractive templates to generate nanostructures in water. These molecules can self assemble into a range of morphologies by altering the media (pH, solvent quality, or temperature), or by altering the size of each block. A PAAMPSA-PEGMA DHBC was synthesized in two steps. First, PAAMPSA and PEGMA were polymerized via ATRP using either alkyne or azide functionalized initiators, next, the two homopolymers were combined using a copper-catalyzed 1,3 Huigens dipolar cycloaddition (CuAAC) to form the DHBC. The structure of the target polymers was confirmed by NMR, while the M.W. and PDI were obtained by GPC. The molecular weights ranged from 3kDa to 50kDa and the PDI's for the copolymers ranged between 1.2 and 1.3. Data on DHBC self-assembly in aqueous solution and its ability to serve as “nano-reactors” to produce metallic nanoparticles will be discussed.



Polymer	DP	Mol. Wt. (Da)	PDI
PAAMPSA	13	3000	1.20
PEGMA	57	27000	1.25
PEGMA	76	36000	1.27
PEGMA	91	43000	1.27
PEGMA	107	51000	1.26

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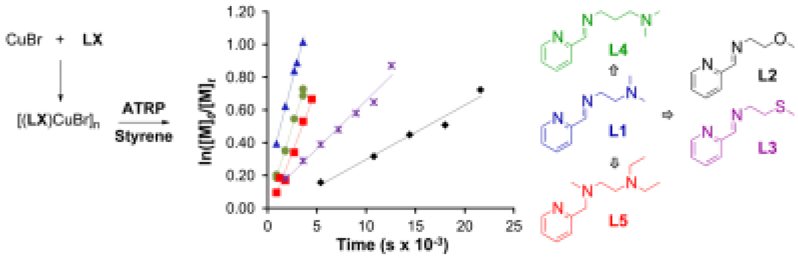
12 - Ligand donor effects of polydentate pyridine-amine ligands for copper(I) in the ATRP of styrene

Sarah L Guillot, *Sarah.L.Guillot@williams.edu, Zachary D. Remillard,* ***Christopher Goh***, *cgoh@williams.edu. Department of Chemistry, Williams College, Williamstown, MA 01267, United States*

Atom transfer radical polymerization (ATRP) is a versatile, metal-mediated method of producing polymers with controlled compositions and molecular weights. Control is attained through the equilibrium between the active radical chain-end state and a dormant state, established by the reduction-oxidation cycling of the metal catalyst. Ligand structure has been shown previously to strongly impact the catalysts' activity and ability to control the polymerization, and polydentate ligands of amine and pyridine donor moieties have produced some of the most active ATRP catalysts.[1,2] Copper(I) bromide complexes of tridentate and tetradentate pyridine-imine and pyridine-amine ligands with additional amine, ether or thioether neutral donor atoms were synthesized and utilized in the ATRP of styrene. We explored how differences in ligand structure for this class of ligands affected the efficiency of ATRP of styrene. Redox potentials of the complexes were determined, and trends in polymerization control and rate of polymer growth relating to ligand design are described.



[ol][li]Matyjaszewski, K. *Macromolecules* **2012** , *45*, 4015.[/li][li]Pintauer, T.; Matyjaszewski, K. *Chem. Soc. Rev.* **2008** , *37*, 1087.[/li][/ol]

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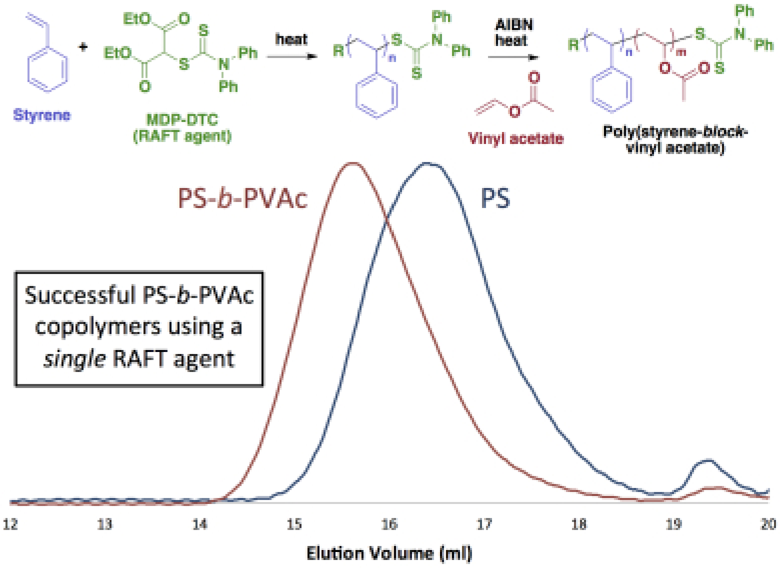
Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

13 - Synthesis of poly(styrene-block-vinyl acetate) using RAFT polymerization with a single mediating agent

Lily A. Dayter, *dayterla@clarkson.edu, Kate A. Murphy, Qin Lou, Devon A. Shipp. Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, NY 13699-5810, United States*

It is shown that reversible addition-fragmentation chain transfer (RAFT) polymerization using malonate *N*,*N*-diphenyldithiocarbamate (MDP-DTC) as the “RAFT agent” controls molecular weight growth in the polymerization of vinyl acetate (VAc) and styrene, monomers with disparate reactivities. Block copolymers containing styrene and VAc were successfully synthesized. Styrene was initially polymerized, yielding a polystyrene macro-RAFT agent. This was subsequently used in the polymerization of VAc, resulting in the polystyrene-block-PVAc. Chain transfer constants for the MDP-DTC RAFT agent for each monomer were also determined.



Successful PS-*b*-PVAc copolymers using a *single* RAFT agent

Sunday, April 7, 2013 11:45 AM
Undergraduate Research in Polymer Science (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

14 - Lower ruthenium leaching using PIB-supported metathesis catalyst

Hassan S. Bazzi[1], *bazzi@tamu.edu, Mohammed Al-Hashimi*[1], *David E. Bergbreiter*[2]. *(1) Chemistry, Texas A&M University at Qatar, Doha, Qatar, (2) Chemistry, Texas A&M University, College Station, TX 77842, United States*

Olefin metathesis is a powerful tool in C-C double bond formation having numerous applications in polymer chemistry and material science. Ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM), in particular are versatile methods for the synthesis of functional materials. Ruthenium-based Grubbs and Hoveyda-Grubbs catalysts are certainly the most popular complexes in the field of olefin metathesis. Unfortunately, only a limited number of studies have been conducted where both recycling and ruthenium waste content are examined. Moreover, numerous papers do not report on the levels of contamination in the product, which clearly is a drawback when developing olefin metathesis for industrial procedures. The separation of the polymeric product and the catalyst is one of the major challenges facing metathesis polymerization. This process currently requires extra steps or additional chemical processes. Alternative processes that avoid a second process step, thus remain of interest. Our approach uses a scheme in which the solubility of the Ru catalyst byproducts is differentiated from the solubility of the product polymer. This strategy employs soluble polyisobutylene (PIB)-supported NHC-ligated Ru catalysts and a liquid/liquid biphasic separation of catalyst residues from the polymer products after a reaction. We will discuss the activity of PIB-supported 2nd generation Hoveyda-Grubbs complex in a series of ring opening metathesis polymerizations yielding high-molecular weight polymers with narrow polydispersities. The PIB-supported Ru complex is phase selectively soluble in the heptane phase of thermomorphic mixtures of heptane and polar solvents. The separability of these catalysts leads to lower Ru contamination (167 ppm levels) in the polymer products (white figure 1) in comparison to the non-supported Hoveyda-Grubbs catalyst (4764 ppm, black figure1).

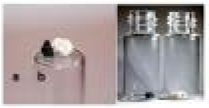


Figure 1: Photographs of polymer – a) Prepared by using 2nd generation Hoveyda-Grubbs complex.
b) Prepared by using PIB supported complex.

Sunday, April 7, 2013 08:00 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)

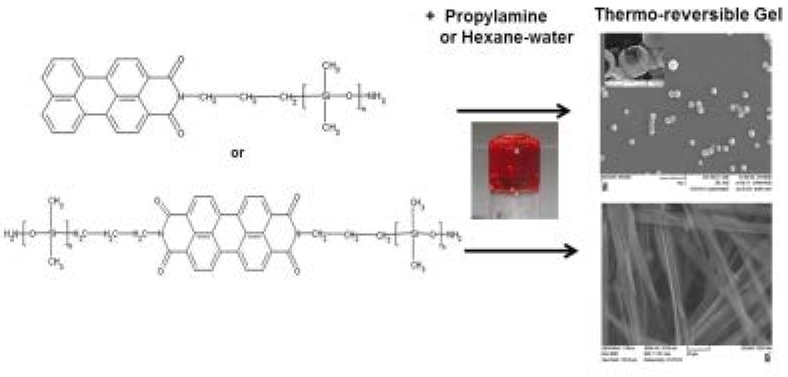
Location: Hilton Riverside

Room: Ste. B, Sec 9

15 - Thermo-reversible gelation of rod-coil and coil-rod-coil molecules based on poly (dimethyl siloxane) and perylene diimide

P Sundararajan, *Sundar@Carleton.ca, Elianne Dahan. Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada*

Thermo-reversible gels of polymers entail non-covalent network formation, immobilizing a solvent. Self-assembly of perylene diimide (PTCDI) via pi interaction is well known. Using such a large aromatic molecule as part of an amphiphilic polymer system, we have prepared gels of PDMS-PTCDI and PDMS-PTCDI-PDMS with propylamine as the solvent. With the rod-coil PDMS-PTCDI, the gel consists of micellar aggregates, while a network of fibres is seen in the gels of the coil-rod-coil molecule PDMS-PTCDI-PDMS. Thermo-reversibility was confirmed using DSC analysis.

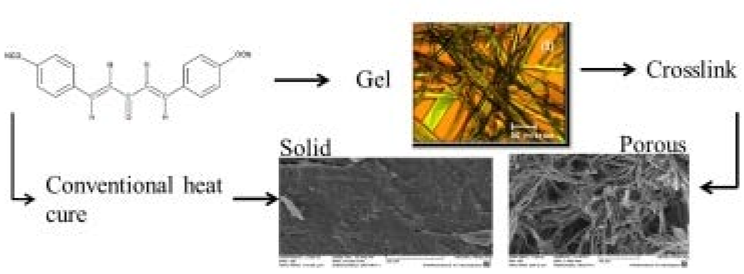


Sunday, April 7, 2013 08:20 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

16 - Porous cyanate ester resins via organogel route and their porous nano-composites with carbon nanotubes

P R Sundararajan[1], *Sundar@Carleton.ca, Rakesh Samikannu*[1,2], *Muthusamy Sarojadevi*[2]. *(1) Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada, (2) Chemistry, Anna University, Chennai, Tamil Nadu 600 025, India*

A method is described for the preparation of porous cyanate ester network in which the self-assembly of the cyanate ester monomer leads to gels having fibrous morphology. The gels with different cyanate ester monomers were prepared using a polar aprotic solvent. The gel fibers are then cured to prepare porous cyanate ester resins. Carbon nanotubes were also incorporated during gelation to prepare porous cyanate ester/CNT composite resins. The cure time of CNT-cyanate ester decreases with CNT loading.



Sunday, April 7, 2013 08:40 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)

Location: Hilton Riverside

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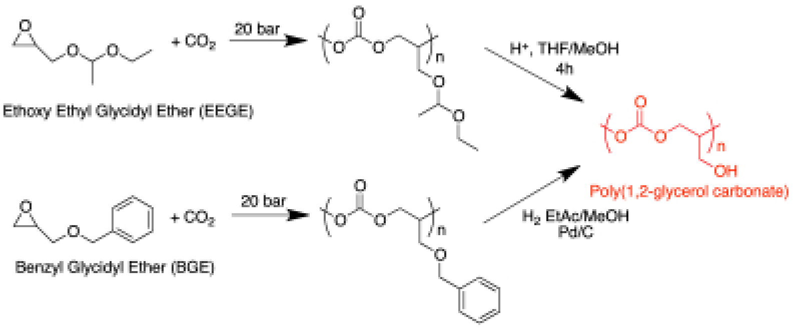
17 - Multifunctional CO_2 containing poly(carbonate) copolymers with tailored number of hydroxyl groups

Jeannette Geschwind[1,2], *geschwij@uni-mainz.de, Holger Frey*[1]. *(1) Department of Organic Chemistry, Johannes Gutenberg University, Mainz, Germany, (2) Graduate School Materials Science in Mainz, Mainz, Germany*

Multifunctional aliphatic poly(carbonate)s with varied number of hydroxyl groups were prepared by the combination of glycidyl ether chemistry with CO_2. For example the fundamental poly(1,2-glycerol carbonate) structure was obtained by combination of glycidyl ether chemistry with CO_2 via two different approaches. The polymer was obtained by a two-step procedure from copolymerization of ethoxy ethyl glycidyl ether (EEGE) or benzyl glycidyl ether (BGE) with CO_2, followed by removal of the respective protecting groups either through acidic cleavage or hydrogenation.



Sunday, April 7, 2013 09:00 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton Riverside
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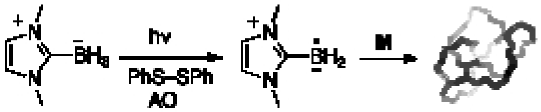
18 - Boron-based initiators for the photopolymerization of acrylates

Emmanuel Lacôte[1], *emmanuel.lacote@univ-lyon1.fr, Jacques Lalevée*[2], *Dennis P. Curran*[3]*. (1) Department of chemistry, catalysis, polymers and processes, CNRS - CPE Lyon - Université de Lyon, Villeurbanne, France, (2) UHA - ENSCMu, Mulhouse, France, (3) Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, United States*

Complexation of boryl radicals by N-Heterocyclic carbenes leads to stabilized nucleophilic radicals. We will describe how these intermediates can be photogenerated and used to initiate polymerization of acrylates for type I and type II photopolymerizations (UV and visible light). Mechanistic investigations supporting the initiation mechanism will be given

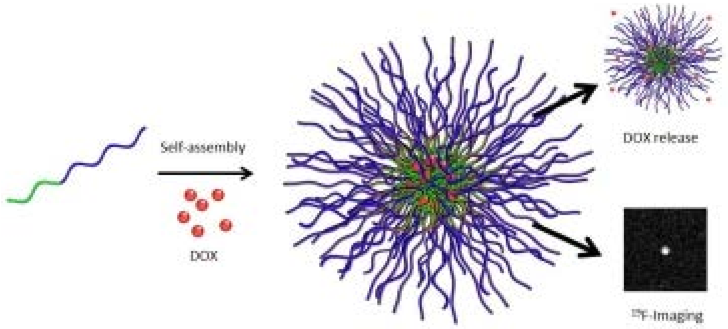


Sunday, April 7, 2013 09:20 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

19 - ^{19}F-based polymer nanoparticles as breast cancer theranostics

Christian Porsch[1], *porsch@kth.se, Yuning Zhang*[2], *Eva Malmström*[1], *Andreas M Nyström*[2]. *(1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden, (2) Neuroscience, Karolinska Institutet, Stockholm, Sweden*

Polymers offer a unique possibility to tailor the design of theranostic delivery platforms. In the present work, we have employed ATRP to synthesize a library of theranostic, well-defined core/shell polymer nanoparticles (NPs) with fluorine atoms incorporated in their hydrophilic corona. This enables NPs with high fluorine content, which shows good performance in ^{19}F-MRI. Furthermore, the influence of the hydrophobic core architecture to the NPs self-assembly, size, and drug delivery characteristics has been evaluated.



Sunday, April 7, 2013 09:40 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)

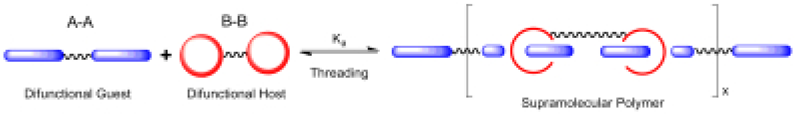
Location: Hilton Riverside

Room: Ste. B, Sec 9

20 - Functionalization of highly efficient hosts and their use in polypseudorotaxane macromolecular self-assembly systems

Terry L. Price, Jr., *terryp24@vt.edu, Daniel V. Schoonover, Harry W. Gibson. Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States*

In the ongoing journey to the development of highly efficient polymeric pseudorotaxane systems, we have chosen to expand upon the pyridyl cryptand - paraquat, host - guest system.[1] Here we present work pertaining to the functionalization of pyridyl cryptands for the production of A-A/B-B supramolecular polymer systems (A=cryptand and B=paraquat). Investigated areas include complexation studies, supramolecular polymerization and characterization.



References:

(1) Pederson, A. M. P.; Ward, E. M.; Schoonover, D. V.; Slebodnick, C.; Gibson, H. W. *J. Org. Chem.* **2008** , *73*, 9094-9101.

Sunday, April 7, 2013 10:00 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton Riverside
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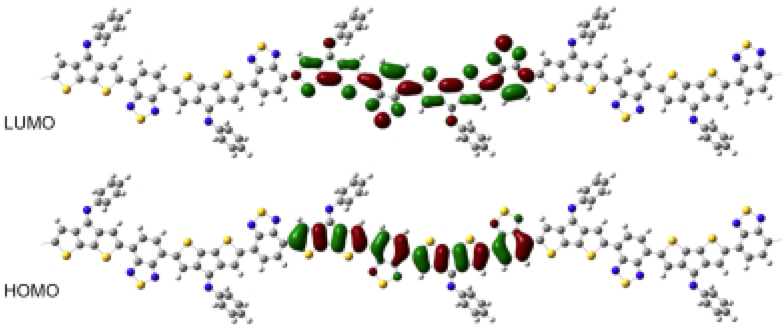
21 - Bridgehead imine substituted cyclopentadithiophene derivatives: Toward a better understanding charge transport phenomena in semiconducting polymers

Jason D. Azoulay[1,2], *jdazoul@sandia.gov, Guillermo C. Bazan*[2]*, Dustin Murtagh*[1]*, Joseph G. Cordaro*[1]*. (1) Materials Chemistry, Sandia National Laboratories, Livermore, CA 94550, United States, (2) Departments of Chemistry & Biochemistry and Materials, University of California at Santa Barbara, Santa Barbara, CA 93106, United States*

A major challenge in the development of models for a predictive understanding of the relationship between molecular and electronic structure arises from the many degrees of freedom in advanced materials development. Bridgehead imine substituted semiconducting polymers offer a unique opportunity in this regard. The imine substituent can *systematically* influence the electron density along the main chain, aromatic stabilization of the constituent copolymer segments, the relative co-planarity of the conjugated backbone and degree of intermolecular coupling in the solid state.



Pictorial representations of the projected single electron HOMO and LUMO wavefunctions of a donor-acceptor copolymer as determined at the B3LYP/6-31G** level of theory.

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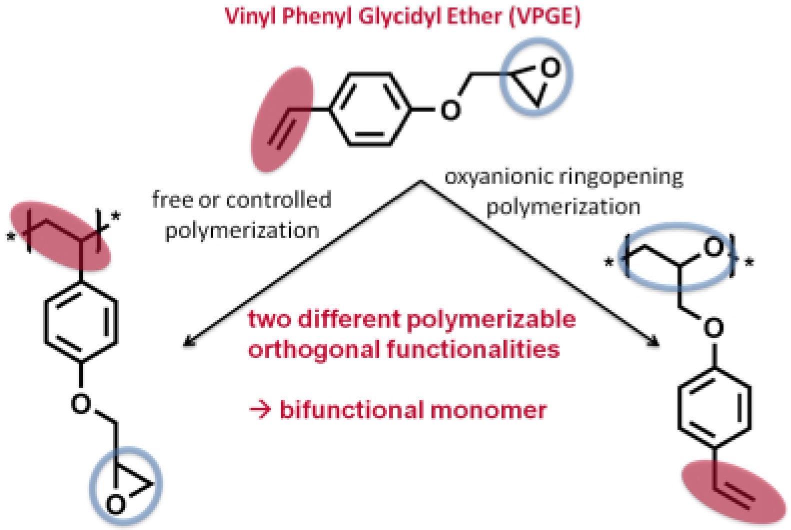
22 - Bifunctional epoxy-styrene monomer for applications from nanoparticles to networks

Mathias Werre[1,2], *werrem@uni-mainz.de, Holger Frey*[1]*. (1) Institute of Organic Chemistry, Johannes Gutenberg University, Mainz, Germany, (2) Graduate School Materials Science in Mainz, Mainz, Germany*

Vinyl phenyl glycidyl ether (VPGE) has two orthogonal polymerizable functionalities, which can be polymerized either via the styrene function in a free/controlled radical fashion or via a ring opening anionic polymerization of the epoxy group.



The remaining orthogonal functionalities can be used for further derivatizations or as crosslinking points. Copolymerization with other styrene or epoxy monomers leads to a variety of possible applications, e.g. for the preparation of nanoparicles and polymer networks.

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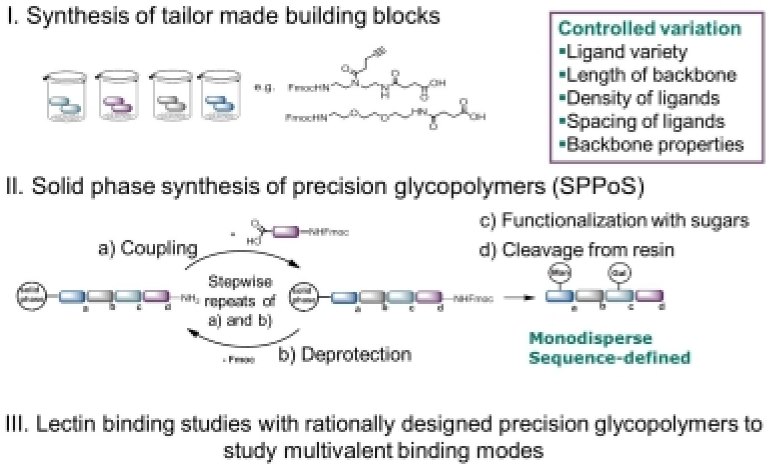
23 - Investigating multivalent binding modes of precision glycopolymers

Daniela Ponader, *daniela.ponader@mpikg.mpg.de, Daniel Pussak, Maria Glanz, Stephan Schmidt, Felix Wojcik, Laura Hartmann. Max Planck Institute of Colloids and Interfaces, Potsdam, Brandenburg 14424, Germany*

Multivalency is a key principle in nature *e.g.* for intercellular recognition or pathogen identification involving carbohydrate-receptor interactions. One tool which has been used for investigations of multivalent binding are neoglycopolymers. However synthesized by standard polymerization techniques these compounds are inherently polydisperse. In order to correlate the chemical structure to the resulting binding activity, monodisperse, sequence defined structures are necessary. Such structures are available by the recently developed *S*olid *P*hase *Po*lymer *S*ynthesis (SPPoS). These rationally designed scaffolds exhibit alkyne moieties which can react readily with sugar azides and give monodisperse, sequence-defined glycopolymers. We systematically varied scaffold parameters such as the number and sequence of sugar ligands and performed binding studies with different lectins such as Concanavalin A or PA-IL lectin from the pathogenic bacterium *Pseudomonas aeruginosa.* We can show strong influence of the number and spacing of ligands as well as an influence from backbone properties on the resulting binding affinity.



Sunday, April 7, 2013 11:00 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)

Location: Hilton Riverside

Room: Ste. B, Sec 9

24 - Photoresponsive Coumarin based polymers: Controlled drug release and micropattering applications

Murthy V. S. N. Maddipatla, *msriram@uakron.edu, Abraham Joy. Department of Polymer Science, The University of Akron, Akron, OH 44325, United States*

Photoresponsive materials are advantageous in many applications due to the spatiotemporal control that they provide. Much attention has been focused on materials that exhibit both photo- and biodegradability due to their extensive applications in environmental and biomedical research. In this context, we have synthesized a new class of photoactive, coumarin-based polymers in which the coumarins are part of the polymer backbone. These polymers undergo two types of photochemical transformations such as photocrosslinking at 350 nm and photodegradation at 254 nm irradiation. In addition, these polymers are mechanically robust, stable in the absence of light, non-toxic and are biodegradable. These combined properties make them valuable for many biomedical applications. For example, controlled drug delivery devices such as ocular implants and dermal patches could be designed from such polymers. In addition, polymeric 2D and 3D structures with micropatterned architectures can be fabricated

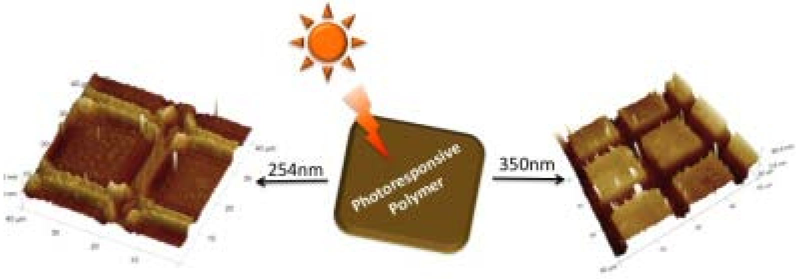


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Fig 1: AFM images of the polymer irradiated at 254nm (left) and at 350nm (right) using a TEM grid as a photomask

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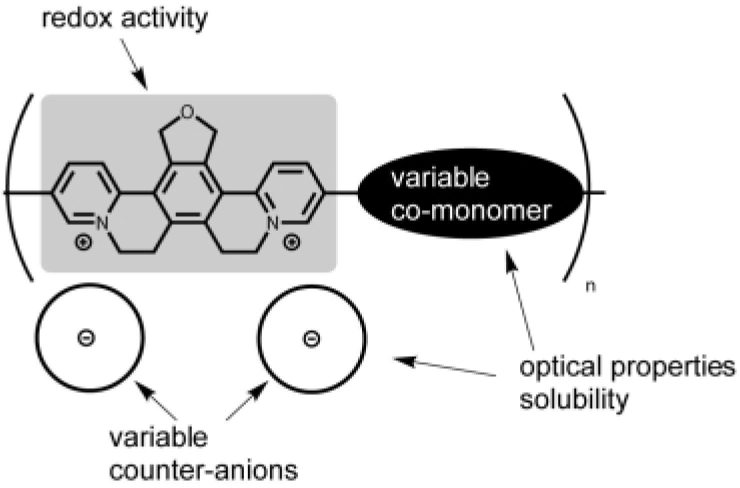
25 - Cationic conjugated polymers: Synthesis and sensing applications

Sébastien Rochat, *srochat@mit.edu, Timothy M. Swager. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

A series of poly(pyridinium phenylene) conjugated polymers was synthesized by the cross-coupling of an easily accessible pyridinium-based monomer with different co-building blocks, followed by an internal quaternizative cyclization. The influence of the constituents on the polymer properties was investigated and is illustrated in the appended scheme. The polymers were found to possess tunable solubility and optical properties, as well as appealing electrochemical characteristics. The use of some of these materials for the detection of electron-rich analytes was investigated.

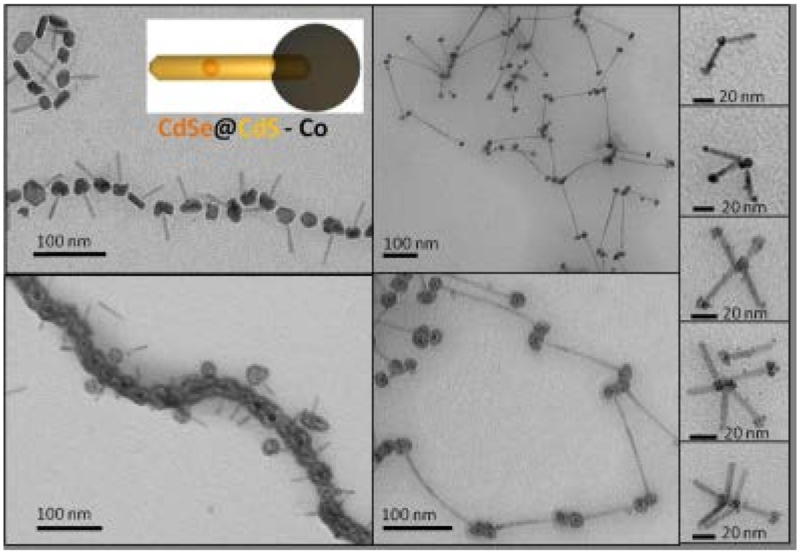


Sunday, April 7, 2013 11:40 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

26 - Synthesis and colloidal polymerization of Janus nanoparticles: New concepts for colloidal monomer design

Lawrence J Hill[1], *ljhill@email.arizona.edu, Jeffrey Pyun*[1,2]. *(1) Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721, United States, (2) Department of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea*

Novel monomers for colloidal polymerization have been developed based on ferromagnetic Janus-type polymer-coated cobalt nanoparticles asymmetrically attached to semiconducting nanorods. Colloidal polymerization afforded p-type semiconducting cobalt oxide nanowires incorporating n-type CdSe@CdS nanorods. Control of monomer morphology enabled synthesis of colloidal copolymers incorporating both AB and A_2B_2 magnetic colloidal monomers for the first time. Particle asymmetry enabled differential functionalization and additional control of self-assembly behavior. Alternative routes to colloidal polymers are emerging in the form of stars and hyperbranched structures.

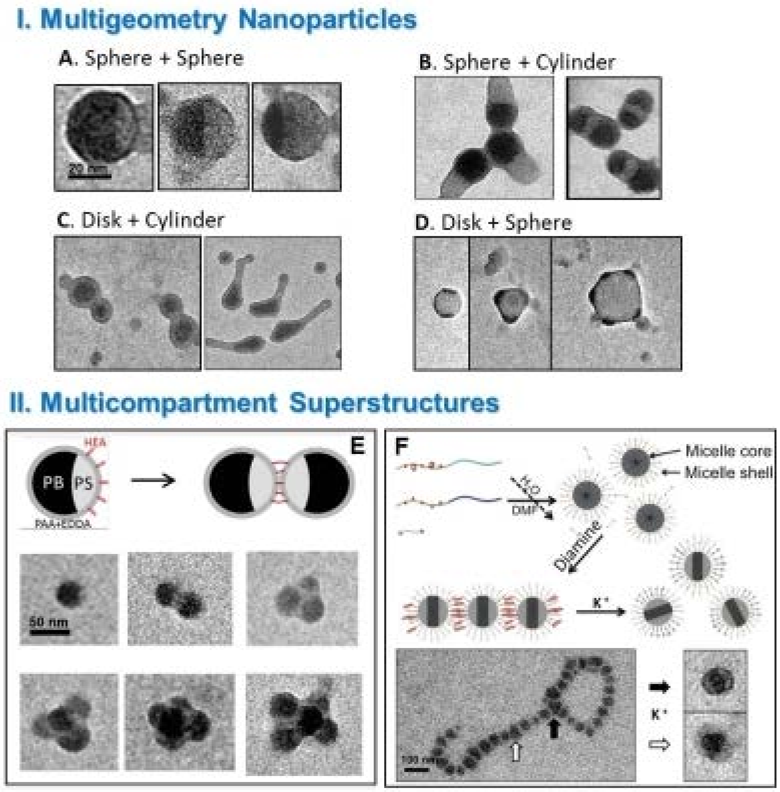


Sunday, April 7, 2013 08:35 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

27 - Multigeometry nanoparticle and multicompartment superstructure construction from block copolymers: Molecular design, assembly, hierarchy, and kinetics

Jiahua Zhu[1], *jhzhu@udel.edu, Karen Wooley*[2], *Darrin Pochan*[1]. *(1) Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States, (2) Department of Chemistry, Texas A&M University, College Station, TX 77843, United States*

Multigeometry nanoparticles, due to segregation of unlike-shaped block copolymer molecules trapped within the same micelle structures, have been produced via assembly of amphiphilic block copolymer mixtures in tetrahydrofuran/water solution. Both size and shape of subdomains can be precisely tuned to produce a class of multigeometry nanoparticles, including sphere-sphere, sphere-cylinder, cylinder-cylinder, cylinder-disk, and sphere-disk hybrid nanoparticles. Furthermore, hierarchical multicompartment superstructures have been built up from multigeometry nanoparticles by taking advantage of their surface anisotropy and particle-particle association *via* either covalent or non-covalent bindings due to different chemical modifications.



Sunday, April 7, 2013 09:00 AM

Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)

Location: Hilton Riverside

Room: Ste. C, Sec 15

28 - Block copolymer templated nitrogen-enriched porous nanocarbons: From synthesis, characterization, to applications

Mingjiang Zhong, *mzhong@andrew.cmu.edu, Tomasz Kowalewski, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

Nitrogen-enriched porous nanocarbons were synthesized by thermal treatment of nanophase-separated block copolymers containing polyacrylonitrile and poly(butyl acrylate) (PAN-*b*-PBA) upon which PBA phase was thermally degraded, generating nanoscale porosity, while PAN phase was carbonized. Characterization by SAXS, AFM, N_2 adsorption, and XPS, revealed that copolymers with bi-continuous morphology yielded high surface area nanocarbons with high content of nitrogen heteroatoms originating from PAN. Such prepared nanocarbons exhibited high performance as electrode materials for supercapacitors, electrocatalysts for oxygen reduction, and CO_2 sorbents.

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Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)
Location: Hilton Riverside
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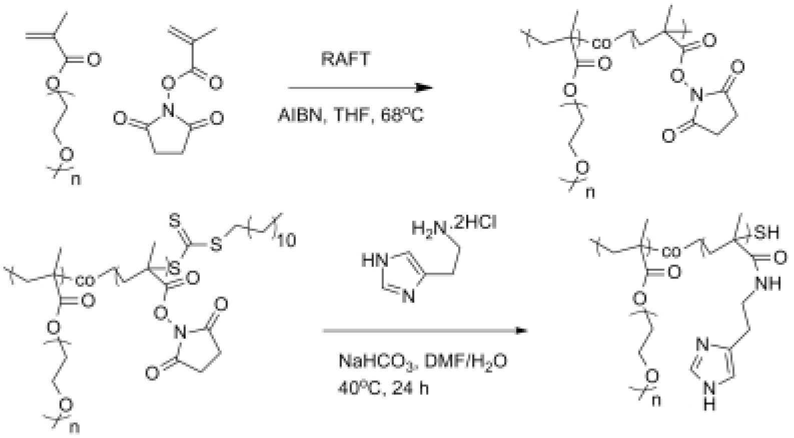
29 - Novel synthetic approaches for imidazole functionalized copolymers

Anand Viswanath, *viswanaa@email.sc.edu, Brian C Benicewicz. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States*

Several synthetic approaches have been designed for functionalizing water soluble Several synthetic approaches have been designed for functionalizing water soluble PEG based copolymers with imidazole moieties using the RAFT technique. One of the more versatile methods involved using the N-methacryloxy succinimide (NMS) monomer along with PEG-methacrylate to produce copolymers with variable loadings of NMS. The kinetics of this copolymerization was investigated with different ratios of the monomer and the reactivity ratios were calculated. Simple postmodification reactions with amine terminated imidazoles provided copolymers capable of attaching to CdSe based quantum dots. Other methods used involved methacylamide based imidazole monomers capable of polymerizing directly through the RAFT technique, and methacrylate based PEG monomers with imidazole groups. These techniques provide a toolbox of synthetic methodologies to precisely tailor the amount of imidazole units and have broad applicability to the loading of any amine/hydroxyl based compounds onto water soluble copolymers. Hence, the biological applicability of such polymers can be expanded to include previously incompatible moieties.

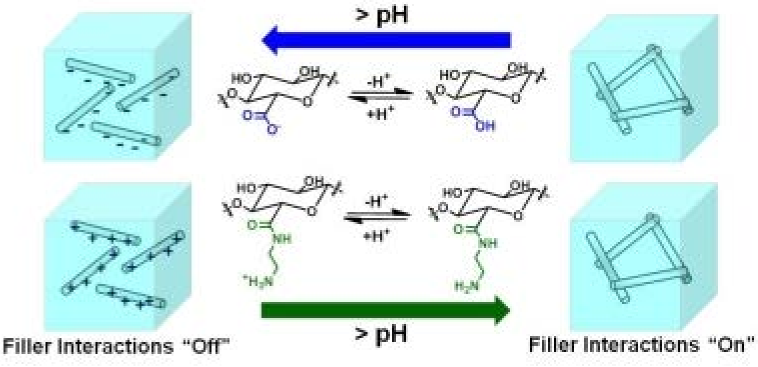


Sunday, April 7, 2013 09:50 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

30 - Surface interactions of functionalized cellulose nanocrystals

Amanda E Way[1], *aew38@case.edu, Lorraine Hsu*[1], *Kadhiravan Shanmuganathan*[1], *Christoph Weder*[2], *Stuart J Rowan*[1]. *(1) Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106, United States, (2) Polymer Chemistry and Materials, Univeristy of Fribourg, Fribourg, Switzerland*

Cellulose nanocrystals (CNCs) have attracted attention as potential green reinforcing fillers for polymer nanocomposites. A key aspect of these materials is the interactions between the CNC and matrix polymer as well as between the CNCs themselves. We have previously shown that charged CNCs allow access to water-responsive mechanically-dynamic materials. We are currently investigating the effect that chemical functionalization of the CNCs has on the properties of its nanocomposites. We have prepared CNCs functionalized with carboxylic acid (**CNC-CO$_2$H**) and amine (**CNC-NH$_2$**) moieties and shown that the modulus of the CNC dispersions is sensitive to pH. **CNC-CO$_2$H** dispersions increase in strength as pH is decreased, while **CNC-NH$_2$** dispersions decrease in strength as pH is decreased. When these CNCs were used as fillers in poly(vinyl acetate) nanocomposites it was demonstrated that pH-responsive films are obtained. Furthermore, grafting thermo-responsive polymers onto the CNC surface, via RAFT polymerization, has allowed access to reversible thermally-stiffening nanocomposites.



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Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)

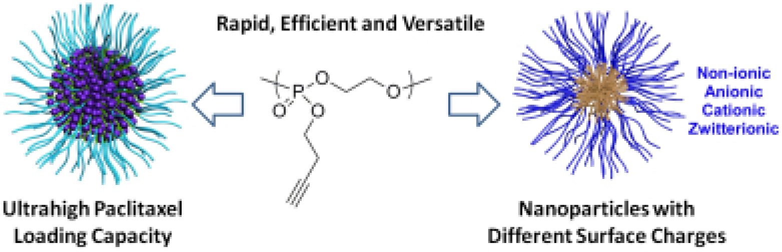
Location: Hilton Riverside

Room: Ste. C, Sec 15

31 - Versatile construction of polyphosphoester-based nanostructures for different biological applications

Shiyi Zhang[1,2], *shiyi.zhang@chem.tamu.edu, Fuwu Zhang*[1], *Jiong Zou*[1], *Mahmoud Elsabahy*[1,3], *Karen L Wooley*[1]. *(1) Departments of Chemistry and Chemical Engineering, Texas A&M University, College Station, TX 77842, United States, (2) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States, (3) Department of Pharmaceutics, Assiut University, Assiut, Egypt*

In this presentation, two degradable nanoparticle systems based on functionalized diblock polyphosphoesters and their applications in treating different diseases, such as pulmonary infections, injuries and cancers, will be discussed. The two nanoparticle systems were derived from a stable alkyne-functionalized phospholane monomer. In the first system, functional paclitaxel (PTX) drug conjugates were densely attached onto the poly(ethylene oxide)-*block*- poly(butynyl phospholane) by “click” type azide-alkyne Huisgen cycloaddition reactions with exceptionally high efficiency. The product drug conjugates could achieve a PTX loading capacity as high as 65 wt% and a water solubility at equivalent PTX concentration of 6.2 mg/mL. In the second system, the stable alkyne-functionalized phospholane monomer was polymerized into a hydrophobic-functional AB diblock polyphosphoester copolymer and the incorporated alkyne-functionalized block was further functionalized into four different charged hydrophilic block segments by “click” type thiol-yne reactions. The resulting four amphiphilic diblock copolymers were self-assembled into water directly, to afford uniform nanometer-sized non-ionic, anionic, cationic and zwitterionic micelles, respectively. The anionic and zwitterionic nanoparticles were designed to load silver ions to treat pulmonary infections. The cationic nanoparticles were applied to regulate lung injuries by a nanoparticle/siRNA delivery approach. This presentation will discuss the detailed design, synthesis, characterization and applications of those two nanoparticle systems, and will highlight the rapid, efficient and versatile chemistry involved in each stage of the production and utilization of these unique functional polymers and nanomaterials.



Sunday, April 7, 2013 10:55 AM

Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)

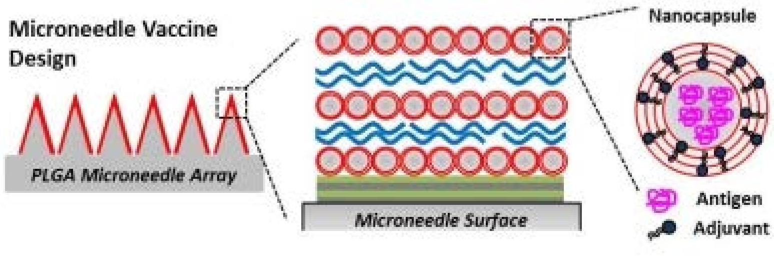
Location: Hilton Riverside

Room: Ste. C, Sec 15

32 - Layer-by-layer assembly of lipid nanocapsules on microneedles for enhanced transcutaneous vaccine delivery

Peter C DeMuth[1], *pcdemuth@mit.edu, James J Moon*[1,4], *Heikyung Suh*[1,4], *Paula T Hammond*[2,4,5], *Darrell J Irvine*[1,3,4,5,6,7]. *(1) Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (2) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (3) Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (4) Koch Institute for Integrative Cancer Research, Cambridge, MA 02139, United States, (5) Institute for Soldier Nanotechnology, Cambridge, MA 02139, United States, (6) Ragon Institute of MGH, MIT, and Harvard, Charlestown, MA 02129, United States, (7) Howard Hughes Medical Institute, Chevy Chase, MD 20815, United States*

Functional vaccine coatings were assembled on the surface of poly(lactide-*co*-glycolide) microneedles using layer-by-layer deposition of degradable poly(beta-amino-esters) with lipid nanocapsules containing protein antigen and immune-stimulatory adjuvants. This process allowed controllable encapsulation of intact nanocapsules into microneedle-based surface-films. Application of vaccine-coated-microneedles *in vivo* gave rapid implantation of films into the skin forming depots to sustain vaccine release through poly(beta-amino-ester) degradation. Microneedle-vaccines generated localized influx/activation of immune cells, cell uptake of vaccine-nanocapsules, and induced enhanced antigen-specific antibody responses.



Sunday, April 7, 2013 11:20 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

33 - Recent developments in polymerisable liquid crystals

Owain L Parri, *owain.parri@merckgroup.com, Joe Sargent, Kevin Adlem, Eduardo Beltran, Laura Ramon. Chilworth Technical Centre, Merck Chemicals Ltd, Southampton, Hampshire SO16 7QD, United Kingdom*

Over the past few years, the market size for optical films consisting of anisotropic networks formed from polymerisable liquid crystal via the process of in-situ photopolymerisation has increased significantly. This paper aims to discuss the latest developments in polymerisable liquid crystal materials.

It is well known that liquid crystals have significant wavelength dispersion which is related to the material properties of the liquid crystal. New polymerisable formulations with controllable wavelength dispersion properties have been developed. These formulations allow optical films with tuneable wavelength dispersion to be prepared.

Figgure 1: SEM, polarised optiocal microscopy and AFM of a anisotropic optical and shaped partical with proposed LC director structure.

It has also been reported in the literature that polymerisable liquid crystals can be processed into micron-sized particles which possess internal anisotropy. Recently it has been demonstrated that these particles can be synthesised by a processed which can be considered scalable. Furthermore, particles with interesting properties including shape anisotropy can be synthesised using this method.

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Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
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34 - In-situ polymerized liquid crystal networks: 25 years of research on their formation, properties, and applications

Dick Broer, *D.Broer@tue.nl, Chemical Engineering & Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*

Anisotropic polymer networks have found applications in optics, electronics and mechanics. A preferred way of making them is by photopolymerization of monolithically aligned liquid crystal monomers. The lecture will provide a short historic overview on their development in a framework of properties and applications. Special attention in the lecture will be paid to the structure-property relationships of the monomers and the networks that they form; still being relevant for applications that are currently under development. In addition the lecture will discuss early applications as optical fiber coatings, polarizing beamsplitters, color filters, optical retarders, transflective retarders, reflective polarizers and viewing angle improving films for LCDs.

Sunday, April 7, 2013 08:30 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
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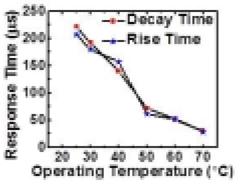
35 - Submillisecond-response and scattering-free liquid crystal spatial light modulators

Shin-Tson Wu, *swu@ucf.edu, College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816-2700, United States*

We demonstrate a scattering-free polymer network liquid crystal spatial light modulator with submillisecond response time and 2-pi phase change in the short-wavelength infrared region. As shown in Fig.1, when the operation temperature increases from 25^{o}C to 70^{o}C, the response time decreases from 220 µs to 30 µs, but the operating voltage at l=1.06 µm increases from 70V to 90V. Meanwhile, hysteresis is suppressed from 7.7% to 2%. If reflective mode is employed, operating voltage can be further reduced.



Sunday, April 7, 2013 09:00 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

36 - Liquid crystal lasers: From materials to realization

***Harry J Coles**, hjc37@cam.ac.uk, Centre of Molecular Materials for Photonics and Electronics, Electrical Engineering, University of Cambridge, Cambridge, Cambridgeshire CB3 0FA, United Kingdom*

Liquid Crystal Lasers are now recognised [1] in many forms, band -edge, random, defect mode to name but a few. Lasing has been observed in Blue Phases, Chiral Nematic, Defect Doped Nematics and Chiral/Achiral Smectics. We have found that Long-Wavelength Band Edge Lasing in Chiral Nematics give the highest slope efficiency (~70%), where, slope efficiency is defined as the lasing energy output/energy input/pulse [2]. We describe the background to Microscopic Liquid Crystal lasers, based on dye doped Chiral Nematics, their *modus operandi* and then consider the key materials properties of the liquid crystal host & cavity design that lead to such high slope efficiencies, low laser thresholds (~25nJ/pulse), narrow line widths (<0.01nm), laser outputs continuously tunable over a 450 to 850 nm wavelength range and quasi-continuous working (3kHz pulse rate) giving average powers of 5mW per pixel or laser spot. Laser pulse widths are typically 1-5ns.

The birefringence, the elastic constants and the orientational order parameters of the liquid crystals and the fluorescent light harvesting dye are the key parameters that influence markedly the performance of such LC lasers. 2-D lenslet arrays of up to 100 by 100 spots have been used to give a quasi- continuous working wide colour gamut RGB laser output [3] with powers of Watts in the far field. Such outputs may be combined to give “white light” laser based outputs. These lasers may be continuously wavelength tuned and we will discuss how they may be deposited from emulsions and ink-jet printed on to polymer substrates leading to novel laser geometries with a wide range of spectroscopic applications.

[1] H.J. Coles, S.M. Morris, Nature Photonics, **4** , 676 (2010).

[2] C. Mowatt, S.M. Morris, T.D. Wilkinson, and H.J. Coles, Appl. Phys. Lett. **97** , 251109 (2010).

[3] S.M. Morris, et al, Optics Express, **16** (23), 1882(2008)

Sunday, April 7, 2013 09:30 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

37 - Tailoring polymer stabilized liquid crystal alignment for device applications

Liang-Chy Chien, *lchien@kent.edu, Jeoung-Yeon Hwang. Department of Chemical Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, United States*

We propose and demonstrate a new approach of liquid crystal alignment for achieving enhanced electro-optical performance for device applications. Our approach makes use of a polymer stabilization alignment (PSA) by forming polymer nanostructures (spikes or fibrils) localized at the substrate surface and with a unidirectional orientation. The morphological studies depict that the spatially oriented polymer nanostructures have diameter smaller ranging from 20 to 100 nm and length of 50 nm to few hundred nanometers, and in some case, the nanostructures have a few microns depending on the concentration of polymer (see Fig. 1). We also show that the physical, dielectric and electro-optical properties a PSA device can be significantly improved due to the increase in strength of surface anchoring. Furthermore, the PSA devices maintain the same level of light transmission as that of the device without PSA.

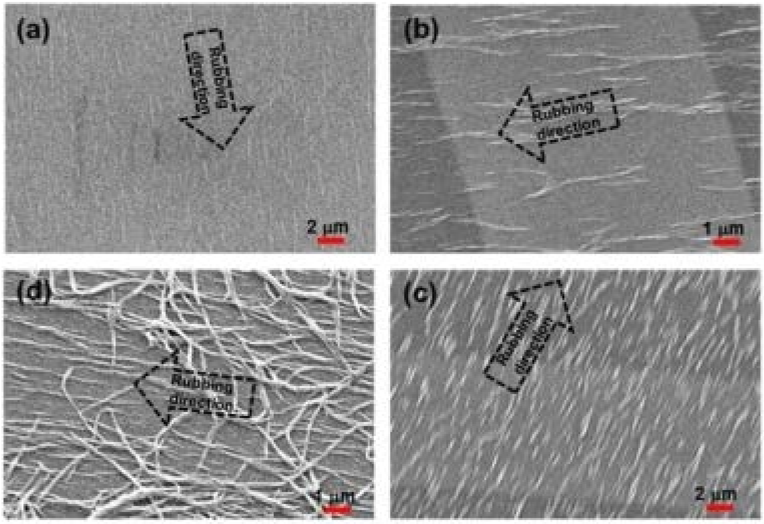


Figure 1: SEM images of the top view of (a) 0.2% polymer nanofilbrils, (b) 1% polymer nanofilbrils, and (c) 3% polymer nanofilbrils, with a preferential orientation following the PI rubbing direction, and (d) top view of a 5% polymer fibrils with a preferential orientation following the PI rubbing direction.

Sunday, April 7, 2013 10:15 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

38 - Dynamic reflection notch broadening in polymer stabilized cholesteric liquid crystals

Lalgudi V Natarajan[2], *Nakaseni@gmail.com, Vincent P Tondiglia*[2], *Kyungmin Lee*[1], *Mike McConney*[1], *Timothy J Bunning*[1], *Timothy J White*[1], *Chad M Keister*[1]. *(1) Air Force Research Laboratory, Materials and Manufacturing Ditrectorate, WPAFB, Dayton, OH 45433, United States, (2) SAIC, DAYTON, OH 45431, United States*

A dynamic broadened reflection band was achieved when a weakly polymer stabilized cholesteric liquid crystal containing a negative dielectric anisotropy nematic was subjected to a low DC field (< 3V/µm). The broadening effect was significant as the notch bandwidth enlarged symmetrically up to 3 times from its original value. A seven fold increase in bandwidth was observed for 22 mm thick cells which contained LCs with small birefringence (~0.04). The broadening effect is proportional to the strength of the applied DC field and relaxes to the original bandwidth when the DC field is removed. Fields, greater than a critical value cause a blue shift of the broadened band. The cholesteric mixture consisted of the chiral dopant S811, the negative dielectric LC ZLI-2079, 5% LC diacrylate monomer RM257 and 0.05% of UV initiator Irgacure 369. The weakly polymer stabilized network was formed by UV curing. Monomer concentrations were varied from 2 to 10 percent by weight showing best performance at concentrations of about 5 percent. The response times were on the order of ~10 secs and the relaxation ~ 2 secs. Addition of small amounts of a less viscous chiral dopant Limonene significantly reduced the response times. Different mechanisms for the broadening effects will be discussed to experimental results.

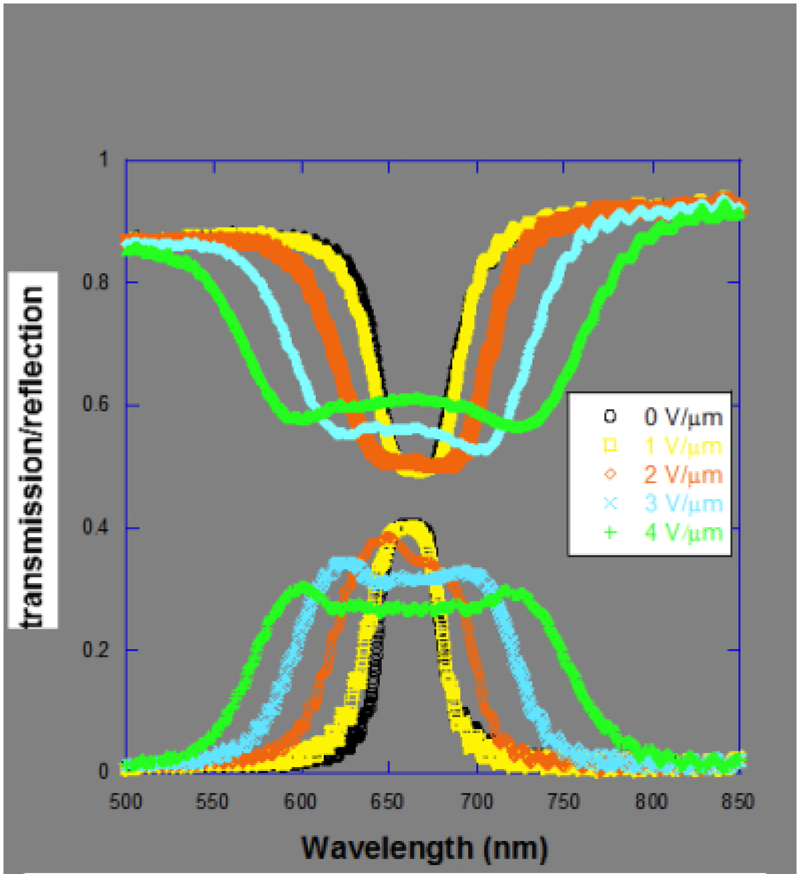


Figure 1:Reflection and transmission spectra showing symmetrical broadening at low DC fields. A 3.7 fold increase in bandwidth seen.

Sunday, April 7, 2013 10:45 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

39 - Large reflection notch tuning of cholesteric liquid crystals stabilized by chiral liquid crystal polymers

Kyung Min Lee[1,2], *kyungmin.lee@wpafb.af.mil, Lalgudi V Natarajan*[1,3], *Vincent P Tondiglia*[1,3], *Michael E McConney*[1,2], *Timothy J Bunning*[1], *Timothy J White*[1]. *(1) Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, OH 45433, United States, (2) Azimuth Corporation, Dayton, OH 45458, United States, (3) Science Applications International Corporation, Dayton, OH 45431, United States*

Manipulating the reflection color of cholesteric liquid crystals has potential utility in optics, photonics, and displays. We report here on red-shifting tuning of the reflection notch of a polymer stabilized cholesteric liquid crystal upon application of a DC field. The utilization of chiral liquid crystal monomers in the fabrication of the polymer network is shown to be the key enabler to this observation. The pre-polymer syrup consisted of a chiral dopant R1011, a negative dielectric nematic LC ZLI-2079, a LC chiral diacrylate and a UV photoinitiator. To understand the role of polymer network chirality to enabling the large range color tuning, PSCLCs were prepared with various ratio of LC achiral vs. LC chiral monomers. Large red tuning behaviors are reported by chiral monomer content in the polymer network, as can be seen in Figure 1. Sample preparation methods to reduce scatter will also be discussed.

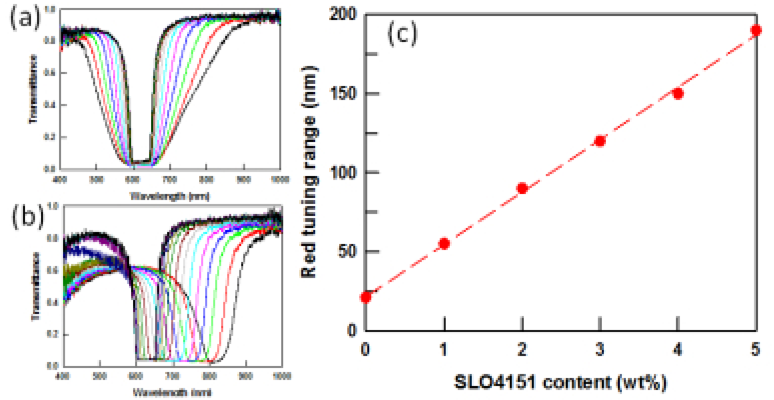


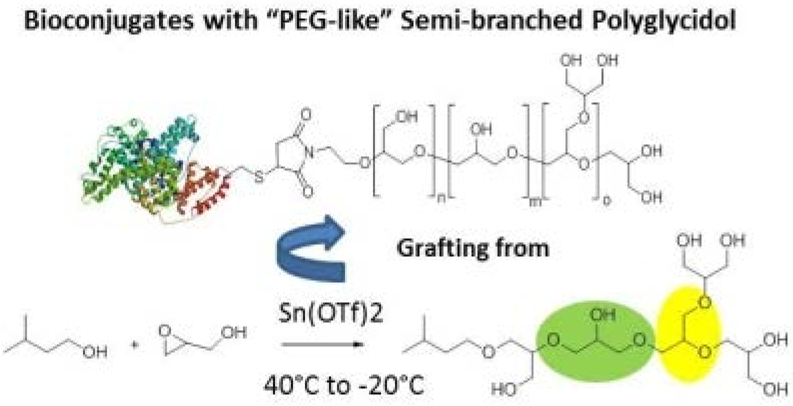
Figure 1. Electro-optical responses of PSCLCs with (a) achiral monomer (RM257) and (b) chiral monomer (SLO4151) when subjected to 0 to 65 V DC at room temperature. (c) Red-tuning range of the PSCLCs is plotted against the concentration of the chiral monomer SLO4151.

Sunday, April 7, 2013 11:05 AM
Liquid Crystals and Polymers (08:00 AM - 11:25 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

40 - Release dynamics in nanosponge materials and the formation of "peg" like polyglycidols

Eva Harth, *eva.harth@vanderbilt.edu, David M Stevens, Benjamin Spears, Guangzhao Li, Ghazal Hariri. Chemistry, Vanderbilt University, Nashville, Tennessee 37235-1822, United States*

Supramolecular nanosponges prepared from bottom up approaches are optimized towards the anticpated release rate and the structure property relationship is discussed. Crosslinking density, polyester and polycabonate backbone length are one of the measures that determines the release kinetic. Integrated functional groups enable practical conjugation of targeting units and dyes. To solubilize and stabilize protein therapeutics in a grafting-from approach semibranched polyglycidols were grown to form in situ "PEG" like surface shells to function as advanced pegylations.

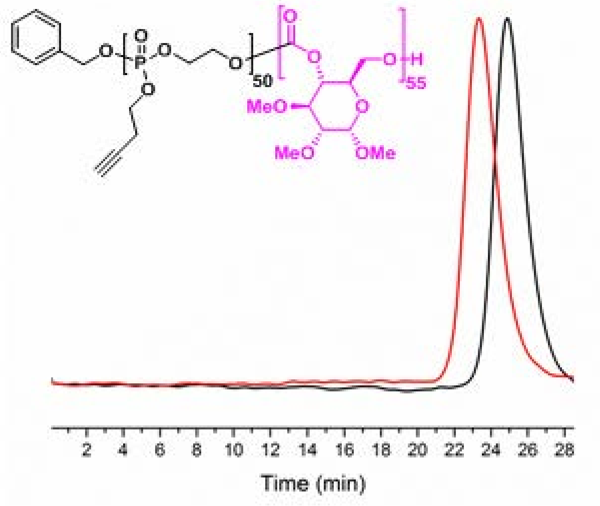


Sunday, April 7, 2013 08:35 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

41 - New generation of polycarbonate biomaterials from cyclic carbonate monomers of glucose

Tiffany P Gustafson, *tiffany.gustafson@chem.tamu.edu, Alexander T Lonnecker, Shiyi Zhang, Karen L Wooley. Department of Chemistry, Texas A&M University, College Station, TX 77842, United States*

Degradable polymeric nanostructures based upon polycarbonates, polyesters and polyanhydrides are widely utilized in the design of polymeric materials for biomedical applications. Upon hydrolytic degradation these materials form potentially toxic, inflammatory and corrosive degradation products. To develop the next generation of polymeric biomaterials we aim to design monomers which can form materials based upon nature's building and energy storage materials, cellulose and starch. The result is a new bioresorbable polycarbonate designed from a natural product based cyclic carbonate monomer of D-glucose which undergoes degradation to the D-glucose starting material and CO_2. This polycarbonate has been utilized to design novel block copolymers with applications ranging from nanomedicine to biomedical engineering of implantable materials. The ability to control the chemical functionality of these polymers through thiolene and thiolyne click chemistry has lent itself to the development of shell crosslinked knedel-like (SCK) nanoparticles which are being utilized in the design of theranostic agents for treatment of acute lung injury and cancer.

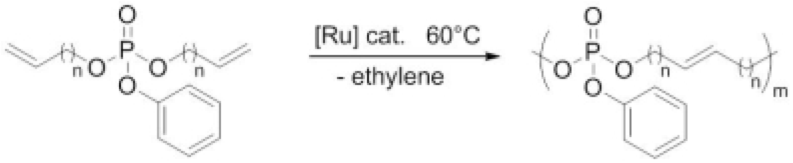


Sunday, April 7, 2013 09:05 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

42 - Tailored to degrade: Novel poly(phosphoester)s for bioapplications

Frederik R. Wurm[1], *wurm@mpip-mainz.mpg.de, Evandro Alexandrino*[1], *Filippo Marsico*[1], *Tobias Steinbach*[1,2], *Sandra Ritz*[1], *Volker Mailänder*[1], *Katharina Landfester*[1]. *(1) Max Planck Institute for Polymer Research, Mainz, Rheinland Pfalz 55128, Germany, (2) Department of Organic Chemistry, Johannes Gutenberg-Universität, Mainz, Rheinland Pfalz 55128, Germany*

The need for biodegradable polymers is self-evident; not only for plastics but moreover for biological relevant and other applications the degradation of polymeric materials is crucial. Typically the research is focused on polyesters based on carboxylic acids like lactic acid or similar. We are investigating novel synthetic strategies to poly(phosphoester)s which have many advantages over the classical polyesters, such as tunable solubility, functionality and degradation with respect to drug delivery and nanoparticle synthesis.



Sunday, April 7, 2013 09:25 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

43 - Synthesis of core-corona type nanosphere having thermoresponsive polymers with controlled chain length and their thermoresponsive behavior

Takuya Matsuyama, *takuya827@hotmail.co.jp, Taka-Aki Asoh, Akihiko Kikuchi. Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan*

We report about synthesis and characterizations of thermoresponsive core-corona type nanosphere with controlled corona chain length. Nanospheres having PNIPAAm cilia with narrow polydispersity were prepared by copolymerization of PNIPAAm macromonomer and styrene. In addition, effect of PNIPAAm molecular weight on sphere diameters was investigated using SEM. As a result, PNIPAAm have important role as a dispersant. Finally, we investigated that dispersion stability of thermoresponsive nanospheres. Obtained nanospheres were colloidally stable at 20^{o}C, but precipitated at 37^{o}C.

Sunday, April 7, 2013 09:45 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

44 - Bioinspired soft materials to direct stem cell function and tissue regeneration

Kevin E. Healy, *kehealy@berkeley.edu, Departments of Bioengineering and Materials Science & Engineering, University of California, Berkeley, Berkeley, CA 94720, United States*

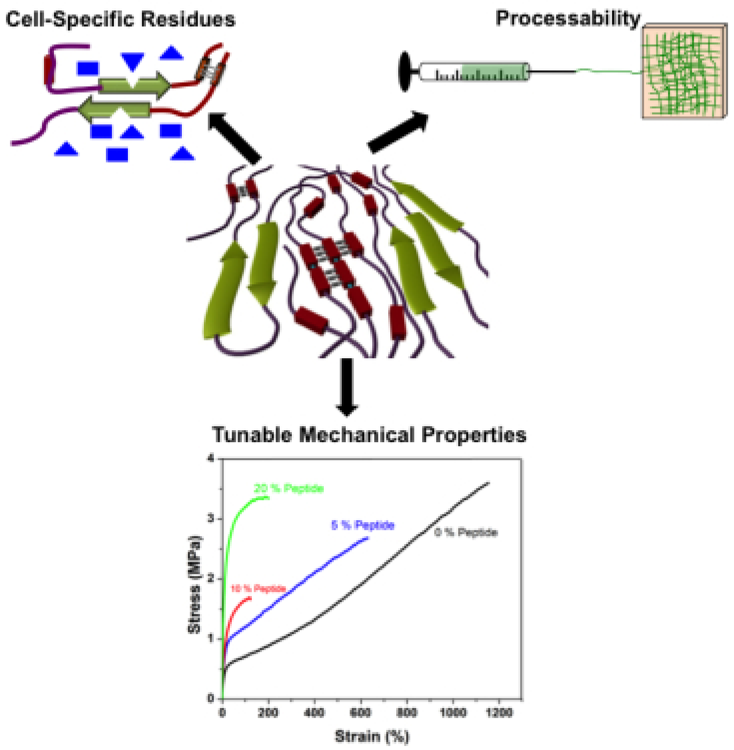
Highly regulated signals in the stem cell microenvironment, such as growth factor presentation and concentration, matrix stiffness, and ligand adhesion density have been implicated in modulating stem cell proliferation and maturation. Therefore, it is desirable to have independent control over both the biochemical and mechanical cues presented to cells to analyze their relative and combined effects on stem cell function. Accordingly, we have developed synthetic hydrogels to assess the effects of adhesion ligand presentation and material moduli spanning physiologically relevant ranges (10 to 10,000 Pa) on stem cell function. Employing these soft materials, we have demonstrated that the mechanical and biochemical properties of a stem cell microenvironment can be tuned to regulate the self-renewal and differentiation of different types of stem cells including human embryonic, neural, and mesenchymal stem cells. We have further modified these tunable biomimetic hydrogels with matrix metalloproteinase labile crosslinkers (e.g. MMP-2, 9 &13), to be used as an assistive microenvironment for transplantation of stem cells into diseased or damaged tissue such as the infracted myocardium. We hypothesize that injectable bioinspired hydrogels, designed with a range of mechanical and biological properties, will yield material-dependent improvements in cardiac function post myocardial infarction. Injection of cells alone created a transient improvement in LV function that declined over time, while the hydrogel without cells experienced a gradual increase in cardiac function and resulted in the highest LV function at 6 weeks. The bioinspired hydrogel succeeded in both mechanically supporting the injured myocardium and modestly enhancing donor cell survival. This bioinspired hydrogel system also provides a foundation for systematic development of “pro-survival” microenvironments for cell transplantation and has the potential to improve the long-term results of cardiac therapies.

Sunday, April 7, 2013 10:20 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

45 - Reinforcement of bio-inspired elastomers via control of secondary structure

*J. Casey Johnson, Nandula D Wanasekara, **LaShanda TJ Korley**, lashanda.korley@case.edu. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

We have utilized a bio-inspired approach, particularly the incorporation of ordered regions, to generate functional, polymeric hybrids with tunable mechanical properties. Multi-block copolymers, which mimic the microstructure of numerous natural materials, are ideal systems with which to explore 'soft' domain ordering via variations in secondary structure of polypeptide-based block copolymers. A new class of elastomeric polyurethane/ureas have been synthesized that incorporate either a purely amorphous soft segment or a b-sheet dominated, peptidic soft segment. These materials exhibit a range of mechanical responses, are processable in film and fiber form, and offer opportunities to tailor degradation pathways and to incorporate cell-specific sequences for applications in tissue engineering scaffolds and smart coatings.



Sunday, April 7, 2013 10:50 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

46 - Multiblock copolymemrs based on PEGylated poly(amino acid)s

Carmen Scholz[1], *cscholz@chemistry.uah.edu, Michihiro Iijima*[2], *David Ulkoski*[1]. *(1) Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, United States, (2) Department of Chemistry, Oyama National College of Technology, Oyama, Tochigi 323-0806, Japan*

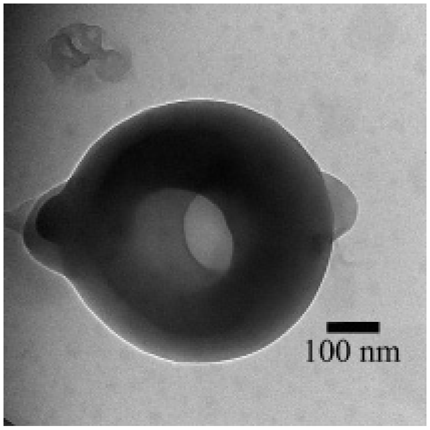
Using amino-terminated poly(ethylene glycol), PEG, as macroinitiator, block copolymers consisting of PEG and poly(amino acids), paa's, are produced by the ring-opening polymerization, ROP, of amino acid N-carboxyanhydrides, NCA's. The use of a-methoxy-w-amino poly(ethylene glycol), leads to the formation of asymmetrical ABC terpolymers where the B and C blocks constitute a paa copolymer. Since the ROP of amino acid NCA displays living characteristics under the conditions used here (low temperature, 0.1 M urea) the paa BC copolymer can be synthesized as a block copolymer or a random copolymer. Using telechelic PEG diamine leads to the formation of symmetrical BAB and CBABC multiblock copolymers, where the B and C blocks are again paa's and the A block constitutes PEG. Poly(*L*-glutamate), pGlu, and poly(*L*-leucine), pLeu, were used as poly(amino acids)locks and formed the hydrophobic moiety of the resulting amphphilic block copolymers. The protection/deprotection chemistry of the g-carboxyl group of pGlu allows for further fine-tuning the hydrophilic-hydrophobic balance of the resulting copolymers. While ABC terblock copolymers form polymeric micelles, the CBABC pentablock copolymers are expected to form “flower-like” micelles with PEG loops with the possibility of nanostructure bridging. Bridges form when polymer chains are exchanged between individual micelles thus forming connections between the nanostructures. The synthesis and self-assembly properties of the resulting block copolymers will be discussed.

Sunday, April 7, 2013 11:20 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

47 - Bioinspired polymeric catalytic template for structured silica and catalytically active titania formation

*Chetan C. Hire[1], Homer C. Genuino[2], Steven L. Suib[2], **Douglas H. Adamson**[1,2], Adamson@UConn.edu. (1) Institute of Materials Science Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United States, (2) Department of Chemistry, University of Connecticut, Storrs, CT 06269-3036, United States*

Previous studies of the enzyme silicatein a have shown that serine and histidine are critical to the catalytic function of the enzyme for tetraethyl orthosilicate (TEOS) hydrolysis. Incorporating these functional groups into a synthetic block copolymer, we show the templated and catalyzed formation of silica and titania. Further, the titania is shown to be catalytically active with a morphology differing from sol-gel produced material. Silica is shown to templated at both the nanometer and micrometer scale.



Sunday, April 7, 2013 11:40 AM

Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 12:00 PM)

Location: Hilton Riverside

Room: Ste. C, Sec 13/16

48 - Synthesis of amino acid containing block copolymers

Alexander J. Lou, *alexander.j.lou@williams.edu, Nai Chien Yeat, Elizabeth E. Hwang, Charles E. Seipp,* ***Sarah L. Goh****, sgoh@williams.edu. Department of Chemistry, Williams College, Williamstown, MA 01267, United States*

Chemotherapy is plagued by poor drug specificity and retention rates, resulting in excessive dosing and death of healthy cells. By encapsulating hydrophobic drugs in self-assembled micelles formed by amphiphilic block polymers, we can create a vessel that addresses both problems simultaneously through the enhanced permeation and retention effect. Diblock copolymers were synthesized using the reversible addition fragmentation chain transfer polymerization technique. Poly(acrylic acid) served as the hydrophilic domain. For the hydrophobic block, phenylalanine and valine monomers were functionalized at their N-terminus with a methacrylate group. The effects of amino acid and end group identity on micelle formation were explored. Copolymers exhibited low critical micelle concentrations on the order of 10 m*M*. Dynamic light scattering confirmed the presence of micelles approximately 30 nm in diameter. Due to their self-assembling nature, these polymers have promise for drug delivery applications.

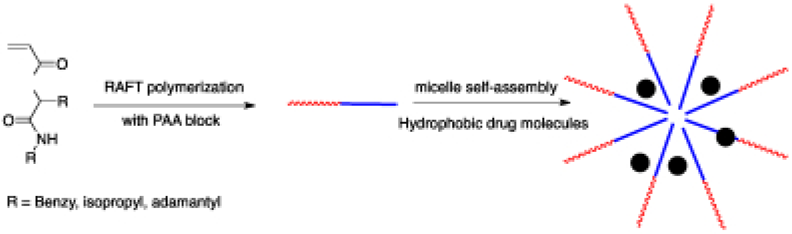


Figure 1. Synthesis of diblock copolymers and micelles.

Sunday, April 7, 2013 01:30 PM

Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)

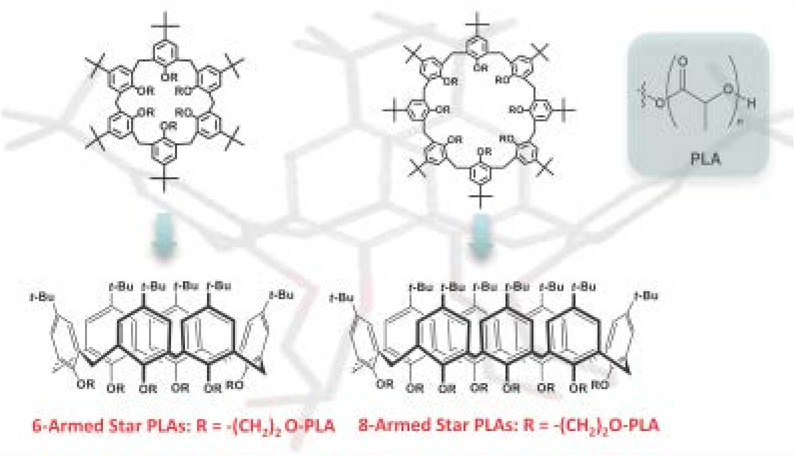
Location: Hilton Riverside

Room: Ste. A, Sec 6

49 - Synthesis, characterization, and degradation of multi-armed calixarene-core polylactide star polymers

Anna C Falls, *pcorbin@ashland.edu, Mei Li, Perry S Corbin. Department of Chemistry, Ashland University, Ashland, OH 44805, United States*

Polylactide (PLA) and related polyesters have been employed in biomedical applications and are becoming more prominently used in commercial packaging materials. One potential method of expanding the properties of this class of renewable, biodegradable plastics is to prepare PLAs with varied architectures and with cores that can be further functionalized. As such, six- and eight-armed calixarene-core star L-PLAs were synthesized. The synthesis was accomplished by preparing calixarene initiators with six and eight primary alcohol functional groups. Polymers with varying numbers of repeat units per arm were then synthesized in solution by Sn(II)-catalyzed ring-opening polymerizations of L-lactide using the macrocyclic initiators. The star PLAs were characterized by GPC and were found to have low PDIs and M_n's close to those targeted. Moreover, end-group analysis by ^{1}H NMR spectroscopy supported star polymer production. DSC studies have, in turn, revealed that the crystallization rates of lower M_n six- and eight-armed calixarene-core PLAs are slower than their linear counterparts and that the percent crystallinity can be finely adjusted with annealing. This observation suggests that the degradation rates of the lower M_n PLAs might be readily tuned. Along these lines, the degradation of low M_n six- and eight-armed PLAs and previously prepared four-armed calixarene-core PLAs were studied in basic solution. Rapid surface degradation that depended upon the initial crystallinity of the PLAs was observed. Further degradation studies under physiological conditions are in progress.

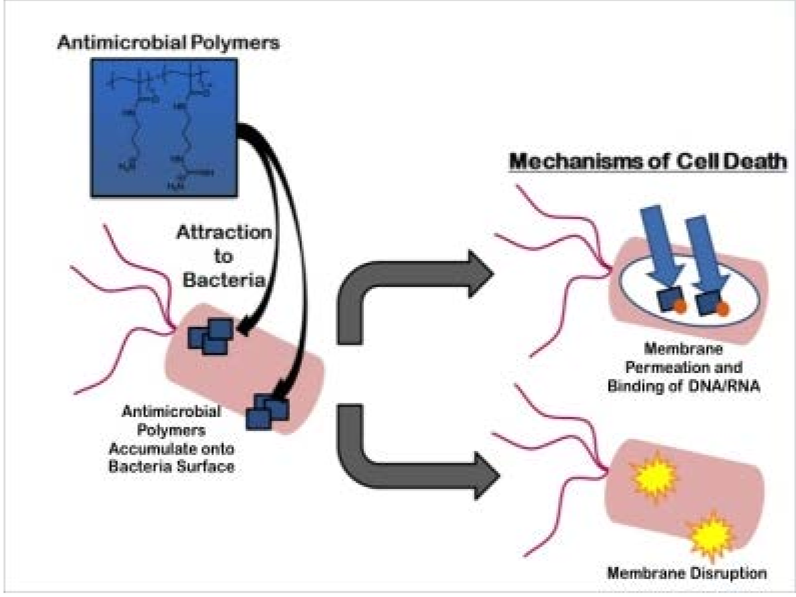


Sunday, April 7, 2013 01:45 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

50 - Synthesis of guanidino and primary amine functional copolymers to mimic antimicrobial peptides

Nicholas D Posey[1], *poseyn@xavier.edu, Paslay C Lea*[2]*, Brooks A Abel*[2]*, Andrew C Holley*[2]*, Charles L McCormick*[2]*, Sarah E. Morgan*[2]*. (1) Department of Chemistry, Xavier University, Cincinnati, Ohio 45207, United States, (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Antimicrobial Peptides (AMPs) selectivly eliminate bacteria while exhibiting minimal toxicity to eukaryotic tissues. Recently, interest in mimicking AMPs synthetically has emerged. In this research, AMP-mimicking moieties were incorporated into copolymers in order to emulate these naturally occurring peptides. A homopolymer of N-(3-aminopropyl) methacrylamide (APMA) was synthesized via RAFT polymerization and characterized via ^{1}H NMR and ASEC-MALLS. To convert the primary amines of PAPMA to guanidine moieties the homopolymer was reacted with N,N'-di-Boc-1H-pyrazole-1-carboxamidine (PCA) at varying primary amine to PCA ratios.

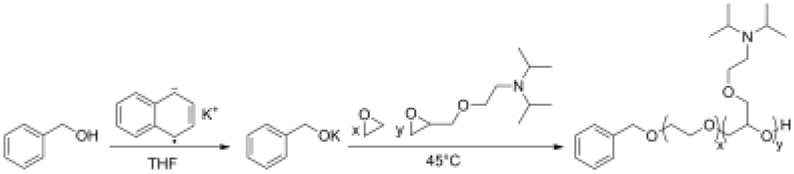


Sunday, April 7, 2013 02:00 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

51 - Synthesis of pH-responsive poly(ethylene oxide) derivatives for applications in biomedicine

Annabelle Lee, *annabelle@mrl.ucsb.edu, Pontus Lundberg, Daniel Klinger, Nathaniel A Lynd, Craig J Hawker. Department of Materials, University of California Santa Barbara, Santa Barbara, California 93106, United States*

Poly(ethylene oxide) (PEO) is widely used in biomedical applications today. By introducing responsive moiety to the PEO backbone, materials can be tailored for emerging applications in drug-delivery and nanomedicine. By using anionic ring opening polymerization, statistical and block copolymers of ethylene oxide (EO), allyl glycidyl ether (AGE), and N,N-diisopropyl ethanolamine glycidyl ether (DIEAGE) were synthesized. The pH- and thermal responsiveness of these copolyethers could be controlled by the relative incorporation of EO, AGE, and DIEAGE into a single polyether material.

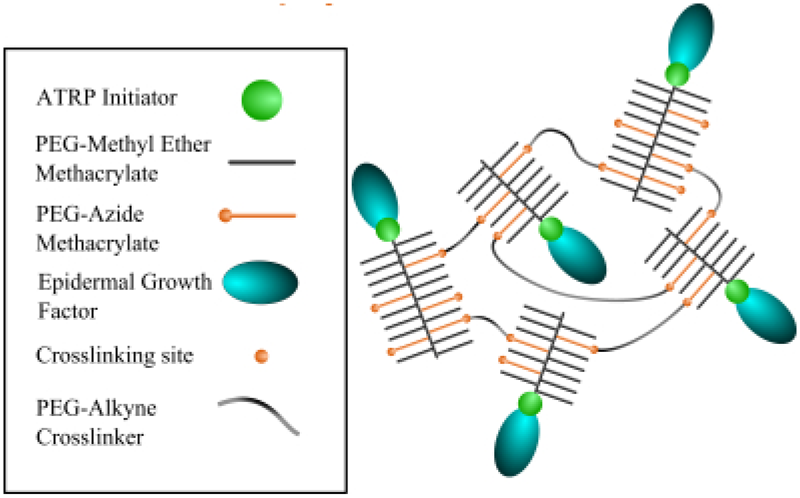


Sunday, April 7, 2013 02:15 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

52 - Controlled release of genetically engineered epidermal growth factor from poly(ethylene glycol methacrylate) hydrogels in response to matrix metalloproteinases

John F Edelbrock, *jfe26@case.edu, Si Eun Kim, Jonathan Pokorski. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

Proteins have great potential as therapeutic tools owing to their high bioactivity and specificity, but translating these therapies to the clinic is difficult due to the limited bioavailability of proteins administered systemically. Programmed release of proteins from bulk polymeric materials would greatly improve their usefulness within implantable devices. We have synthesized cross-linked poly(ethylene glycol methacrylate) hydrogels grafted-from genetically engineered epidermal growth factor using atom transfer radical polymerization and report their release profiles in response to biologically relevant proteases.

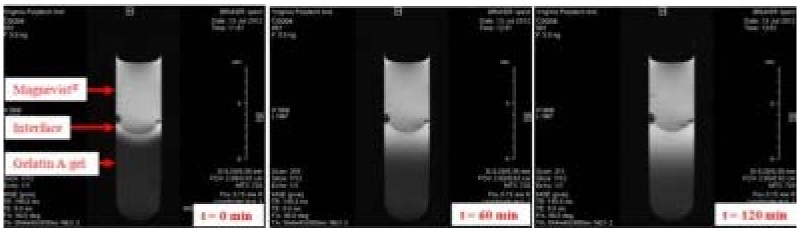


Sunday, April 7, 2013 02:30 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

53 - MicroMRI transport study of polymer beacons for combined DNA delivery and image contrast

Monica D. Boatwright[1], *monica.boatwright22@gmail.com*, *Xiaoling Wang*[2], *Carmen Scholz*[1], *Louis A. Madsen*[2]. *(1) Chemical Engineering, The University of Alabama in Huntsville, Huntsville, Alabama 35806, United States, (2) Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States*

Polymer beacon “theranostics” have been developed that allow the simultaneous delivery of DNA therapeutics and tracking of the delivery vehicle through Magnetic Resonance Imaging (MRI). We aim to determine transport mechanisms of polymer beacons by controlled *in vitro* experiments to optimize theranostic agents. We are developing a method utilizing microMRI to measure the diffusion and flow properties of theranostic agents through artificial human tissue mimics. In initial studies, self-diffusion was determined to be the driving force of contrast agent infusion.

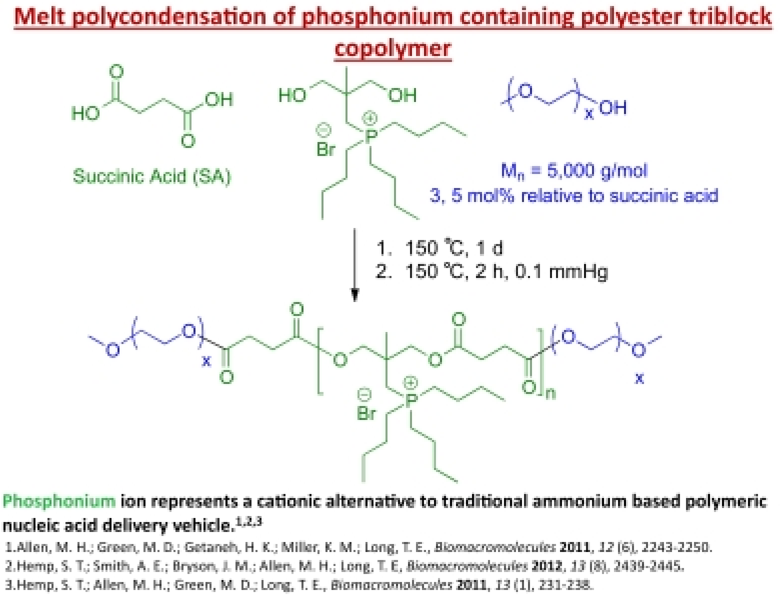


Sunday, April 7, 2013 02:45 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

54 - Novel phosphonium containing polyester triblock copolymers for nucleic acid delivery

Richard Nicholas Carmean[1], *cmean17@vt.edu, Musan Zhang*[2], *Timothy Long*[2]. *(1) Department of Biochemistry, Virginia Tech, Blacksburg, VA 24060, United States, (2) Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24060, United States*

Phosphonium-containing triblock copolyesters

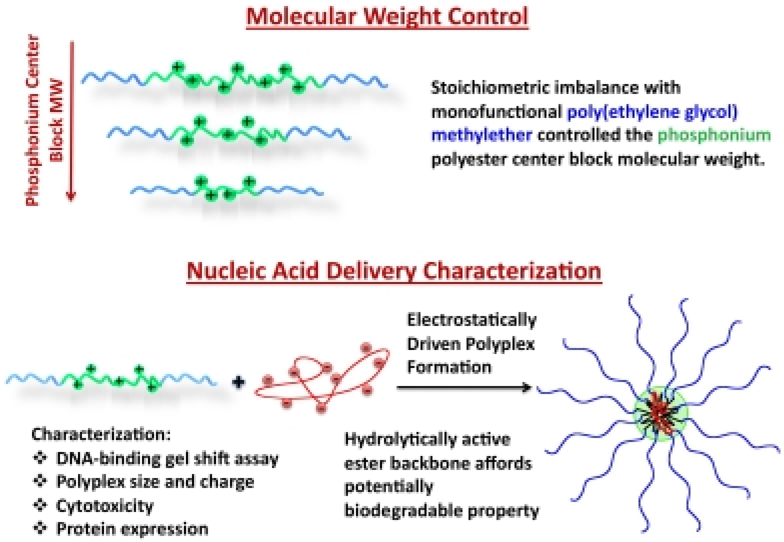


Melt polycondensation of phosphonium containing polyester triblock copolymer

Phosphonium ion represents a cationic alternative to traditional ammonium based polymeric nucleic acid delivery vehicle.[1,2,3]

1.Allen, M. H.; Green, M. D.; Getaneh, H. K.; Miller, K. M.; Long, T. E., *Biomacromolecules* **2011**, *12* (6), 2243-2250.
2.Hemp, S. T.; Smith, A. E.; Bryson, J. M.; Allen, M. H.; Long, T. E, *Biomacromolecules* **2012**, *13* (8), 2439-2445.
3.Hemp, S. T.; Allen, M. H.; Green, M. D.; Long, T. E., *Biomacromolecules* **2011**, *13* (1), 231-238.

for non-viral gene delivery



Molecular Weight Control

Stoichiometric imbalance with monofunctional poly(ethylene glycol) methylether controlled the phosphonium polyester center block molecular weight.

Nucleic Acid Delivery Characterization

Characterization:
- DNA-binding gel shift assay
- Polyplex size and charge
- Cytotoxicity
- Protein expression

Hydrolytically active ester backbone affords potentially biodegradable property

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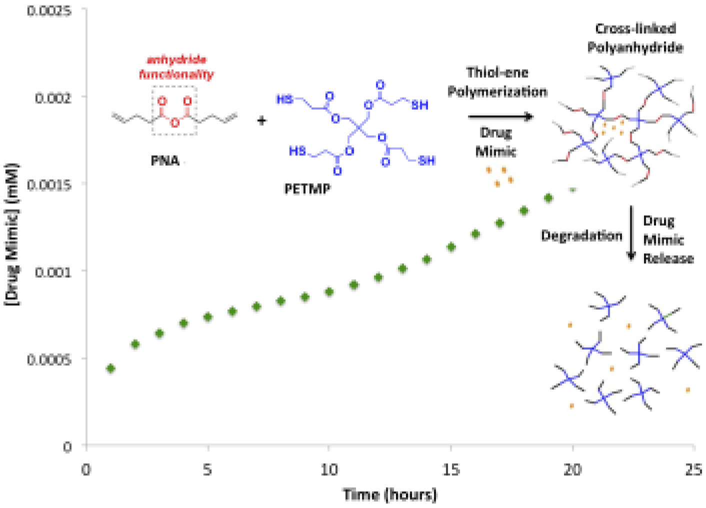
Sunday, April 7, 2013 03:15 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

55 - Drug release kinetics from cross-linked polyanhydrides

Nicole A Traphagen, *traphana@clarkson.edu, Katie L. Poetz, Devon A. Shipp. Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, NY 13699-5810, United States*

Most polymer-based drug delivery systems contain polymers that degrade by bulk erosion. Often the release of therapeutics from these bulk-eroding polymers cannot be easily modeled. Using surface eroding polymers instead can overcome many of these problems. Polyanhydrides typically erode by surface erosion and are usually biocompatible. In this work, we synthesized polyanhydrides by thiol-ene polymerization. We studied the release kinetics of drug mimics from these polyanhydrides, and monitored the effect of crosslink density on release kinetics.



Sunday, April 7, 2013 03:30 PM

Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)

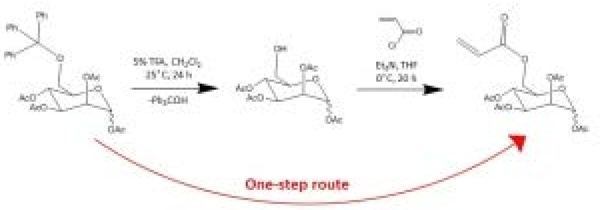
Location: Hilton Riverside

Room: Ste. A, Sec 6

56 - Functionalization of monosaccharaides for polymer synthesis

Sarah L Blosser[1,2], *sarahbloss@gmail.com, Cesar Lopez-Gonzalez*[1], *Coleen Pugh*[1]. *(1) Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States, (2) Department of Chemistry, The College of Wooster, Wooster, Ohio 44691, United States*

A new method to functionalize monosaccharides has been explored. Varying hexoses in pyranose form (manopyranose, glucopyranose) were protected to synthesize 1,2,3,4-tetra-O-acetyl-6-O-trityl-D-monosaccharides. Tritylated, acetylated monosaccharides were then reacted with electrophiles to functionalize with ester, silyl ether, and ether groups at the 6th position (primary alcohol). To date 1,2,3,4-tetra-O-acetyl-6-O-trityl-D-manopyranose, and 1,2,3,4-tetra-O-acetyl-6-O-trityl-D-glucopyranose, have been synthesized and treated with multiple electrophiles. Preliminary results indicate that this method of functionalization is successful and, significantly, avoids the deprotection step typically required for functionalization of a monosaccharide, therefore reducing the number of synthetic steps required to reach functionalization.



Sunday, April 7, 2013 03:45 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

57 - Synthesis of mannose-functionalized polymeric micelles

Lauren L. Agoubi, *lla2@williams.edu*, *Bianca A. Ulloa*, *Michelle M. McRae*, *Olivia W. Foley*, ***Sarah L. Goh***, *sgoh@williams.edu.*
Department of Chemistry, Williams College, Williamstown, MA 01267, United States

Self-assembling glycopolymers have garnered increased attention from the scientific community as an effective solution to the complications presented by current therapeutics. Using glycopolymers to encapsulate highly toxic drugs, targeted delivery can be achieved by exploiting the enhanced permeation and retention (EPR) effect and by functionalizing polymers with sugar moieties specific to receptors present on tumor-associated cell lines. With this combination of passive and active targeting in mind, amphiphilic diblock copolymer poly(2-(a-D-mannosyloxy)ethyl methacrylate)-co-poly(tert-butyl acrylate), or pMannHEMA-co-ptBA, was synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization. A critical micelle concentration of 0.00734 mg/mL was observed in 0.1 M phosphate buffer of pH 8.0. By dynamic light scattering, micelles were 31.6 nm in diameter. The binding behavior of the copolymer with concanavalin A (ConA) was also examined by measuring the turbidity change rate. Using a 1.0 mg/mL solution of pMannHEMA-co-ptBA in HEPES buffer, the copolymer displayed increased absorbance in the presence of ConA, indicating receptor recognition (Figure 1). Consequently, this work provides a general synthetic route to self-assembling glycopolymers. pMannHEMA-co-ptBA demonstrated self-assembling behavior with a low critical micelle concentration. In addition, the copolymer exhibited positive binding behavior with a mannose-binding protein, distinguishing the copolymer as a potentially clinically relevant molecule.

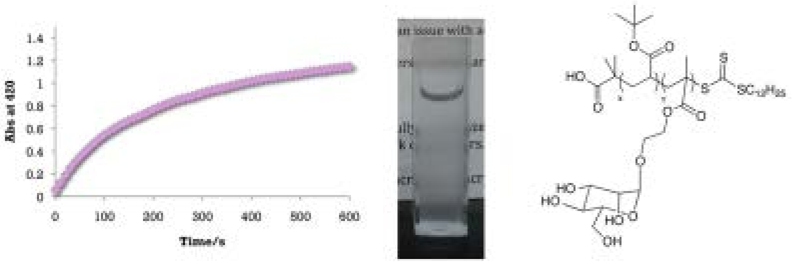


Figure 1. Time course of optical density at 420 nm in mixtures of concavalin A and pMannHEMA-co-ptBA and copolymer structure.

Sunday, April 7, 2013 04:00 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

58 - Biopolymeric hydrogels for cardiovascular therapies

Kristi L Kiick, *kiick@udel.edu, Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States*

Biopolymers have long served as inspiration in the design of responsive materials for biomedical applications. Our group has employed a combination of recombinant synthesis and simple bioconjugation strategies to produce a variety of biopolymeric materials capable of guiding cell behavior. In one area, multivalent polymers have been used to produce stimuli-responsive hydrogels that show tunable mechanical properties and excellent cell viability relevant for the development of cell-instructive scaffolds for cardiovascular therapies and targeted delivery. Recent developments in this area will be discussed.

Sunday, April 7, 2013 04:15 PM
Undergraduate Research in Polymer Science (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

59 - Design features of polymers for organic solar cells

Jean M.J. FRECHET[2], *jean.frechet@kaust.edu.sa, Olivia LEE*[1], *Jessica DOUGLAS*[1], *Mark CHEN*[1], *Alan YIU*[1], *Jeremy NISKALA*[1]. *(1) Dept of Chemistry and Dept of Chemical Engineering, University of California Berkeley, Berkeley, California 94720-1460, United States, (2) KAUST Division of Physical Sciences, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*

Selected design features of polymers suitable for applications in organic solar cells are explored. Issues such as the control of band gap, the thermal stability of bulk heterojunctions and the solubility of the electroactive polymers are considered. For example photocrosslinking of the polymer **[Figure 1]** contributes to enhanced stability, while the use of furan moieties as replacement for thiophene units may contribute to higher solubilities.

Sunday, April 7, 2013 01:15 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

60 - Deconstructing polymer semiconductors for single molecule break junctions

Luis M Campos, *lcampos@columbia.edu, Department of Chemistry, Columbia University, New York, NY 10025, United States*

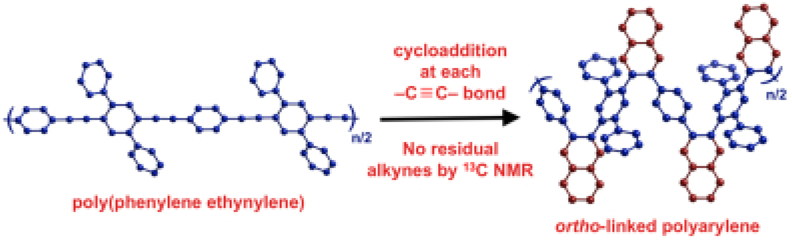
One of the most ubiquitous moeities in organic electronics is the thiophene unit. However, details of charge transport in oligothiophene--based devices are still lacking due variations in crystal packing arrangements, stability, and processability. The scanning tunneling microscope break junction (STM--BJ) technique has become a powerful tool in recent years for probing the conductance of single molecules. This method provides insight into the charge transport properties of molecules, and therefore is an important addition to the arsenal of techniques used by material chemists to predict the behavior of molecules in devices. This paper will present our research on the charge transport properties of oligothiophenes, and other derivatives, using the STM-BJ technique.

Sunday, April 7, 2013 01:40 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

61 - Benzannulation of conjugated polymers

William R Dichtel, *wdichtel@cornell.edu, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States*

Polyphenylenes containing *ortho*-substituted aromatic linkages are attracting increased interest for their well-defined conformational behavior and because they are precursors of nanostructured forms of graphene. However, current transition metal-catalyzed cross-coupling polymerizations to form *o*-arylene linkages proceed with insufficient efficiency to prepare high molecular weight polymers. Here we describe a new approach to introduce *ortho*-substitution patterns into polyarylene backbones by using a benzannulation reaction at each carbon-carbon triple bond of readily available poly(phenylene ethynylene)s. The benzannulation reaction proceeds efficiently, as demonstrated by a model study as well as by NMR, infrared, UV/Vis, and fluorescence spectroscopies performed on the polymer before and after the benzannulation reaction. The benzannulation tolerates bulky aromatic substituents adjacent to the alkyne functions, providing unique access to highly substituted polyarylene architectures that might serve as precursors to graphene nanoribbons of precise width and edge structure. Molecular dynamics simulations of the benzannulated polymer confirm that steric hindrance between its adjacent aromatic moieties gives rise to a compact solution structure suggested by its size exclusion chromatogram. The high efficiency and steric tolerance of the benzannulation reaction suggest that other molecular and polymeric phenylene architectures might
be accessed using this approach.



Sunday, April 7, 2013 02:05 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

62 - Organizing conjugated polymer heterostructures by solution crystallization

Ryan C. Hayward, *rhayward@mail.pse.umass.edu, Department of Polymer Science & Engineering, University of Massachusetts, Amherst, MA 01003, United States*

Conjugated polymers, such as regioregular poly(3-alkyl thiophenes), are well known to crystallize as extended one-dimensional nanowires or fibrils. These structures are not only important in determining the charge transport characteristics of device layers, but can also provide a driving force to assemble different semiconducting components into nanoscale heterostructures of well-defined architecture. We have studied a variety of routes to assemble such structures that rely on solution-state crystallization of poly(3-hexyl thiophene) (P3HT). In one example, we have co-organized of P3HT fibrils with CdSe nanoparticles through both co-crystallization of freely dissolved and particle-bound P3HT, as well as through nanoparticle adsorption to ligand-functionalized nanowire surfaces. In another case, we have studied the formation of hybrid nanostructures during simultaneous crystallization of P3HT and conjugated small molecules. We seek to understand the mechanisms by which these heterostructure form and the influence on photophysical properties of the constituent materials.

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ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

63 - Developing synthetic strategies for non-linear semiconducting polymers and organic-inorganic hybrid materials

Christine Luscombe, *luscombe@uw.edu, Materials Science and Engineering Department, University of Washington, Seattle, WA 98195-2120, United States and Molecular Engineering and Sciences Institute, University of Washington, Seattle, WA 98195-2120, United States*

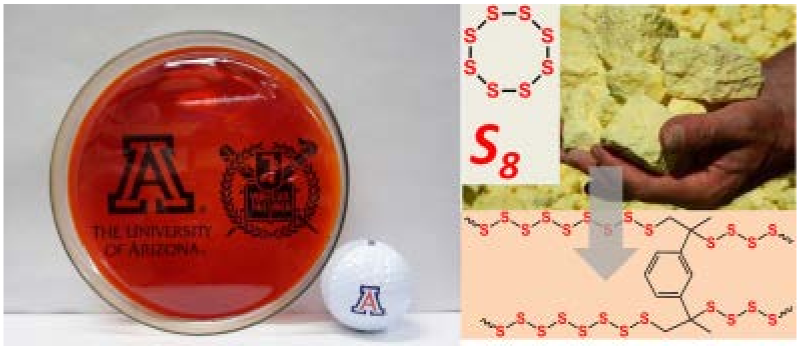
The ability of chemists to design and synthesize p-conjugated organic polymers with precise control over the molecular weight with narrow polydispersities remains one of the keys to using polymeric materials in electronic and photonic devices. Being able to synthesize well-defined block copolymers, star shaped polymers and surface grafted polymers will expand the structural library of semiconducting polymers which will allow us to obtain a more in-depth knowledge of the relationship between the structure-property relationship of semiconducting polymers. Extensive research for nonlinear polymers has been conducted to prepare multifunctional molecular architectures with higher dimensionalities such as star-shaped, disk-like, and hyperbranched polymers. Their intrinsic compact structures and globular shape predetermine their unique properties in comparison with linear polymers, such as low viscosity and high solubility. In this talk, the synthetic advances that have been made in creating star and hyperbranched semiconducting polymers will be discussed.

Sunday, April 7, 2013 02:55 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

64 - Yellow Chemistry: Polymerizing sulfur for batteries and photonics

*Woo Jin Chung[1], Adam G Simmonds[1], Jared J Griebel[1], Eui Tae Kim[2], Richard G Glass[1], Patrick Theato[3], Yung-Eun Sung[2], Kookheon Char[3], **Jeffrey Pyun**[1,3], jpyun@email.arizona.edu. (1) Department of Chemistry & Biochemistry, University of Arizona, Tucson, Arizona 85721, United States, (2) School of Chemical & Biological Engineering, World Class University Program, Seoul National University, Gwanak-gu, Seoul 151-744, Republic of Korea, (3) Institut für Technische und Makromolekular Chemie, Universität Hamburg, Hamburg, Germany*

We will present our recent work on novel sulfur utilization chemistry for polymeric materials. Elemental sulfur is manufactured at a level of 70 million tons every year, which is primarily produced via hydrodesulfurization of crude petroleum. However, there are only a few utilization technologies for sulfur, hence, over 6 million tons of elemental sulfur is generated in excess, which creates exciting opportunities to develop new chemistry and processing to utilize sulfur as a feedstock for polymers. We will present our recent efforts in the direct utilization of sulfur to prepare thermosetting polymeric sulfur that exhibit enhanced processing and electrochemical properties. These types of polymeric materials exhibit very high charge capacity again Li-insertion and have tremendous potential as inexpensive, high performance cathodes for Li-S batteries. Furthermore, these sulfur-rich copolymers exhibit unusually high refractive indices (n = 2.0) and can be easily processed in thin films, or molded objects.

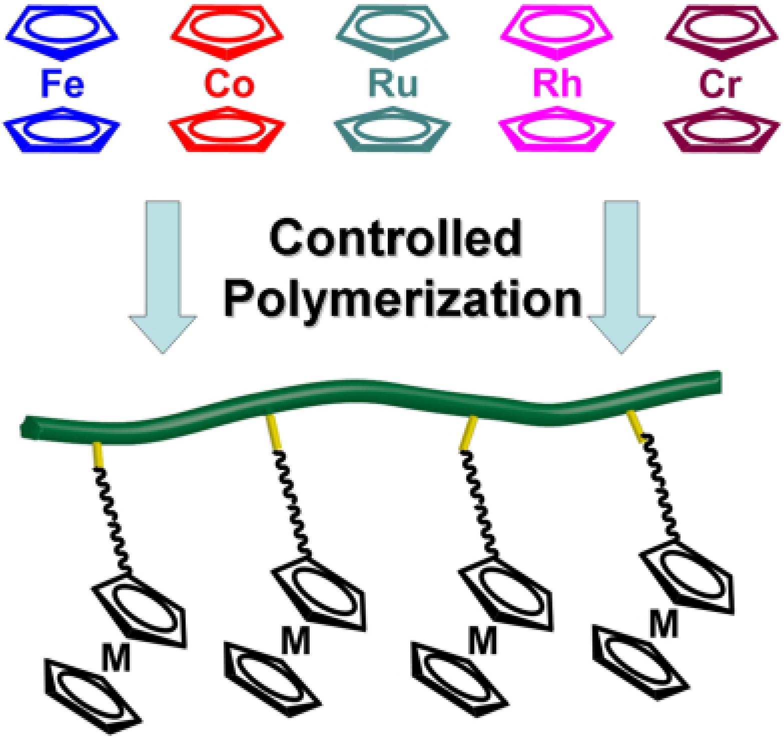


Sunday, April 7, 2013 03:20 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

65 - Novel metallocene-containing polymers: Progress and challenges

Chuanbing Tang, *tang4@mailbox.sc.edu, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States*

Metallocene-containing polymers have promising applications in the areas of catalysts, sensors, magnetic materials, lithography, and biomedical systems. This presentation will highlight recent progress in synthesis and applications of side-chain metallocene-containing polymers with diverse architectures by controlled polymerization.



Sunday, April 7, 2013 03:45 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

66 - Topographically directed self-assembly of nanoparticles via spin coating

Alshakim Nelson, *alshak@us.ibm.com, IBM Almaden Research Center, San Jose, C 95120, United States*

Nanoparticles represent a versatile set of building blocks for constructing functional materials with properties that can be exploited for both existing and emerging technologies. Although many of these applications would significantly benefit from the organization of nanoparticles into higher order architectures, the precise placement and arrangement of nanoparticles over large areas of a surface remain a challenge. Large area nanomanufacturing of these nanomaterials with high throughput and reproducibility is critical to the commercialization success of these technologies. This seminar will begin with a discussion of the core-shell FMNPs that we have developed for self-assembled magnetic storage media. While these particles are suitable for developing prototype magnetic media, we have also discovered that these well-defined particles can also be utilized as a model system for investigating solvent-driven directed self-assembly of nanomaterials on patterned substrates. Thus, a general method for rapidly organizing nanoparticles on patterned surfaces will also be presented.

Sunday, April 7, 2013 04:10 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

67 - Hydrogen peroxide-responsive polymeric nanoparticles for diagnostics and drug delivery in inflammatory disease

Caroline de Gracia Lux[1], *Shivanjali Joshi-Barr*[1], *Enas A. Mahmoud*[1], ***Adah Almutairi***[1,2], *aalmutairi@ucsd.edu. (1) Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, United States, (2) Departments of NanoEngineering and Materials Science, University of California, San Diego, United States*

To target drug delivery to inflamed tissue, we sought to develop a polymeric nanoparticle that responds to hydrogen peroxide. Since no current system is sensitive to disease-relevant concentrations, a new molecular design was required. We report a biocompatible polymeric particle, bearing ether-linked boronic ester groups, capable of undergoing backbone degradation and thus release upon exposure to either 50 µM H_2O_2 or activated neutrophils. Further, the particles are equally as nontoxic as PLGA and degrade into small molecules that should be easily cleared. We are now exploring specific applications of this material in diagnostics and therapeutics; the polymer promises a broad impact on the study of inflammation and should lead to new advances in bioresponsive materials.

Sunday, April 7, 2013 04:35 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

68 - Award Address (ACS Award in Polymer Chemistry sponsored by ExxonMobil Chemical Company). New approaches to molecular building blocks and macromolecular architectures

Craig Hawker, *hawker@mrl.ucsb.edu, Chemistry and Materials, University of California, Santa Barbara, CA 93106, United States*

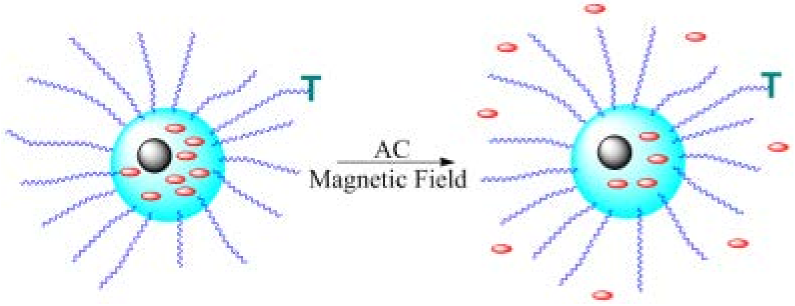
Polymer chemists, through advances in controlled polymerization techniques and reliable post-functionalization methods, now have the tools to create materials of almost infinite variety and architecture. Many relevant challenges in materials science, however, require not only functional polymers but also on-demand access to the properties and performance they provide. The power of such temporal and spatial control of polymerization can be found in Nature, where the production of proteins, nucleic acids, and polysaccharides helps regulate multicomponent systems and maintain homeostasis. We will illustrate the considerable potential for this emerging field and provides a coherent vision and set of criteria for pursuing future strategies for regulating controlled polymerizations.

Sunday, April 7, 2013 05:00 PM
ACS Award in Polymer Chemistry: Symposium in Honor of Craig J. Hawker (01:15 PM - 05:25 PM)
Location: Hilton Riverside
Room: HEC C

69 - Polymer micelles for a targeted, magnetothermally triggered drug delivery system

Amanda L Glover[1], *alglover@crimson.ua.edu, Jesse A Gettinger*[1], *Lindsey N Cobb*[1], *M. Adam Beg*[1], *Margaret P Johnson*[1], *Jacqueline A Nikles*[2], *Christopher S Brazel*[3], *David E Nikles*[1]. *(1) Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, United States, (2) Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35290-1240, United States, (3) Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL 35487-0203, United States*

Our goal is to design micelles that can be loaded with anti cancer drug, magnetic nanoparticles and be targeted to cancer cells. Diblock copolymers and triblock terpolymers, containing poly(ethylene glycol), polycaprolactone and/or poly(lactic acid) blocks were designed that form spherical micelles in water. The degree of polymerization for different blocks was systematically varied. The critical micelle concentration (CMC) and the temperature dependence of the CMC was determined. Micellar phase behavior was studied in solution using differential scanning microcalorimetry (DSC) which showed semicrystallinity of the micelles' PCL core in solution. Either doxorubicin or dibucaine, were loaded into the micelles and the drug loading capacities and isothermal released profiles were determined. For a magnetothermally triggered drug delivery system, the drug release will be heating the micelles above their melting points and allowing the drug to diffuse out. Magnetic nanoparticles either 9 nm or 24 nm were loaded into the cores of the micelles with and without drug. The micelle solutions were heated in an ac magnetic field, using quantum dots as nanothermometers to determine the local temperature of the micelles when an ac magnetic field was applied. A cyclic RGD peptide was conjugated to the terminus of some of the poly(ethylene glycol) molecules, thus giving targeted micelles.



Sunday, April 7, 2013 01:50 PM

Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)

Location: Hilton Riverside

Room: Ste. C, Sec 15

70 - Assembling, disassembling, and switching nanoparticles in vivo to program the phamacokinetics of therapeutic and diagnostic delivery vehicles

Miao-Ping Chien, *m1chien@ucsd.edu, Matthew Thompson, Nathan Gianneschi. Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92037, United States*

It has been shown that the morphology of nanomaterials greatly impacts the pharmacokinetic profile of the material, with larger objects having longer circulation times while smaller nanomaterials show a greater rate of internalization into cells. We have developed two nanoparticle systems (DNA- and peptide-polymer micellar systems) that combine these properties and allow us to program pharmacokinetics *in vivo* by virtue of morphology switches via endogenous or exogenous stimuli. We show, the circulation half-life of DNA containing polymeric micelles in blood *in vivo* can be modulated via a programmed morphology switch triggered by an exogenously injected DNA stimulus.

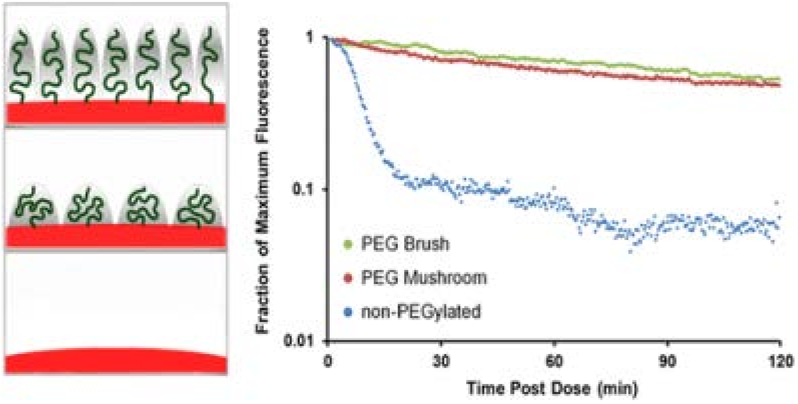
The second system utilizes peptide polymer amphiphiles that is responsive to specific cancer-associated enzymes. We have shown that these materials undergo a morphology switch from small sphere to large aggregate in tumor tissue *in vivo* resulting in the accumulation of the materials in the diseased tissue. These two systems have broad implications for the design of nanoscale materials in drug delivery and diagnostics applications where tunable pharmacokinetics can play a role in enhanced targeting and clearance.

Sunday, April 7, 2013 02:15 PM
Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

71 - PEGylation density effects on protein binding, macrophage association, biodistribution, and pharmacokinetics

Kevin G. Reuter[1], *kreuter@email.unc.edu, Jillian L. Perry*[9], *Marc P. Kai*[10], *Kevin P. Herlihy*[1,9], *Stephen W. Jones*[2], *J. Chris Luft*[1,5,8,9], *Mary Napier*[1,4,5,8,9], *James E. Bear*[2,7,9], *Joseph M. DeSimone*[1,3,5,6,8,9,10,11]. *(1) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (2) Cell and Developmental Biology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (3) Department of Pharmacology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (4) Department of Biochemistry and Biophysics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (5) Carolina Center of Cancer Nanotechnology Excellence, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (6) Institute for Advanced Materials, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (7) Howard Hughes Medical Institute, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (8) Institute for Nanomedicine, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (9) Lineberger Comprehensive Cancer Center, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (10) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States, (11) Sloan-Kettering Institute for Cancer Research, Memorial Sloan-Kettering Cancer Center, New York, New York 10021, United States*

Particle Replication in Non-wetting Templates (PRINT®) is one of the most versatile techniques in particle fabrication. In this study, we scaled-up PRINT and fabricated hydrogel-based 80 nm x 80 nm x 320 nm particles. We then varied PEGylation density on the surface of hydrogel PRINT nanoparticles and systematically observed the effects on protein adsorption, macrophage uptake, and circulation time. Interestingly, the density of PEGylation necessary to promote a long-circulating particle was dramatically less than what has been previously reported.

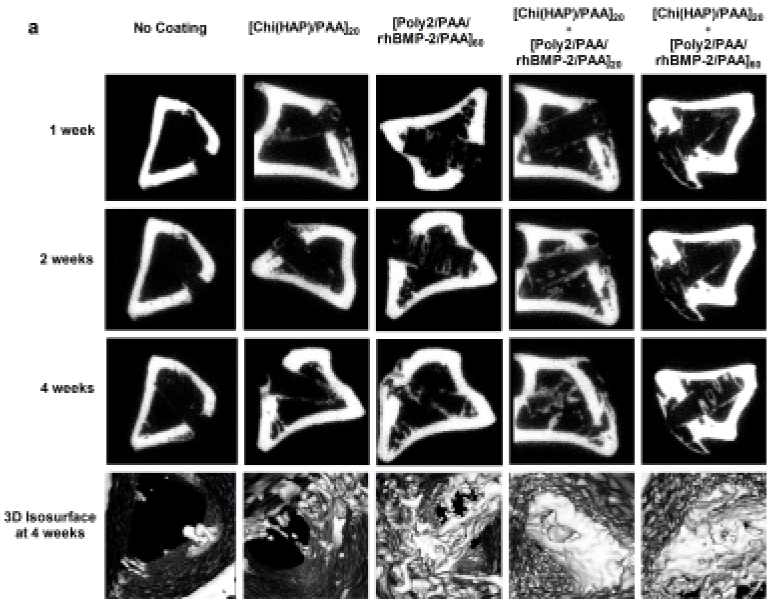


Sunday, April 7, 2013 02:40 PM
Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

72 - Self-assembling biomaterials for bone tissue regeneration

Nisarg J Shah[1,2]*, nisarg@mit.edu, Md. Nasim Hyder*[1,2]*, Paula T Hammond*[1,2,3]*. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (2) Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (3) Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The functional success of biomedical implants critically depends on stable bonding with the host tissue. We have developed a self-assembled, nanoscale, osteogenic polymer coating for the stable mechanical fixation of an implant to the host bone tissue. A few nanolayers are sufficient to tune cellular interactions and enable desired cell attachment or function. The incorporation of relatively simple biomolecular components influences the biocompatibility, surface chemistry and mechanical properties of the surface that induces direct bone deposition and stable implant fixation.



Sunday, April 7, 2013 03:05 PM

Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)

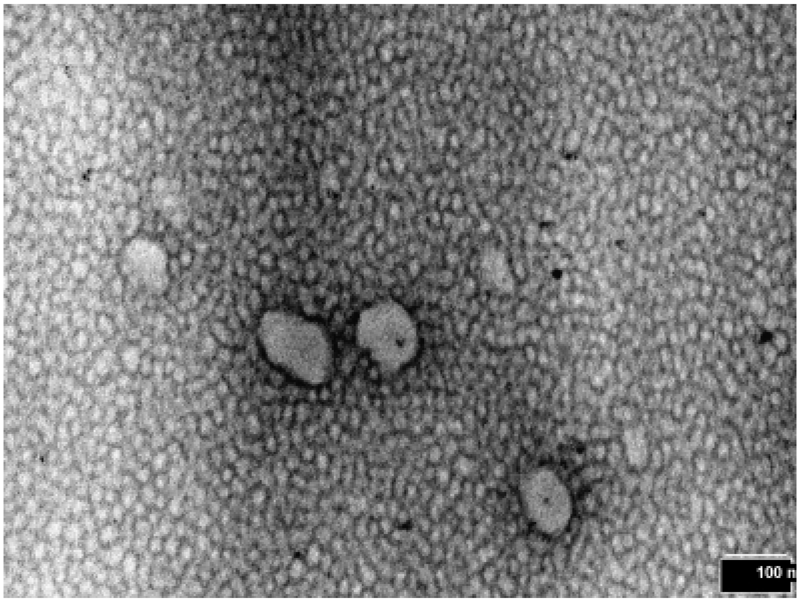
Location: Hilton Riverside

Room: Ste. C, Sec 15

73 - Thermoplastic elastomeric block-copolymers via controlled radical polymerization of soybean oil

Nacu B Hernandez[1], *nacu23@iastate.edu, Eric W Cochran*[1], *Chris Williams*[2]. *(1) Department of Chemical and Biological Engineering, Iowa State University, Ames, IOWA 50011, United States, (2) Department of Civil Engineering, Iowa State University, Ames, IOWA 50011, United States*

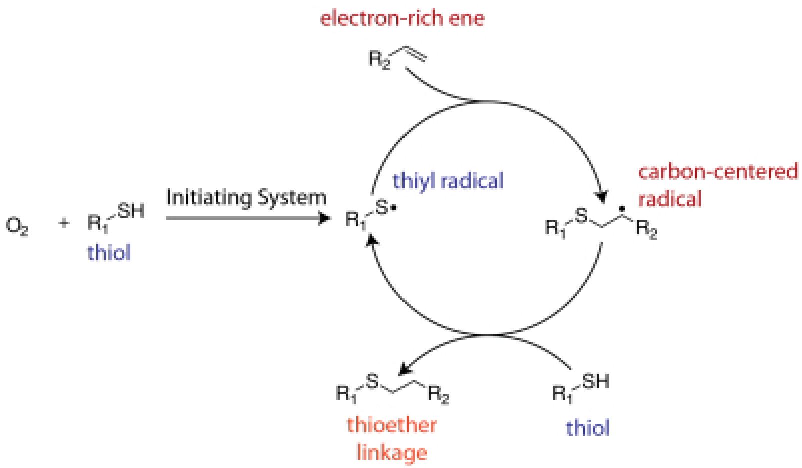
This contribution presents the controlled radical polymerization of a vegetable oil into thermoplastic rubber, and the incorporation thereof into triblock copolymers with polystyrene to form thermoplastic elastomers. Over the past two decades, the production of bio-based polymers from plant oils has successfully brought forth thermoset materials through the application of traditional cationic and free radical polymerization routes yielding highly crosslinked polymers. We have discovered that under appropriate conditions controlled radical polymerizations such as Atom Transfer Radical Polymerization can sufficiently limit the polymerization of triglyceride so that it terminates at a desired molecular weight and block composition, yielding a lightly branched, semi-ordered thermoplastic elastomer (see attached figure). We present multiple synthetic methods for these bio-based elastomeric block copolymers comprised of poly(acrylated epoxidized soybean oil) and polystyrene. We investigate the viability of these materials as bitumen modifiers. Initial findings have concluded thus far that our biopolymers can match and even exceed the performance of traditional petroleum-based polymers.



Sunday, April 7, 2013 03:45 PM
Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

74 - In situ polymerization via environmentally-borne initiation stimuli

Scott R Zavada[1], *szavada@umich.edu*, *Timothy F. Scott*[1,2]. *(1) Program for Macromolecular Science and Engineering, University of Michigan - Ann Arbor, Ann Arbor, Michigan 48109, United States, (2) Department of Chemical Engineering, University of Michigan - Ann Arbor, Ann Arbor, Michigan 48109, United States*



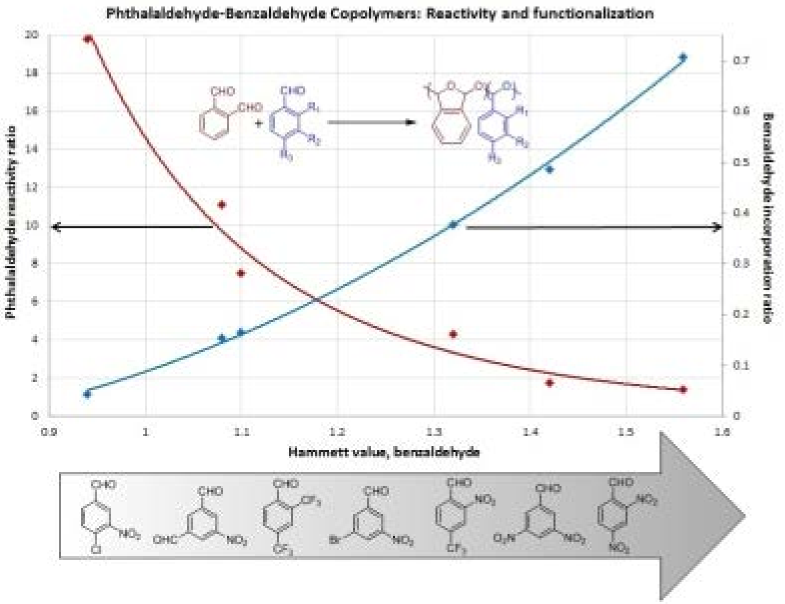
The thiol-ene polymerization, a radical-mediated, step-growth reaction between multi-functional thiols and electron-rich enes that proceeds via alternating propagation and chain-transfer steps, has emerged as a leading approach in the design of new, in situ-polymerizable materials owing to its capacity for rapid and selective reactivity. Our research involves the examination of oxygen-mediated radical-initiation schemes for thiol-ene materials such that the formulated resin will remain liquid while stored under anaerobic conditions and will only polymerize upon exposure to the atmosphere.

Sunday, April 7, 2013 04:10 PM
Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

75 - Phthalaldehyde-benzaldehyde copolymers: Reactivity and functionalization

Joshua A Kaitz, *kaitz2@illinois.edu, Jeffrey S Moore. Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

The burgeoning field of stimuli-responsive self-immolative polymers has garnered significant interest in recent years. Poly(phthalaldehyde) [PPA], an important member of this family, displays rapid head-to-tail depolymerization upon trigger cleavage. Further utilization of PPAs in various applications is limited as functionalizable phthalaldehyde-based monomers are not commercially available and their synthesis is cumbersome. Herein, we introduce a general route for the preparation of functional PPAs by a phthalaldehyde-benzaldehyde copolymerization approach. Effect of benzaldehyde structure on reactivity and copolymer functionalization will be discussed.

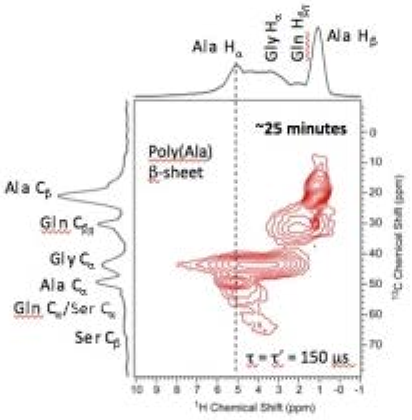


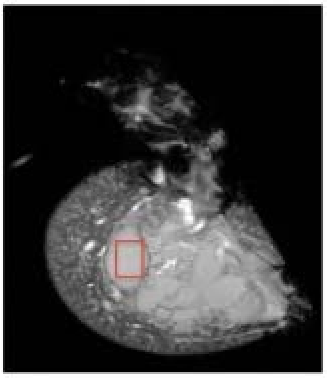
Sunday, April 7, 2013 04:35 PM
Excellence in Graduate Polymer Research (01:30 PM - 05:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

76 - Elucidating the structure and dynamics in spider silks and related protein biopolymers using magnetic resonance

Jeff Yarger, *jyarger@gmail.com, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, United States and Magnetic Resonance Research Center, Arizona State University, Tempe, AZ 85287-1604, United States*

Spiders produce up to six different types of silk that have extraordinary mechanical properties exceeding most other natural and synthetic fibers. Spider silk is composed almost entirely of protein and in the case of dragline silk from orb and cob weavers, contains two proteins. Thus, spider dragline silk can be referred to as nature's co-biopolymer. The origin of the silk's impressive mechanical properties lies in the molecular structure, dynamics and organization of the two proteins that make up the silk: major ampullate spidroin 1 (MaSp 1) and major ampullate spidroin 2 (MaSp2). Our research group has made considerable strides in isotopically ($^{2}H/^{15}N/^{13}C$) enriching a variety of silk fibers from a number of spider species enabling multi-nuclear, multi-dimensional solid-state NMR studies. Using advanced ssNMR methods along with magnetic resonance imaging (MRI) and x-ray diffraction, we are able to get a detailed understanding of the molecular protein structure and dynamics of spider silks.





Sunday, April 7, 2013 01:35 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)

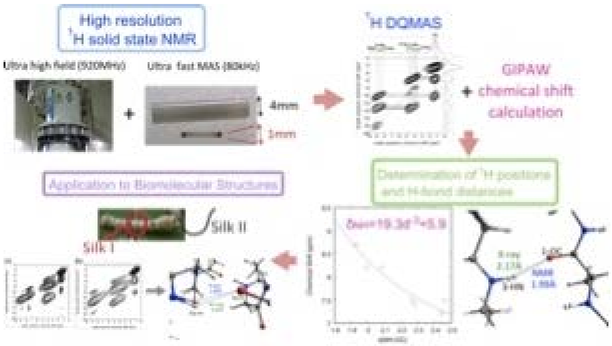
Location: Hilton Riverside

Room: Ste. C, Sec 18

77 - Probing intermolecular structures of biomolecules in solid state: High resolution ^{1}H solid state NMR analysis under ultra high speed MAS

Koji Yazawa[1], *kyazawa@cc.tuat.ac.jp, Yusuke Nishiyama*[2], *Katsuyuki Nichimura*[3], *Hironori Kaji*[4], *Tetsuo Asakura*[1,3]. *(1) Department of Biotechnology, Tokyo University of Agriculture and Technology, Tokyo, Japan, (2) JEOL Resonance, Akishima, Japan, (3) Institute for Material Science, Okazaki, Japan, (4) Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

The well-resolved ^{1}H solid state NMR spectra of alanine tripeptide (Ala$_3$) with anti-parallel and parallel b sheet structures are assigned by using double-quantum magic-angle-spinning (DQMAS) measurements with ultra high field and ultra fast MAS NMR. The observed ^{1}H chemical shifts are in excellent agreement with the ^{1}H chemical shifts calculated by first principles gauge-including projector augmented wave (GIPAW) method for ^{1}H geometry optimized structures, indicating the accurate ^{1}H positions of the structure. The chemical shifts of the amide protons are described by the inverse third power of inter-molecular NH¼OC direct hydrogen bond distance. We applied this relationship to evaluate the inter-molecular hydrogen bond distances of silk structures, silk I and silk II.



Sunday, April 7, 2013 02:00 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)

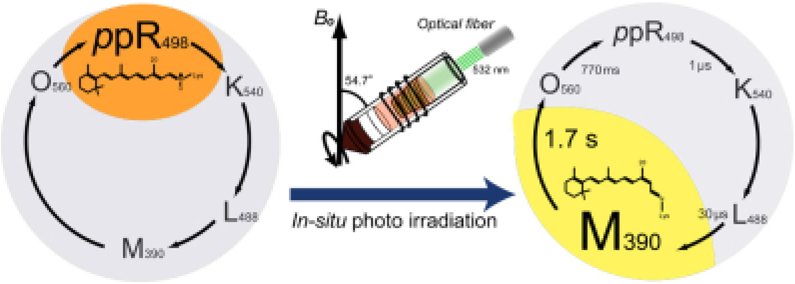
Location: Hilton Riverside

Room: Ste. C, Sec 18

78 - Photo-induced structural changes of photoreceptor membrane proteins as revealed by in-situ photo-irradiated solid-state NMR

Akira Naito, *naito@ynu.ac.jp, Graduate School of Engineering, Yokohama National University, Yokohama, Kanagawa 240-8501, Japan*

Pharaonis phoborhodopsin (*p*pR) is a negative phototaxis receptor of *Natronomonus* pharaonis and forms a 2:2 complex with the cognate transducer (*p*HtrII), which transmits the photosignal into cytoplasm. Light absorption of *p*pR initiates *trans*-*cis*photo-isomerization of the retinal chromophore followed by cyclic chemical reaction consisting of several intermediates (K, L, M and O). We have successfully trapped and observed the M intermediate by using newly developed photo-irradiated solid-state NMR system and a new photo-cycle will be presented.



Sunday, April 7, 2013 02:25 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)

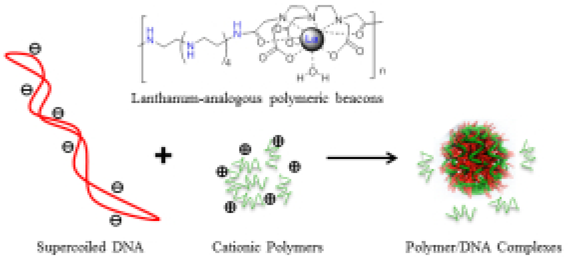
Location: Hilton Riverside

Room: Ste. C, Sec 18

79 - Quantifying bound vs. free polymer in polymeric delivery beacons using NMR

Xiaoling Wang[1], *mbcocoa@vt.edu*, *Sneha S Kelkar*[1], *Louis A Madsen*[1], *Theresa M Reineke*[2]. *(1) Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States*

Polymer-based non-viral nucleic acid delivery vehicles are promising alternatives to viral-based vectors, and may also be combined with imaging “beacons” for tracking these theranostic agents in vivo. So far, no method has yielded reliable information about the concentration of free polymer in a given polyplex (polymer-DNA complex) formulation. This information will be critical for safe administration of these agents and for FDA approval. Here we describe an NMR method to sensitively determine the quantity of free polymer in polyplex dispersions. By carefully integrating the intensity of the broad resonance originating from nanometer-sized polymer/DNA complexes relative to the intensity of the resonance lines of free polymer from proton NMR, we can measure the amount of unbound polymer. We have measured 25kDa linear poly(ethyleneimine)/DNA complexes at an N/P ratio of 7:1 and lanthanide-chelated oligoethyleneamine/DNA complexes at N/P 40:1. Our results show that ~20% of the poly(ethyleneimine) molecules are in the free form in Tris buffer at pH 7 and ~26% of the lanthanide-chelated oligoethyleneamines appear as free polymer in H_2O at 37°C. These results agree with another method we have devised using ^{1}H-NMR quantitation with an internal chemical reference. We will present the workings of these methods, along with a survey of free vs. bound polymer in other DNA polyplex systems. This technique may also be used to monitor the dissociation of polymer/DNA complexes.



Formation of Polymer/DNA complexes

Sunday, April 7, 2013 02:50 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

80 - Solid-state NMR studies of the interplay of protein and water dynamics

Michael Vogel, *michael.vogel@physik.tu-darmstadt.de, Institute of Condensed Matter Physics, Technical University Darmstadt, Darmstadt, Germany*

We use ^{13}C CPMAS NMR, including the DIPSHIFT experiment, to study protein dynamics as a function of water concentration. We find that the internal dynamics of a protein are activated as soon as 1-2 water layers cover its surface. However, the enhanced dynamics of hydrated proteins with respect to dry proteins vanishes when the temperature is decreased towards 200 K. At the same time, cooling leads to a crossover from isotropic motion to anisotropic motion for the water molecules in the hydration shell, as observed in 1D and 2D ^{2}H NMR.

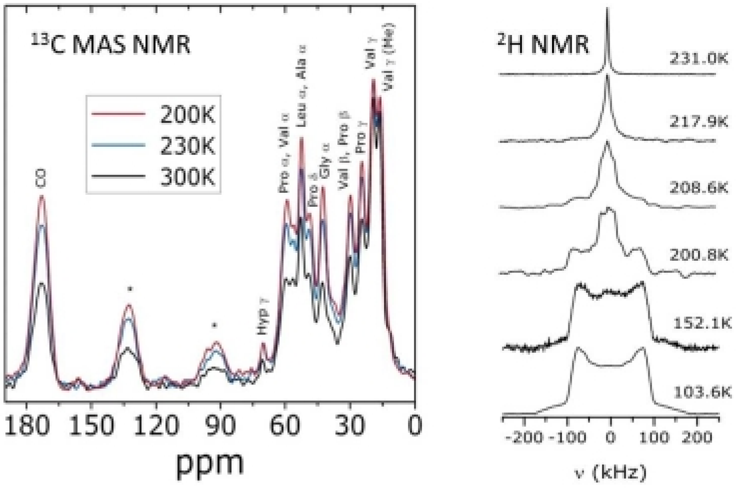


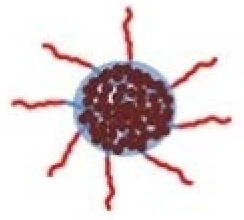
Fig. 1: ^{13}C NMR spectra of hydrated elastin and ^{2}H NMR spectra of hydrated myoglobin for various temperatures. The former and the latter provide insights into protein dynamics and water dynamics, respectively

Sunday, April 7, 2013 03:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

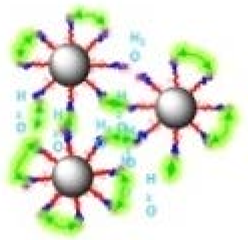
81 - Structure-relaxivity relationships of well-defined magnetite clusters for sensitive magnetic resonance imaging

Sharavanan Balasubramaniam[1], *shravan1@vt.edu*, *Sanem Kayandan*[1,2], *Nipon Pothayee*[1], *Nan Hu*[2], *Yin-Nian Lin*[2], *Nikorn Pothayee*[4], *Alan P Koretsky*[4], *Michael J House*[5], *Robert C Woodward*[5], *Timothy G St. Pierre*[5], *Judy S Riffle*[1,2], *Richey M Davis*[1,3]. *(1) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24060, United States, (2) Department of Chemistry, Virginia Tech, Blacksburg, VA 24060, United States, (3) Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24060, United States, (4) Laboratory of Functional and Molecular Imaging, National Institute of Neurological Disease and Stroke, National Institutes of Health, Bethesda, MD 20892, United States, (5) School of Physics, The University of Western Australia, Crawley, Western Australia 6009, Australia*

Magnetic nanoparticles have long been recognized as T_2-contrast agents for MRI. We report colloidally-stable magnetite clusters with hydrophobic and hydrophilic cores, and controlled sizes and compositions. Magnetite nanoparticles (~ 8 nm) were synthesized by the reduction of ferric acetylacetonate in benzyl alcohol. Hydrophobic-core clusters were prepared by rapid nanoprecipitation using an amphiphilic poly(*D*,*L*-lactide)-poly(ethylene oxide) diblock copolymer stabilizer. For the hydrophilic-core clusters, magnetite-poly(ethylene oxide-*b*-acrylate) complexes were synthesized, followed by crosslinking the amine tips of the H_2N-PEO corona with PEO diacrylate. The transverse relaxivities of the two classes of clusters correlated with particle sizes and compositions. Interestingly, the hydrophilic-core clusters had r_2s approaching the static dephasing limit of ~ 600 s^{-1}.mM Fe^{-1} and were more than twice that of the hydrophobic-core clusters at similar sizes and compositions. We posit that the high magnetic field gradients accessible to water protons by diffusion within the core of the hydrophilic clusters lead to the higher relaxivities.



Hydrophobic-core clusters



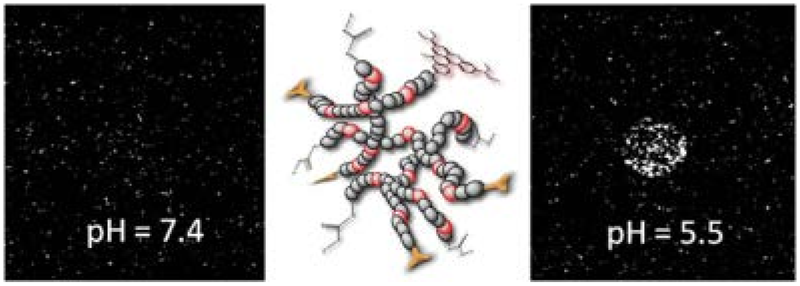
Hydrophilic-core clusters

Sunday, April 7, 2013 03:55 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

82 - Biologically-responsive polymeric ^{19}F MRI agents

Andrew K Whittaker, *a.whittaker@uq.edu.au, Kristofer J Thurecht, Idriss Blakey, Hui Peng. Australian Institute for Bioengineering and Nanotechnology, University of Queensland, St Lucia, QLD 4072, Australia*

The use of ^{19}F MRI for detection of early stages of disease has significant potential advantages over established ^{1}H MRI methodologies. The principal of these is the absence of a confounding background NMR signal. In addition ^{19}F NMR and hence MRI is often sensitive to the local chemical environment, for example the pH or oxygen tension of the environment. In this presentation we introduce a series of branched and linear partially-fluorinated polymers in which the conformation, and hence dynamics of the polymer chains are altered in response to a change in the local environment. The change in dynamics leads to a change in the strength of the dipolar interactions experienced by the fluorine nuclei, and hence a “switch” in the MRI intensity. The polymers have incorporated linkages which are sensitive to either the pH or local reductive potential of the environment.



Sunday, April 7, 2013 04:20 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:45 PM)

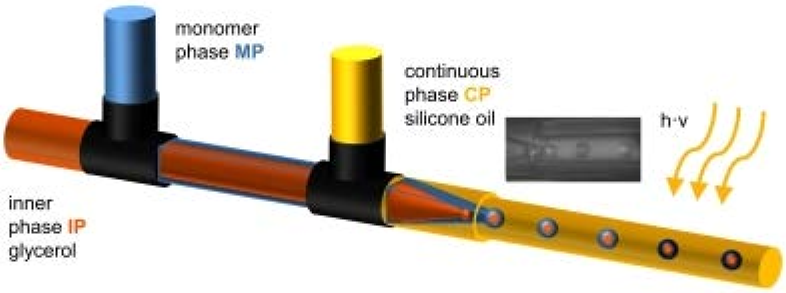
Location: Hilton Riverside

Room: Ste. C, Sec 18

83 - One-piece micropumps from liquid crystalline core-shell particles

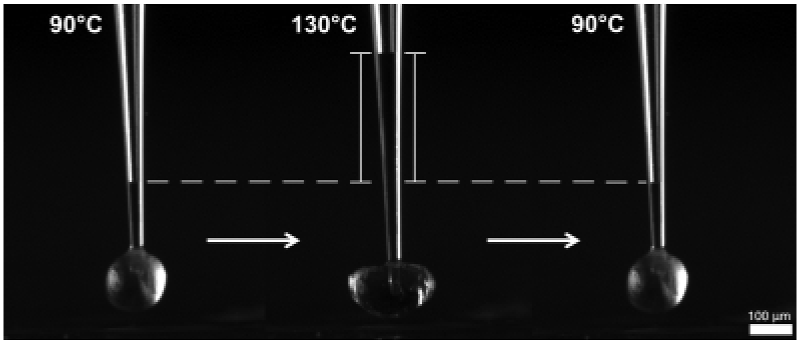
Rudolf Zentel[1], *zentel@uni-mainz.de, Eva-Kristina Fleischmann*[1]*, Hsin-Ling Liang*[1]*, Jan Lagerwall*[2]*. (1) Chemistry, University of Mainz, Mainz, Germany, (2) Graduate School of Converging Science, Seoul National University, Suwon-si, Republic of Korea*

Responsive polymers are low-cost, light-weight, and flexible and thus an attractive class of materials for the integration into micromechanical and lab-on-chip systems. Triggered by external stimuli, liquid crystalline elastomers (LCEs) are able to perform mechanical motion and can be utilised as microactuators. We present the fabrication of one-piece micropumps from liquid crystalline core-shell elastomers via a microfluidic double-emulsion process.



Due to the continuous nature of the deployed microfluidic setup, the fabrication process makes a low-cost and rapid production possible. The elastomer particles are filled with a liquid core, which is reversibly pumped into and out of the particle by actuation of the liquid crystalline shell in a jellyfish-like motion.

The LCE shells have the potential to be integrated into a microfluidic system as micropumps for flow regulation that do not require additional components except the passive channel connectors and the source of the actuation trigger. This renders elaborate and high-cost micromachining techniques otherwise required for obtaining microstructures with pump function unnecessary.

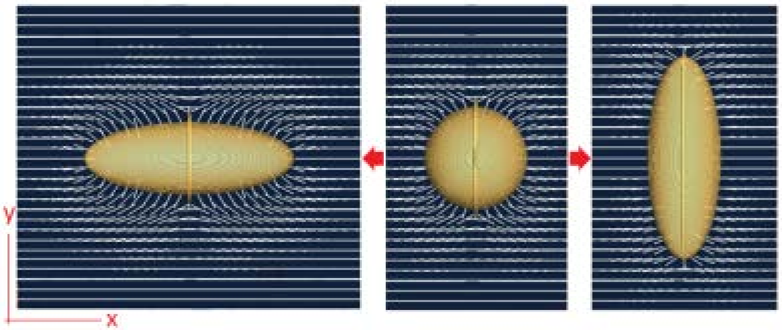


Sunday, April 7, 2013 01:30 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

84 - Shapeable particles in nematic colloids

Slobodan Zumer[1,2,3], *slobodan.zumer@fmf.uni-lj.si, Miha Ravnik*[1,3]. *(1) Department of Physics, University of Ljubljana, Ljubljana, Slovenia, (2) Jozef Stefan Institute, Ljubljana, Slovenia, (3) Center of Excellence NAMASTE, Ljubljana, Slovenia*

Nematic colloids are characterized as topological soft matter where elastic binding of colloidal particles is mediated by defects. Shaping particles' geometry and topology lead to new structures. Using topology and numerical simulations we describe colloids with particles consisting of nematic elastomers that can easily be reshaped by heat or UV-light.



The figure shows changes in nematic fields following an elastomer disorder-order transition turning spheres into ellipsoids elongated along the memorized internal ordering directions parallel to x- (left) or y-axis (right).

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Liquid Crystals and Polymers (01:30 PM - 05:05 PM)

Location: Hilton Riverside

Room: Ste. B, Sec 7/10

85 - Thermal and electrical actuation of nematic liquid crystal elastomeric micropillars

Shu Yang, *shuyang@seas.upenn.edu, Yu Xia, Elaine Lee. Department of Materials Science & Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States*

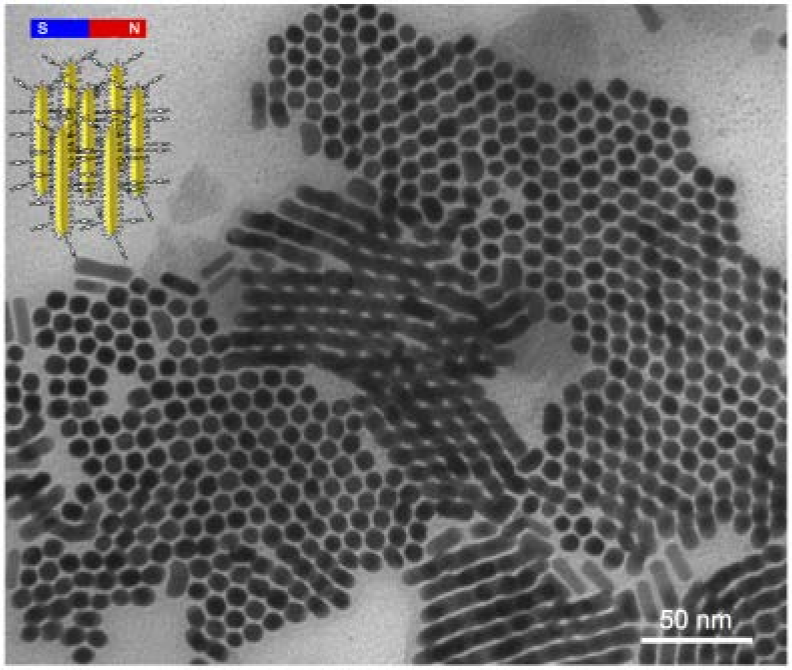
Liquid crystals (LCs) are anisotropic materials with physical properties that depend sensitively on both global and local molecular alignment. The ability to change LC molecular alignment under an external field will lead to dynamic tuning of the mechanical, opitcal and electric anisotropies of LCs, thus, providing powerful tools in controlling the propagation of light and the assembly of soft materials. Here, we fabricated micropillar arrays from nematic liquid crystal elastomers (NLCEs) with diameter of 1-10 mm and aspect ratio (=height/diameter) up to 5 using soft lithography. The LC molecules were found homeotropically aligned along the pillar wall. Upon heating above the isotropic phase or applying an electrical field, the pillars shrank in height but expanded in diameter due to realignment of the LC molecules within the pillars with a strain of ~ 20% (Figure 1). This change was completely reversible upon cooling or release of the electrical field. The actuation of LCE micropillars could be potentially of interest to create sensors and actuators for artificial muscles, heart valves, light switches and displays.

Sunday, April 7, 2013 02:30 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

86 - Self-assembly of mesogen-coated gold nanorods

__Torsten Hegmann__[1], thegmann@kent.edu, S. Umadevi[2], Xiang Feng[2]. (1) Liquid Crystal Institute, Kent State University, Kent, OH 44242, United States, (2) Chemistry, University of Manitoba, Winnipeg, MB R3T 2N2, Canada

We describe a modified approach to decorate gold nanorods with rod-like nematic or discotic liquid crystal molecules, and demonstrate their self-assembly behavior in the bulk and on substrates (i.e. on TEM grids after slow solvent evaporation). The process involves the binding of a trimethoxysilane terminated aliphatic thiol (MPS) on the gold nanorod surface and subsequent addition of either a rod-like nematic (end-on or side-on), a discotic or a bent-core silane followed by the addition of a base to initiate a hydrolysis and dehydration condensation to immobilize the LC silane on the gold nanorod surface. We will discuss the role of the mesogen capping the gold nanorods on the self-assembly, and demonstrate that the resulting arrays can be manipulated via the surrounding mesogens by external magnetic fields.[1]



[1] S. Umadevi, X. Feng, and T. Hegmann, Adv. Funct. Mater., in press.

Sunday, April 7, 2013 02:50 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

87 - SWCNT nanocomposites based on an all-aromatic liquid crystal polyetherimide: Synthesis and characterization

Maruti Hegde[1], *m.hegde@utwente.nl, Ugo Lafont*[1]*, Ben Norder*[2]*, Stephen J. Picken*[2]*, Edward T. Samulski*[3]*, Michael Rubinstein*[3]*, Theo Dingemans*[1]*. (1) Faculty of Aerospace Engineering, Novel Aerospace Materials, Delft University of Technology, Delft, The Netherlands, (2) Faculty of Applied Sciences, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands, (3) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina NC 27599-3290, United States*

An all-aromatic liquid crystal polyetherimide based on BPDA and an aromatic aryletherdiamine (P3) was modified with SWCNTs. SWCNT concentrations as high as 4.4. vol.% could be prepared.

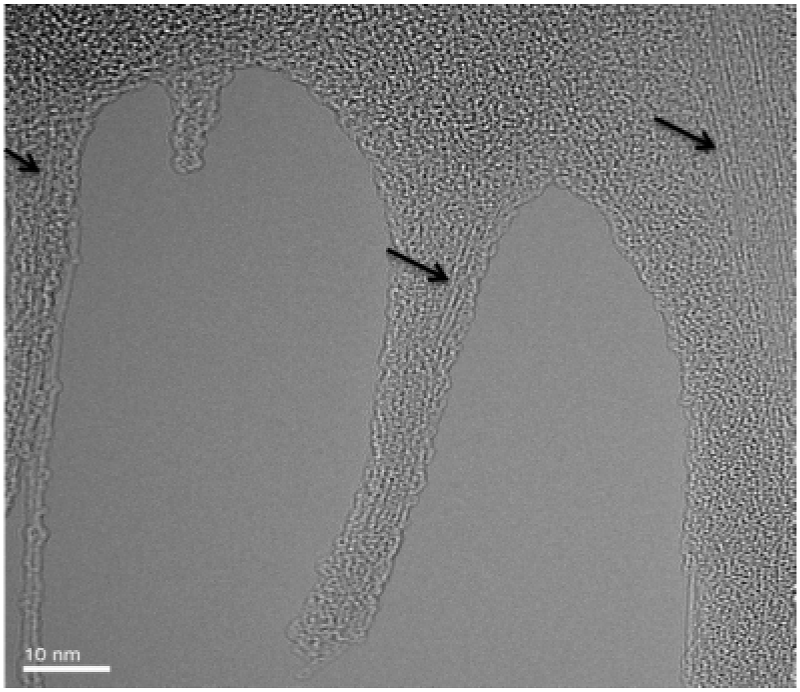


Figure 1. TEM imaging of LC BPDA-P3 with 2.4 vol.% SWCNT showed SWCNT's (indicated by black arrows) surrounded by amorphous polymer domains, which differs from what has been observed for other semi-crystalline polymeric matrices such as PVA and PmPv. Subsequent investigation of the nanocomposite film morphology by DSC and WAXD revealed no change in the degree of crystallinity as compared to the neat polymer.

Storage modulus values at R.T. increased from 3.0 GPa to 6.0 GPa at SWCNT loadings of 4.4 vol.%. Heat treatment of the nanocomposite films above the K-N transition and subsequent quenching resulted in increased storage modulus values. The synthetic details and properties of this new family of LC nanocomposites will be discussed.

Sunday, April 7, 2013 03:10 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

88 - Optical control of reconfigurable shape-morphing liquid crystal elastomeric colloids in nematic and cholesteric liquid crystals

Ivan I Smalyukh, *ivan.smalyukh@colorado.edu, Department of Physics, University of Colorado-Boulder, United States*

Dispersions of complex-shaped nano- and micro-sized colloidal particles in isotropic and liquid crystalline (LC) hosts have attracted a great deal of interest and may offer a means of self-assembly of materials with novel optical and mechanical properties. Methods for optical manipulation of colloidal shapes that would allow one to explore their practical utility and physical underpinnings behind such shape-dependent interactions are in a great demand. This lecture will describe fabrication of colloidal particles with complex three-dimensional shapes and also optical control of shape of LC elastomeric microparticles while they are dispersed in nematic and cholesteric LCs. Elastomeric colloids with cylindrical initial shapes and nematic director along the cylinder axis are obtained by means of soft lithography, polymerization in a strong magnetic field, and subsequent infiltration with gold nanospheres. By utilizing nanoparticle-mediated photothermal energy transfer from laser light to heat and inherent coupling between the temperature-dependent ordering and shape, we bend and morph the elastomeric microparticles to obtain long-term-stable well-controlled complex particle shapes and LC director fields within and around the particles. We show that laser-induced changes of shape of elastomeric colloids are followed by their spontaneous realignment and transformations of dipolar and quadrupolar director structures in the surrounding nematic host. We also demonstrate that elastomeric and metal complex-shaped particles can be rotated and translated using low-frequency electric fields. These findings are explained by use of a simple model based on LC elasticity and may impinge on shape-controlled self-assembly of adaptive composite materials.

Sunday, April 7, 2013 03:45 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

89 - Liquid-crystalline organization as a tool for the elaboration of hybrid functional materials

Daniel Guillon, *daniel.guillon@unistra.fr, Sylvie Bégin, Bertrand Donnio, Alfonso Garcia-Marquez, Arnaud Demortière, Emmanuel Terazzi, Saïwan Buathong. Organic Materials, IPCMS, Strasbourg, France*

Several examples of liquid-crystalline containing dendrimers able to self-organize at the mesoscopic scale and hybrid materials made of metallic nanoparticles functionalized with dendritic moieties will be discussed. In these materials, a mesoscopic organization is generated by mesomorphic phases of different symmetry where the molecular dendrimer shape and the intermolecular interactions between the different constitutive chemical parts play an important role in the establishment of the order.

For the hybrid materials, gold nanoparticles protected by a mixture of thiol dendrimers showing a ferromagnetic behaviour at room temperature, as well as magnetic nanocrystals of ferrite functionalized by luminescent prodendritic ligands will be considered. Finally, we will consider the case of a magnetic and liquid-crystalline polymeric network obtained by using adequately pre-functionalized 3.3 nm-diameter iron oxide nanoparticles to reticulate mesogenic linear oligomers. The magnetic properties remain almost unchanged, despite substantial changes of the environment around the ferrite particles.

Sunday, April 7, 2013 04:15 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

90 - 3D topology of smectic liquid crystals guided by nanoparticle assembly and a patterned substrate

Apiradee Honglawan[1], *apih@seas.upenn.edu, Shu Yang*[1,2], *Daniel Beller*[3], *Randall D. Kamien*[3]. *(1) Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States, (2) Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States, (3) Physics, University of Pennsylvania, Philadelphia, PA 19104, United States*

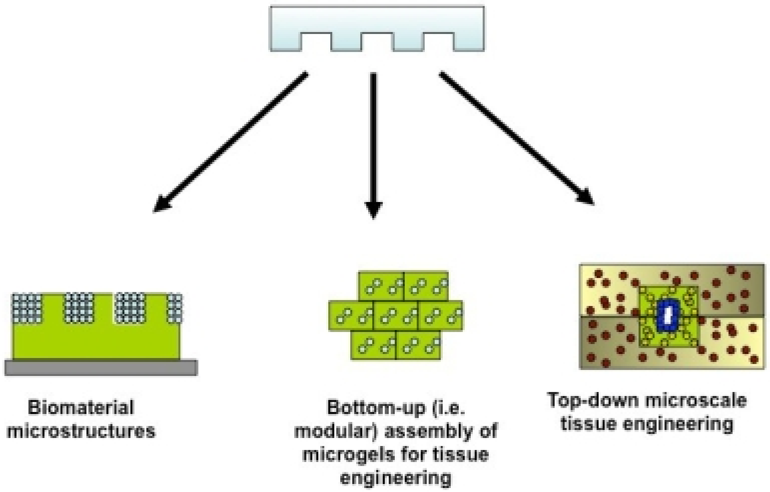
Controlling topological defects and liquid crystal (LC) phases in three dimensions (3D) is of particular interest to the generation of blue phases and other topologically structured materials, which will lead to possibly disruptive display technologies. However, it has been experimentally challenging to realize the 3D topology. Here, we investigate formation of 3D geometries of smectic-A (SmA) LCs guided by nanoparticle assembly and the underlying substrate. When the surface chemistry and substrate geometry (here 1D channels) promoted planar alignment of LC molecules, hexagonal arrays of toric focal conic domains (TFCDs) were formed due to competing effects of planar anchoring at the LC/substrate interface and homeotropic anchoring at the LC/air interface. When the silica nanoparticle surface was functionalized by fluorosilane, they spontaneously phase separated from the SmA LCs and aggregated only in the TFCDs at the LC/air interface, which in turn altered the LC anchoring to planar conditions in these regions. In contrast, unmodified silica particles were found embedded within LC layers, breaking the ordered symmetry of SmA film. By imposing nanoparticles with variable surface chemistry, we added new dimensions to control geometries of smectic LCs in 3D, which could shed new light on ways to engineer functional complex structures.

Sunday, April 7, 2013 04:45 PM
Liquid Crystals and Polymers (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

91 - Microengineered hydrogels for tissue engineering and stem cell bioengineering

Ali Khademhosseini, *alik@rics.bwh.harvard.edu, Harvard Medical School, Harvard-MIT Division of Health Sciences and Technology, Cambridge, MA 02139, United States*

Micro- and nanoscale technologies have been shown to be powerful techniques in addressing the current challenges in tissue engineering and stem cell bioengineering. These technologies have allowed for an unprecedented ability to control cell-cell, cell-microenvironment and cell-soluble factors interactions through miniaturized assays for high-throughput cell-based studies. Hydrogels are excellent scaffolding materials in tissue engineering because they generate three dimensional (3D) hydrated environments for cellular support resembling in vivo conditions. Our lab has been actively involved in merging of complex biomaterials and micro/nanoscale technologies to precisely control cellular microenvironments and create vascularized tissue constructs. Our work encompasses a wide range of scientific subjects from materials science to biology. In this presentation, I will outline our work in the development of microscale hydrogels to modulate cell-microenvironment interactions for tissue engineering and stem cell bioengineering applications. I will also discuss our major biological findings related to tissue engineering and stem cell bioengineering using miniaturized systems.



Sunday, April 7, 2013 01:30 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

92 - Bioactive PEG-hydrogels as 3D scaffolds for wound care applications

Kim Öberg[1]*, kimober@kth.se, Isabella Joelsson Rahmn*[1]*, Jonathan Kelly*[2]*, Michael Malkoch*[1]*. (1) Department of Fibre & Polymer Technology, Coating Technology, Stockholm, Sweden, (2) Mölnlycke Health Care AB, Göteborg, Sweden*

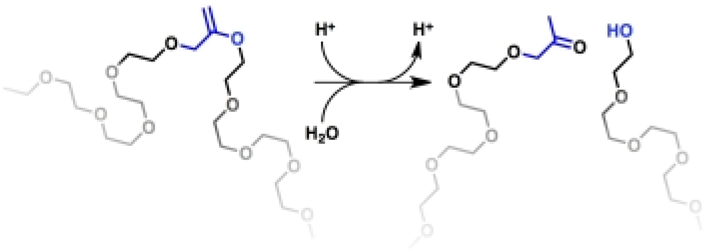
In this work we present a facile route for constructing photo-cross-linkable polyethylene glycol (PEG) hydrogels which can be selectively functionalized with bioactive moieties using the copper-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction. The hydrogel mechanical properties could be accurately tailored by altering the cross-linking density. Hydrogels functionalized with a selection of biologically interesting substances such as D-mannose, L-dopamine and biotin were furthermore evaluated for their interactions with normal human dermal fibroblasts (NHDF).

Sunday, April 7, 2013 02:00 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

93 - Synthesis of hydrolytically-degradable poly(ethylene glycol)

***Nathaniel A Lynd**, lynd@mrl.ucsb.edu, Pontus Lundberg, Sebastiaan A. van den Berg, Eric D. Pressly, Annabelle Lee, Bongjae F. Lee, Morgan Howe, Craig J. Hawker. Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

We report a facile method of imparting hydrolytic degradability to poly(ethylene glycol) (PEG) through the incorporation of methylene ethylene oxide (MEO) repeat units via a controlled chain growth copolymerization followed by a post-polymerization modification. The molecular weight distributions of the degradable PEG materials were narrow, and the incorporation of MEO repeat units could be accurately controlled. The molecular weight after degradation was defined by the molar incorporation of MEO, and the structure of the degradation byproducts was consistent with an acid-catalyzed vinyl-ether hydrolysis mechanism. The hydrolytic degradation of poly[(ethylene oxide)-co-(methylene ethylene oxide)] was pH-sensitive, with degradation at pH 5 being significantly faster than at pH 7.4 at 37 °C in PBS buffer, while longer-term stability could be obtained in either the solid-state or at pH 7.4 at 6 °C.



Sunday, April 7, 2013 02:20 PM

Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)

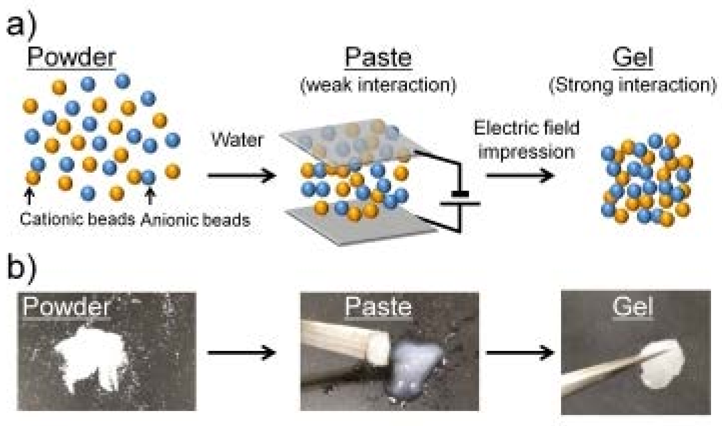
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

94 - Preparation of reconstructible hydrogels by electrophoretic microbead adhesion

Taka-Aki ASOH, *asoh@rs.noda.tus.ac.jp, Akihiko Kikuchi. Department of Materials Science and Technology, Tokyo University of Science, Noda, Japan*

We recently reported the electrophoretic adhesion of oppositely charged hydrogels. Adhesion of hydrogels was achieved through the formation of polyion complex at the interface of the two hydrogels by electric field impression. To apply this electrophoretic adhesion of hydrogels to building materials, the rapid fabrication of hydrogel constructs will be achieved by electric field impression to a precursor.



We prepared a reconstructible hydrogel composed of oppositely charged microbeads by the electrophoretic adhesion of the microbeads to each other.

Sunday, April 7, 2013 02:40 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
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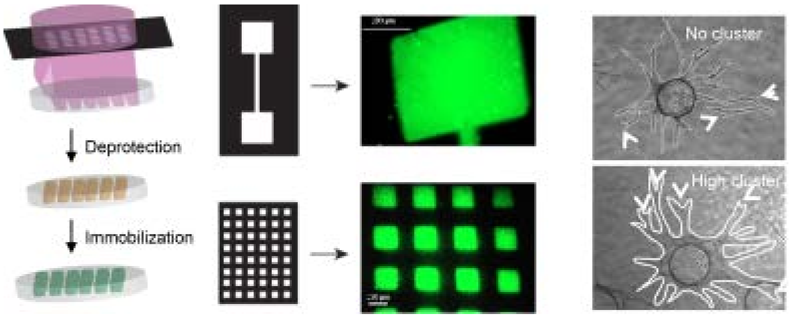
95 - Chemoselective patterning as a toll to study vessel sprouting

***Tatiana Segura**, tsegura@ucla.edu, Chemical and Biomolecular Engineering, University of California Los Angeles, Los Angeles, CA 90024, United States*

Although the natural extracellular matrix (ECM) contains a heterogeneous composition of proteins that are presented to residing cells within discrete pockets (not a homogeneous concentration or distribution) and precise times (determined by the developmental stage of the tissue), engineered ECMs (eECMs) that attempt to recapitulate the natural ECM do not mimic this heterogeneity. We believe that this heterogeneity is important and that is in part the reason why more complex tissue architectures have not been successfully engineered or treated and why there is a gap in knowledge between what is observed in vivo and what we can do in vitro with engineered materials. In this talk, I will describe our efforts to design chemoselective and spatially controlled immobilization of bioactive signals into hydrogel scaffolds. The technology described can be applied to the immobilization of peptides and proteins and would allow us to more precisely test our hypothesis that vascular endothelial growth factor (VEGF) presentation impacts the endothelial cell phenotypic switch.



Sunday, April 7, 2013 03:15 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
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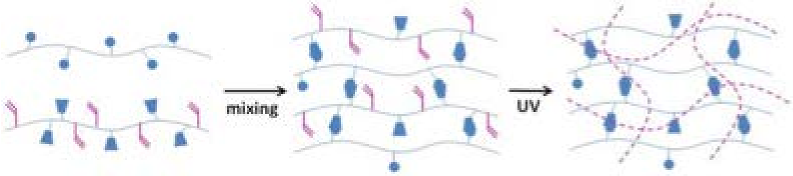
96 - Enhancing hydrogel functionality through the combination of physical and covalent crosslinks

*Christopher B Rodell, **Jason A Burdick**, burdick2@seas.upenn.edu. Department of Bioengineering, University of Pennsylvania, Philadelphia, PA 19104, United States*

Hydrogels are typically defined by the nature of their crosslinks, whether assembled through the physical interactions of polymers or through the formation of stable chemical bonds. Towards biomedical applications, each mode of crosslinking has advantages in terms of delivering to the body or through resistance to degradation and dissolution. Here, we introduce a system that self-assembles into shear-thinning and self-healing hydrogels, but may also undergo a secondary covalent crosslinking, such as through radical polymerization. One specific formulation involves the interaction of hyaluronic acid (HA) modified with either cyclodextran or adamantane that assembles into a network through guest-host interactions. When at least one component also includes a methacrylate group, a secondary free-radical photopolymerization can be used to increase the network crosslinking and stabilize the hydrogel. Such a system is advantageous to form an injectable material and then further crosslink the material to decouple final mechanics and stability from the mode of delivery.

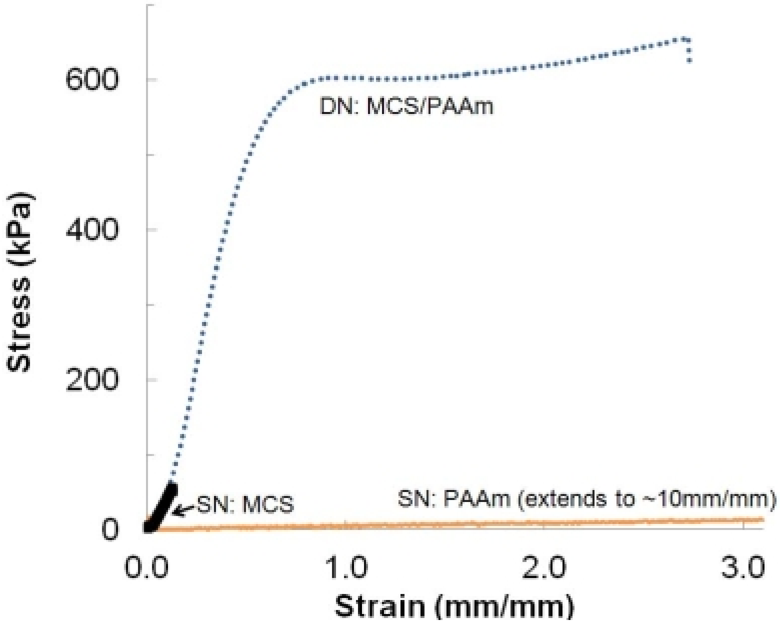


Sunday, April 7, 2013 03:45 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

97 - Improving the fracture properties of glycosaminoglycan hydrogels by double network strategy

Tiffany C. Suekama, *tsuekama@ku.edu, Anahita Khanlari, Michael S. Detamore, Stevin H. Gehrke. Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, Kansas 66045, United States*

Glycosaminoglycan (GAGs) are major components of the mammalian extracellular matrix. GAGs such as chondroitin sulfate (CS) and hyaluronic acid (HA) are widely used in tissue engineering, but a major limitation is the poor mechanical properties. A tough and ductile double-network (DN) biopolymer-based hydrogel was developed and characterized. The DN hydrogel was made using methacrylated chondroitin sulfate (MCS), and polyacrylamide (PAAm) or hyaluronic acid. The major conclusion is that MCS/PAAm DN hydrogels have proved to provide excellent toughness and strength for a biomaterial and are comparable to previously developed tough double-network gels of poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS)/PAAm. Further the MCS/PAAm DN had no hysteresis in the first 15% strain after 12 cycles and showed minimal hysteresis at higher strains. Increasing concentrations of MCS also increases the fracture stress but minimizes the fracture strain and the yielding diminishes the yielding phenomenon. Polyethylene (glycol) diacrylate (PEGDA) was added to the MCS first network. PEGDA was previously found to act as a cross-linker in co-polymerizations of MCS and PEGDA. PEGDA increases the modulus with concentration but reduces the fracture properties. Overall, this is the first demonstration of a tough, ductile biopolymer-based network displaying a substantial necking region, demonstrating the generality of this failure mechanism in such DN gel formulations and can be tuned by changing the concentrations and adding a chemical cross-linker. Future strategies are to develop biocompatible GAG-DNs.



Sunday, April 7, 2013 04:15 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
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98 - Novel quaternary ammonium functionalized polymers with antimicrobial properties

Amit L Garle[1,2], *Bridgette_Budhlall@uml.edu, Bridgette M Budhlall*[1,2]. *(1) Department of Plastics Engineering, University of Massachusetts, Lowell, MA 01854, United States, (2) NSF Center for High-Rate Nanomanufacturing, University of Massachusetts, Lowell, MA 01854, United States*

Various implants such as catheters and cerebrospinal shunts have become indispensable in modern healthcare. But infections associated with biomaterial implants also have serious complications[1]. Modification of existing materials to incorporate antimicrobial properties while retaining their useful properties is one strategy to enhance their applicability in implant applications. Here, we present synthesis and characterization of a novel quaternary ammonium functionalized cyclic lactone (QCL). QCL is polymerized and coupled to poly(e-caprolactone) to form a diblock copolymer. These diblock copolymers are blended with poly(e-caprolactone) in various proportions and the phase separation of the blend is studied by XPS. Using biological assays, it was determined that the copolymer films possessed nearly 100% antimicrobial activity toward Gram-positive bacterium, *S. epidermidis*, without leaching toxic components. For the Gram-negative bacterium, *E. coli*, 60-80% reduction in biofilm retention was observed for all the copolymer films. These novel polymers have potential applications in inhibiting implantable biomedical device associated infections.

Sunday, April 7, 2013 04:35 PM
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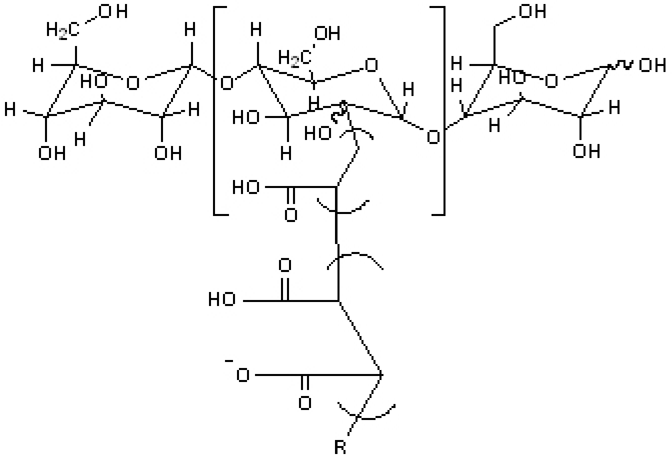
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

99 - Hybrid polymers

Klin Rodrigues, *klin.rodrigues@akzonobel.com, AkxoNobel Surface Chemistry, Chattanooga, TN 37406, United States*

AkzoNobel has developed a new biodegradable biopolymer technology for a variety of industrial applications including the Fabric and Cleaning market. Based upon the combination of selected polysaccharides and synthetic monomers, the Hybrid Polymers (see typical structure below) of this technology biodegrade in the environment, offer a smaller carbon footprint, and are effective in replacing synthetic polymers in formulations such as automatic dishwash systems and laundry detergents. This new technology is different from previous biopolymer attempts in that it makes use of a high amount of polysaccharide (40 to 75 weight percent), and promises to be a new, cost effective approach to a more sustainable future. The paper will present details on the latest developments in Hybrid Polymers. These Hybrid Polymers have been structurally characterized by NMR and other techniques. The analytical data have been used to more fully understand the interaction of these polymers and calcium carbonate surfaces. The polymers modify the growing carbonate crystal surface and minimize scale in industrial systems. The lifecycle analysis performed on a prototypical Hybrid Polymer versus its synthetic polymer analog will be discussed.



Monday, April 8, 2013 08:05 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

100 - How far can we push polymer architectures?

EW (Burt) Meijer, *E.W.Meijer@tue.nl, Departments of Biomedical and Chemical Engineering and Chemistry, Institute for Complex Molecular Systems, Eindhoven, Eindhoven 5600 MB, The Netherlands*

The phrase polymer architectures is often related to the way how atoms are connected within a macromolecular structure, e.g. block copolymers, grafted polymers, networks or dendrimers. With the increasing understanding of supramolecular interactions within or between polymers and the notion that the macroscopic properties of the materials are often dominated by the overall morphology, the issue "How far can we push polymer architecture" is now more related to mastering matter at all mesoscopic length and timescales. Some of the challenges and recent achievements of our laboratories will be demonstrated with examples of controlling supramolecular systems by both intra- and inter-molecular interactions and how cooperativity and multivalency can play a discriminating role.

Monday, April 8, 2013 08:35 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

101 - New low-temperature, non-flammable polyelectrolyte systems for lithium ion batteries

Joseph M DeSimone, *desimone@unc.edu, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States*

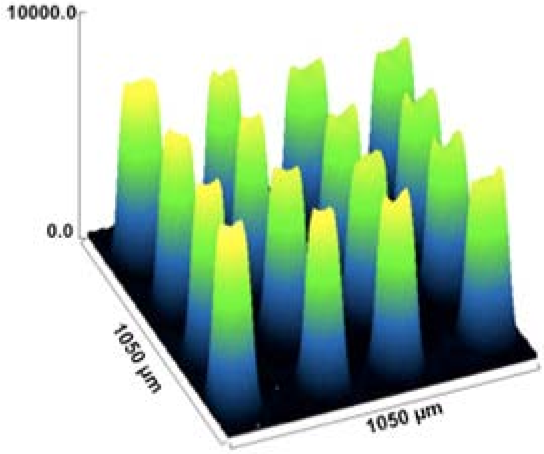
Renewable lithium-ion batteries are promising sustainable alternatives to non-renewable energy resources like petroleum. However, safety concerns, electrochemical stability, and narrow temperature range of operation remain persisting challenges that impede their prominence. In order to circumvent these shortcomings, we will describe herein a new class of lithium ion electrolytes composed of perfluoropolyethers (PFPE) and poly(ethylene oxide) (PEO) mixtures. These polymeric blends are amphiphilic, transparent, homogeneous and demonstrate the ability to solvate different lithium salts. The flammability, degree of crystallinity, ionic conductivity and electrochemical stability of these carbonate-free systems will be discussed.

Monday, April 8, 2013 09:05 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

102 - Attaching proteins to polymers and other things

David A Tirrell, *tirrell@caltech.edu, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

This lecture will discuss several new approaches to protein modification, including the use of non-canonical amino acids and the enzyme N-myristoyltransferase. Protein pegylation, surface conjugation, and reversible attachment to polymer gels, will be described. Applications in protein therapeutics, microarray technology, and high-throughput biochemistry will be explored.

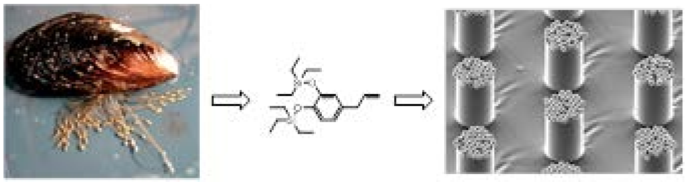


Monday, April 8, 2013 09:35 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

103 - New strategies for bio-inspired wet adhesion

Craig Hawker, *hawker@mrl.ucsb.edu, University of California at Santa Barbara, Santa Barbara, CA 93106, United States*

A facile synthetic strategy for introducing catecholic moieties into polymeric materials based on a readily available precursor - eugenol - and efficient chemistries - tris(pentafluorophenyl)borane catalyzed silation and thiol-ene coupling is reported. Silyl-protection is shown to be critical for the oxidative stability of catecholic moieties during synthesis and processing which allows func-tionalized polysiloxane derivatives to be fabricated into 3-D microstructures as well as 2-D patterned surfaces. Deprotection gives stable catechol surfaces with adhesion to a variety of oxide surfaces being precisely tuned by the level of catechol incorporation. The advantage of silyl-protection for catechol functionalized polysiloxanes is demonstrated and represents a promising and versatile new platform for underwater surface treatments.



Synthetic Bio-Inspired Adhesive Surface

Monday, April 8, 2013 10:20 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

104 - Vitrimers

Ludwik Leibler, *ludwik.leibler@espci.fr, Matière Molle et Chimie, École Supérieure de Physique et do Chemie Industrielles de la Ville do Paris, Paris, France*

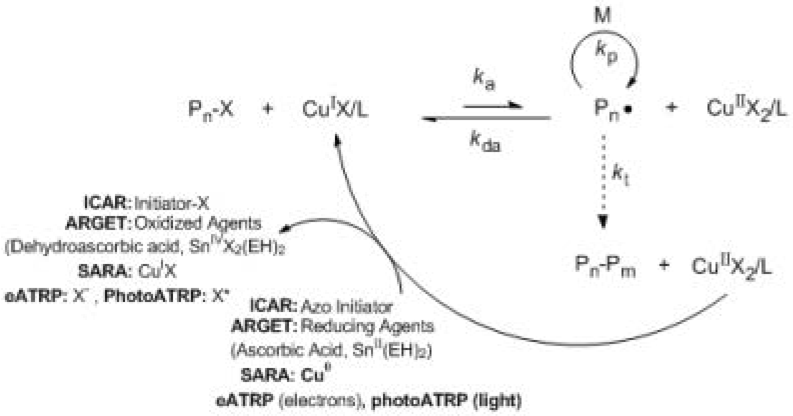
Glass-workers shape marvelous objects without using moulds or precise temperature control because glass is a unique material that transforms from liquid to solid in a very progressive way. Can we imagine other compounds that offer similar opportunities? I will present the concept of solidification by molecular-networks topology freezing and introduce vitrimers, organic materials that behave just like glass. Discovery of vitrimers could profoundly affect many industries that rely on polymers and composites.

Monday, April 8, 2013 10:50 AM
AkzoNobel North America Science Award (08:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: HEC C

105 - Award Address (AkzoNobel North America Science Award sponsored by AkzoNobel). Atom transfer radical polymerization: An efficient synthetic toolbox for complex molecular architecture and for new applications

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu, Chemistry, CMU, Pittsburgh, PA 15213, United States*

Atom transfer radical polymerization (ATRP) is an efficient controlled radical polymerization systems relying on intermittent activation of dormant alkyl halides to propagating radicals, especially in the presence of Cu complexes with various N-based ligands. New ATRP techniques permit reduction of Cu concentration to ppm level in the presence of reducing agents, visible light or electrical current. ATRP of (meth)acrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers provides (co) polymers in a large range molecular weights and with controlled molecular weight distribution . Polymers can be prepared quantitatively in bulk, in solution and in dispersed media. Polymers with complex architecture, such as block, graft, star, gradient, hyperbranched copolymers, as well as gels and networks have been synthesized. The (co)polymers made by ATRP can be used as components of various advanced materials. Design, synthesis, characterization and applications of various polymeric materials enabled by ATRP will be presented.



Monday, April 8, 2013 11:25 AM

AkzoNobel North America Science Award (08:00 AM - 12:00 PM)

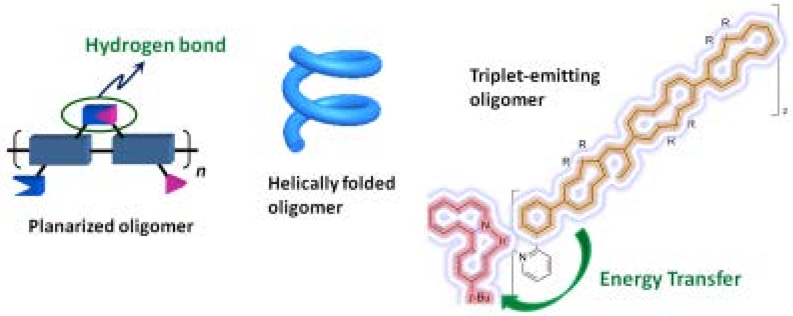
Location: Hilton Riverside

Room: HEC C

106 - Studying conjugated oligomers for electronic and photonic applications

Dahui Zhao, *dhzhao@pku.edu.cn, College of Chemistry, Peking University, Beijing, China*

Conjugated polymers are widely studied and applied for their electronic and photonic properties. Monodispersed conjugated oligomers with precise chemical structures are ideal model systems for their polymeric counterparts. The optical and electronic property change with molecular weight is mainly manifested in the low molecular weight range. The defined structures nonetheless provide unambiguous structure-property correlations. Moreover, as supramolecular structures governed by noncovalent forces are of great importance to the optical/electronic properties, monodispersed oligomers are better suited for relevant studies for exhibiting distinct self-assembly propensity and producing well-defined supramolecular architectures.



Monday, April 8, 2013 07:35 AM

ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (07:30 AM - 12:15 PM)

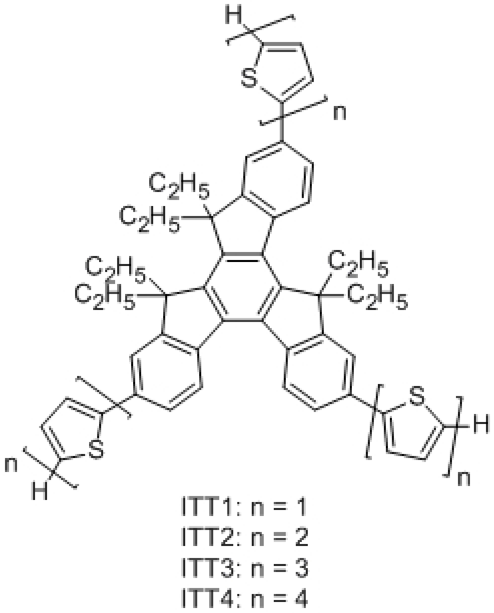
Location: Hilton Riverside

Room: Ste. B, Sec 9

107 - Electropolymerization of star-shaped oligothiophenes

*Hsuan-Yin Chen, Jun-Yun Tsai, **Jye-Shane Yang**, jsyang@ntu.edu.tw. Department of Chemistry, National Taiwan University, Taipei, Taiwan Republic of China*

The morphology and electronic properties of the electropolymerized films of a series of star-shaped oligothiophenes containing an isotruxene core (ITT*n*, *n* = 1-4)



will be discussed in terms of the structure of the monomers. Isotruxene is an excellent branching unit that allows strong electronic coupling between the ortho and the para branches. A combination of isotruxene and oligothiophene leads to two- and three-dimensional scaffolds of efficient charge-transporting in the molecular level.

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ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (07:30 AM - 12:15 PM)
Location: Hilton Riverside
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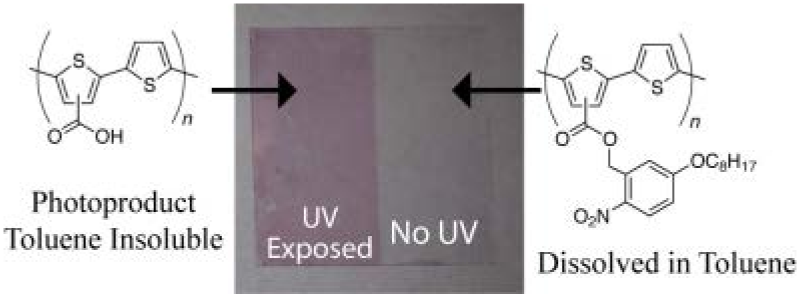
108 - Controlling organic semiconductors with side-chain interactions

Samuel W. Thomas, *sam.thomas@tufts.edu, Zachary C. Smith, Robert H. Pawle. Department of Chemistry, Tufts University, Medford, MA 02155, United States*

This talk will summarize new strategies for controlling the non-covalent interactions of conjugated oligomers and polymers using specifically designed side-chains. Photocleavable side-chains on conjugated structures enable both photoactivated fluorescence enhancement and photoinduced aggregation of materials such as oligo- and polythiophenes.



Side-chain/main-chain interactions of oligo- and poly(phenylene-ethynylene)s control their photophysical properties, including unexpected hypsochromic shifting of optical spectra of these materials in moving from the solution to the solid state, driven by electrostatically favorable cofacial arene-arene interactions.

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Location: Hilton Riverside
Room: Ste. B, Sec 9

109 - Prospecting in Hückel-space for organic electronic materials

John D. Tovar, *tovar@jhu.edu, Chemistry, Johns Hopkins University (?), United States*

Organic electronic materials are now accepted as viable large-area, flexible, low-cost alternatives to inorganic semiconductors for use as functional components of light emitting, energy harvesting and bioelectronic devices. This lecture will highlight fundamental structural considerations relevant to the design of materials that can foster efficient energy/charge migration. One aspect involves the use of unusual aromatic building blocks with relatively low degrees of resonance stabilization that can encourage the intramolecular delocalization of charge carriers. Another aspect deals with alternative ways to control intramolecular delocalization of polymer charge carriers through "evolved aromaticity". A final aspect involves the control of intermolecular delocalization of pi-electron wavefunctions through the use of water-soluble oligopeptides attached to conjugated oligomers that upon self-assembly lead to the formation of 1-D fibrillar nanostructures containing internal pi-stacked electronic conduits. In all cases, the making, breaking and stacking of aromatic rings is of utmost importance.

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ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (07:30 AM - 12:15 PM)
Location: Hilton Riverside
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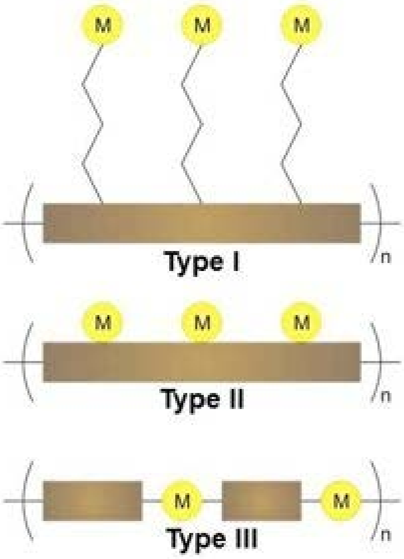
110 - Functional conducting metallopolymer materials

Bradley J. Holliday, *bholliday@cm.utexas.edu, Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, TX 78712, United States*

Our group has developed a series of novel electropolymerizable monomers that utilize specifically designed coordination environments to incorporate well-defined metal complexes directly into conducting polymer backbones. These hybrid materials known as conducting metallopolymers



have a variety of applications including light-emitting devices, photovoltaics, catalysis, and molecular storage/delivery. These materials exploit the properties of both the conducting polymers and the metal centers in a cooperative fashion. The synthesis, electrochemistry, and electrodeposition of a collection of these metallopolymers will be presented.

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ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (07:30 AM - 12:15 PM)
Location: Hilton Riverside
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111 - Designing catalysts for ring-opening alkene and alkyne metathesis of strained annulenes

Colin Nuckolls, *cn37@columbia.edu, Department of Chemistry, Columbia University, New York, NY 10027, United States*

My research group is interested in using the ring-opening alkyne and alkene metathesis reactions to create polymeric precursors to graphene ribbons. In the course of these studies, we have found that for ring-opening alkene metathesis of dibenzocyclooctatetrene to be successful one of the double bonds needs to be kinked into a trans-conformation. For ring-opening alkyne metathesis of strained cyclooctynes, all available catalysts do not have enough chemoselectivity to be useful in producing well-defined polymers. To overcome this limitation, we have developed molybdenum-based catalysts that are selective for reactions with strained alkynes and unreactive towards unstrained alkynes. The key to this selectivity is using ligands on the molybdenum that are multi-dentate. In the course of these studies, we have found a new catalytic system that can be activated to perform ring-opening alkyne metathesis using methanol. This allows, for the first time, alkyne metathesis to be performed on substrates with polar and protic functional groups such as phenols and alcohols.

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Location: Hilton Riverside
Room: Ste. B, Sec 9

112 - Exploring the use of redox-active radicals in optoelectronic devices

Trisha L Andrew, *tandrew@chem.wisc.edu, Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States*

The electronic and morphological factors that affect charge separation events in organic optoelectronic devices have been (and continue to be) widely studied. However, using spin polarization to control charge transport within individual molecules and thin films has received comparatively less attention. We will discuss issues relating to the use of redox-stable organic radicals in the active layers of organic photovoltaic cells and present their resulting effects on device metrics.

Monday, April 8, 2013 11:20 AM
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113 - Novel polymeric membranes for pervaporative purification of 1,3 propanediol from fermentation broths

Baishali Kanjilal[1], *Baishali.Kanjilal@gmail.com*, *Iman Noshadi*[2], *Kyle Hope*[2], *Alexandru Asandei*[1,3], *Richard Parnas*[1,2,3]. *(1) Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States, (2) Chemical, Material and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States, (3) Chemistry, University of Connecticut, Storrs, CT 06269, United States*

The bio-fermentation of crude glycerol to 1, 3-propanediol as a value added product gives a recourse to capitalizing on the current over capacity of glycerol from biodiesel and other industrial processes. The separation of the highly hydrophilic 1,3 propanediol from aqueous fermentation broths amounts to ~60% of the total production cost. This work presents novel membrane structures based on Poly(HEMA), Poly(Styrene-co-Allyl alcohol) and multi functionalized Siloxanes for pervaporative purification of 1,3 propanediol from dilute fermentation broths. The membrane structures are characterized by good separation factors and fluxes. The integration of these structures into separation process could result in energy savings by upto 80% over current conventional processes.

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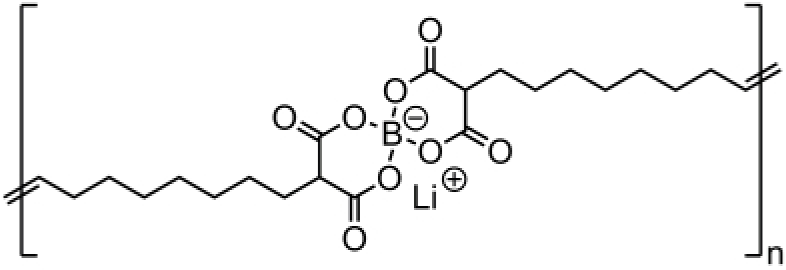
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (07:30 AM - 12:15 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

114 - Lithium single-ion conducting polymers with unusual high-voltage stabilities for battery applications

Ryan L. Weber, *rweber@chem.wisc.edu, Joseph C. Yeager, Robert J. Hamers, Mahesh K. Mahanthappa. Department of Chemistry, University of Wisconsin - Madison, Madison, WI 53706, United States*

Polymeric lithium single-ion conductors (PLSICs), in which mobile Li-ions are associated with a polyanionic backbone, mitigate problems with electrolyte polarization in Li-ion batteries. We have synthesized an electrochemically stable PLSIC by acyclic diene metathesis (ADMET) polymerization of a diolefin monomer containing a lithium bis(malonato)borate functionality. Electrochemical studies of this polymer reveal moderate lithium conductivity and an unusually wide electrochemical window (0.05-8.0 V *vs.* Li/Li^+) due to the formation of a stable solid-electrolyte interphase (SEI) layer.



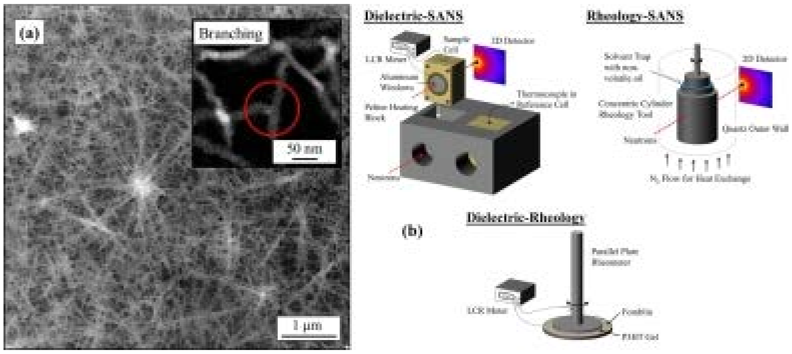
Polymeric Lithium Single-Ion Conductor
Stable to 8.0 V vs. Li/Li^+

Monday, April 8, 2013 08:30 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

115 - Engineering the multi-length scale structure of conjugated polymer networks for enhanced charge transport in organic photovoltaics

Gregory M Newbloom, *newbloog@uw.edu, Danilo C Pozzo. Department of Chemical Engineering, University of Washington, Seattle, WA 98195-1750, United States*

Gelation of conjugated polymers represents one approach towards engineering unique structures that can meet the multi-length scale morphological requirements for efficient organic solar cells. We have demonstrated that both the fiber size and branching network structure of poly(3-hexylthiophene) (Figure 1a) can be tuned by changing the self-assembly conditions. Furthermore, we have determined the gelation mechanism for poly(3-hexylthiophene) by studying the intermediate stages of the self-assembly process using simultaneous combinations of small angle neutron scattering, rheology and dielectric spectroscopy (Figure 1b).

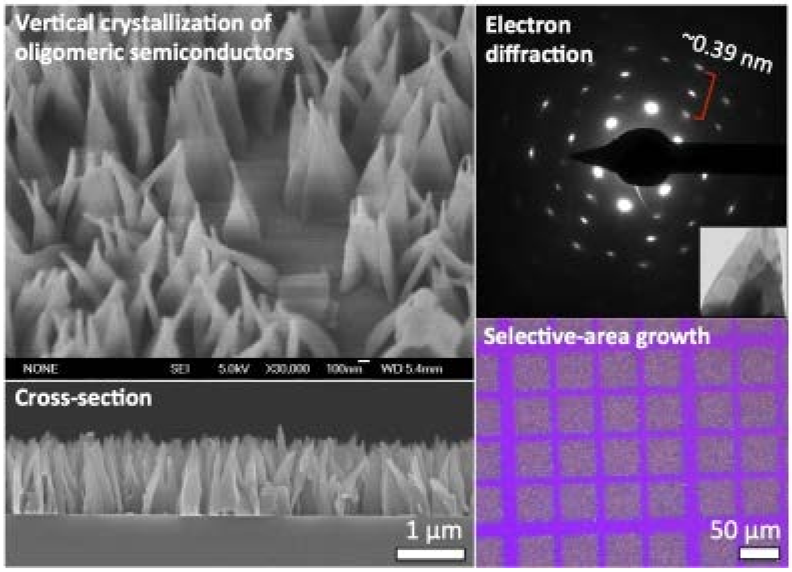


Monday, April 8, 2013 08:55 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

116 - Graphene-assisted growth of vertically oriented oligomeric semiconductor single crystals

Yue (Jessica) Wang[1,2], *yuewang@chem.ucla.edu, Jaime A Torres*[1,2], *Richard B Kaner*[1,2]. *(1) Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States, (2) California NanoSystems Institute, Los Angeles, California 90095, United States*

We demonstrate a simple solution-based approach for growing single-crystalline, vertically oriented arrays of organic semiconductors by using graphene as an epilayer. We demonstrate the exquisite control over the deposition densities and crystal sizes, and the selective-area grown at desired locations by patterning graphene into micrometer-sized arrays. This method has enabled the vertical crystallization of materials including tetraaniline, octaaniline, sexithiophene and bis(*N*-carbazolyl)biphenyl. With graphene directly integrated as the bottom electrode, such heterostructures have great implications in electronics and photonics.

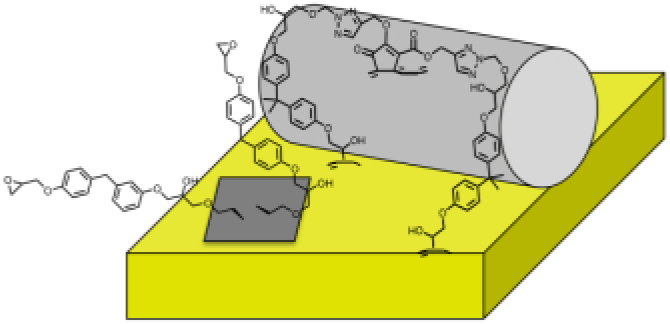


Monday, April 8, 2013 09:20 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

117 - Nanocomposites of epoxy with covalently modified graphene and carbon nanotubes

Stefanie A Sydlik, *ssydlik@mit.edu, Timothy M. Swager. Department of Chemistry and Institute for Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Epoxys are an important class of thermoset polymer used in high performance applications, especially composite materials. Novel functionalization methods for carbon nanotubes (CNT) and graphene have been developed to allow the fascicle preparation of nanocomposites containing CNTs and graphene. Epoxy-functionalized CNT (EpCNT) were synthesized and the addition of 1 weight % one EpCNT (EpCNT2) was found to increase the lap shear strength in aluminum-aluminum bonds by 35% over the leading commercial epoxy and by 27% over the same amount of unfunctionalized CNT. Further studies of the nanocomposites were conducted, examining the effect of filler type and quantity on the shear modulus of the epoxy. 10 weight % of another EpCNT (EpCNT3) was found to increase the plateau shear storage modulus by 101 % (1.96 MPa to 3.94 MPa) and 10 weight % of pristine graphite was found to increase the storage modulus by 15 % (to 2.25 MPa), while the other fillers were found to detract from the shear modulus. Optical micrographs and SEM images reveal a correlation between excellent dispersion and enhancement of shear properties.

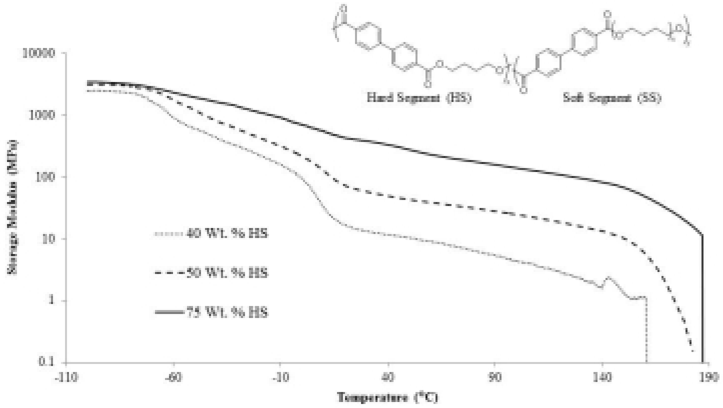


Monday, April 8, 2013 09:45 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

118 - Partially aromatic high-performance polyesters for electronic applications

Ashley M. Nelson, *an53@vt.edu, Richard N. Carmean, Timothy E. Long. Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States*

Electronic applications often require polymers with extreme thermal and ultraviolet light stability. The mesogenic and photoactive moiety 4,4'-dimethyl-*trans*-stilbene dicarboxylate and dimethyl biphenyl-4,4'-dicarboxylate were copolymerized with various diols to investigate the effect of mesogen and spacer length on the thermal, thermomechanical, rheological, and morphological transitions. The hexanediol spacer afforded liquid crystalline copolyesters with high thermal stability. Differential scanning calorimetry and polarized optical microscopy confirmed the liquid crystalline morphology. To increase impact properties, poly(tetramethylene oxide) as a spacer was investigated; affording elastomers.

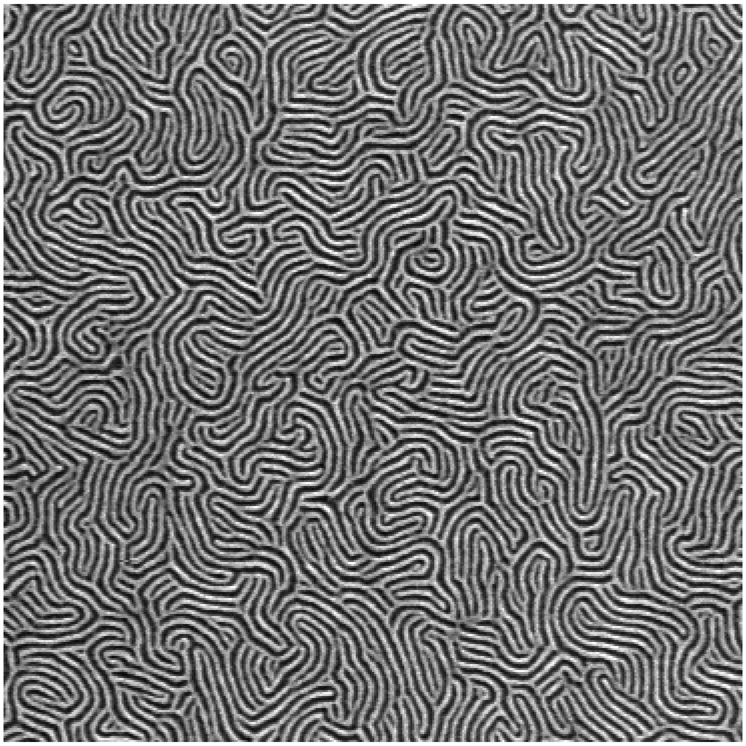


Monday, April 8, 2013 10:25 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

119 - Polarity-switching top coat polymers enable thin film block copolymer orientation control

Christopher M Bates[1], *chrismbates@gmail.com*, *Takehiro Seshimo*[1], *Michael J Maher*[1], *William J Durand*[2], *Julia D Cushen*[2], *Leon M Dean*[2], *Gregory Blachut*[2], *Christopher H Chen*[1], *Christopher J Ellison*[2], *C. Grant Willson*[1,2]. *(1) Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, United States, (2) Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

Block copolymer thin film orientation control remains an important area of research for applications ranging from organooptoelectronics, nanoporous membranes, to advanced lithography. Etch-resistant silicon-containing block copolymers require control of the top interface, which is most often accomplished through the use of solvent annealing. Herein is described a fast thermal annealing process for obtaining perpendicular features of a silicon-containing block copolymer. The process utilizes a polarity-switching top coat polymer and requires only a spin-coater and hot plate.

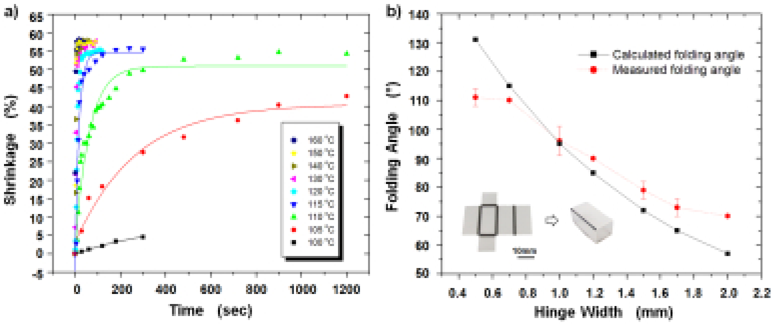


Monday, April 8, 2013 10:50 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

120 - Study of strain relaxation to control self-folding of pre-strained polymer sheets

Ying Liu, *yliu29@ncsu.edu, Michael D. Dickey, Jan Genzer. Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

We demonstrate a simple self-folding technique using pre-strained polymer sheets and inkjet printing. The ink patterned on the sheets via a desktop printer absorbs light, which heats locally the polymer underneath the ink and causes folding within seconds. Here, we combine thermal shrinkage and rheological properties of polymer sheets with finite element modeling, and provide insight into the folding mechanism based on macroscopic relaxation dynamics. The folding angle can be determined by a geometric model of strain relaxation.

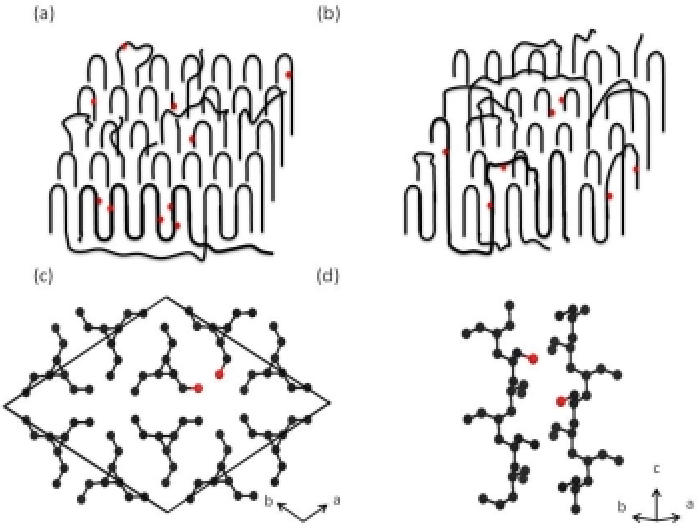


Monday, April 8, 2013 11:15 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

121 - Chain trajectory of semi-crystalline polymers in bulk and single crystals by ^{13}C-^{13}C double quantum NMR

Toshikazu Miyoshi, *miyoshi@uakron.edu, Polymer Science, The University of Akron, Akron, OH 44325-3909, United States*

Semi-crystalline polymers are crystallized as folded chain structures in thin lamellae to form single plate/scrolled crystals in dilute solution and bilayer structures consisting of crystalline and amorphous regions in bulk. ^{13}C-^{13}C DQ NMR is applied to extract detailed chain trajectory of synthetic polymers. Effects of ^{13}C-^{13}C spin number, spin topology, and inter nuclei distance on DQ signals are investigated. Detailed structures such as adjacent re-entry fractions, re-entrance sites, and chain folding numbers are discussed.



Monday, April 8, 2013 09:00 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

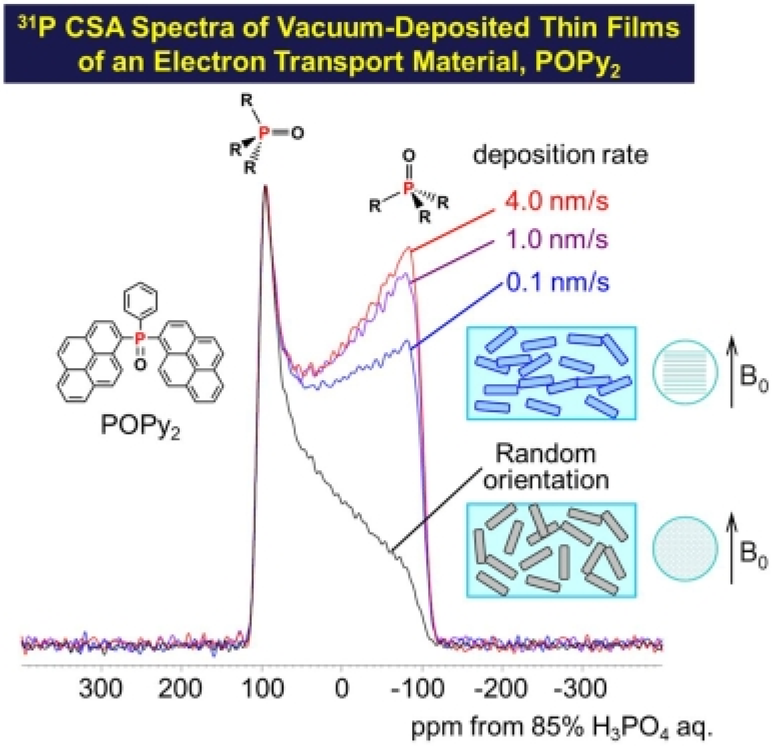
Location: Hilton Riverside

Room: Ste. C, Sec 18

122 - Solid-state NMR and GIPAW approach for organic LEDs and organic solar cells

Hironori Kaji, *kaji@scl.kyoto-u.ac.jp, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

The aim of our research is to understand the performance of organic LEDs (OLEDs) and organic solar cells (OSCs) at the molecular level, and to fabricate new materials and devices with enhanced performance. In the presentation, we will show solid-state NMR and GIPAW analysis of aggregated structures of organic molecules in OLEDs and OSCs, which are considered to be closely related to the device performance. This research is granted by JSPS through FIRST Program, initiated by CSTP.



Monday, April 8, 2013 09:25 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

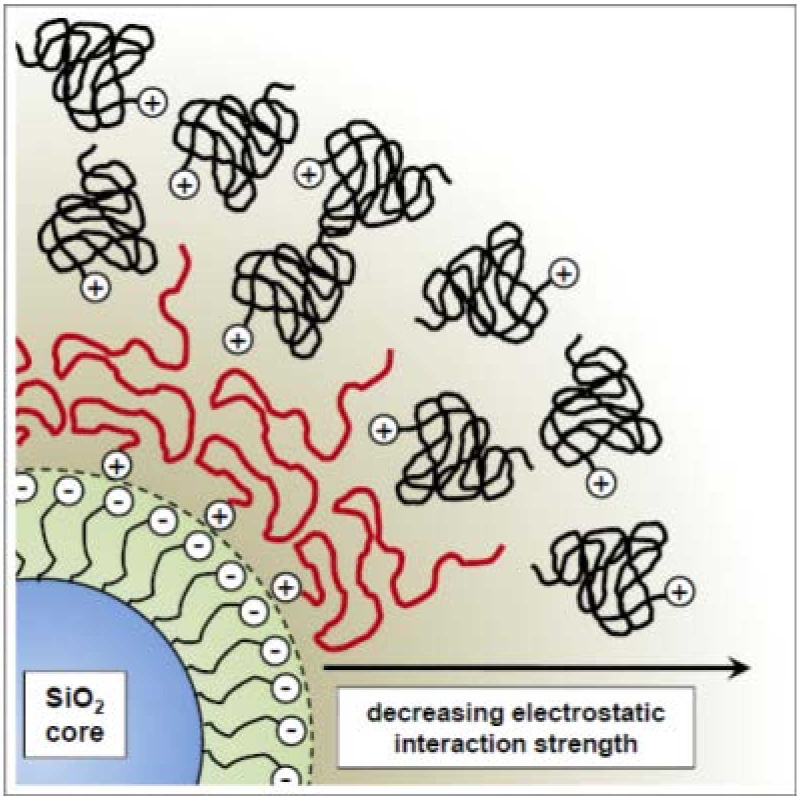
Location: Hilton Riverside

Room: Ste. C, Sec 18

123 - Canopy dynamics of nanoscale ionic materials probed by NMR

Peter A Mirau[1], *peter.mirau@wpafb.af.mil, Michael L Jespersen*[1], *Ernst D von Meerwaal*[2], *Richard A Vaia*[1], *Nikhil J Fernandes*[3], *Emmanuel P Giannelis*[3]. *(1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45434, United States, (2) Department of Physics, University of Akron, Akron, OH 44325, United States, (3) Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, United States*

Nanoscale Ionic Materials (NIMs) are hybrids prepared from ionically functionalized nanoparticles (NP) neutralized by oligomeric polymer counter-ions. NIMs are designed to behave as liquids under ambient conditions in the absence of solvent and have no volatile organic content, making them useful for a number of applications. We have used NMR relaxation and pulse-field gradient NMR to probe local and collective canopy dynamics in NIMs based on silica NP, fullerols and proteins. The NMR studies show that the canopy dynamics depend on the degree of neutralization, the canopy radius of gyration and molecular crowding at the ionically modified NP surface. The viscosity in NIMs can be directly controlled with the addition of ions that enhance the exchange rate for polymers at the NP surface. These results show that NIMs for many applications can be prepared by controlling the dynamics of the NP interface.

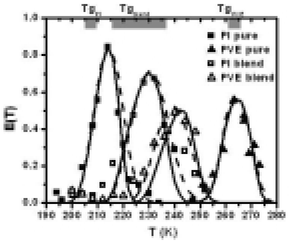


Monday, April 8, 2013 09:50 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

124 - Soft matter poses hard problems: Magnetic resonance as a route to untangling amorphous macromolecular systems

***Jeffery L White**, jeff.white@okstate.edu, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States*

A variety of high molecular weight amorphous macromolecules were examined using time-dependent solid-state NMR methods, with the goal of determining how individual macromolecular chains respond to the formation of intimate mixtures with dissimilar polymer chains. These studies, which relied extensively on CODEX NMR methods, revealed that different polymers retain unique glass transitions, friction coefficients, configurational entropy, and dynamic heterogeneity even in miscible blends mixed on the nanometer length scale. Based on these findings, new experiments involving gradient copolymers have been devised to extract the degree to which bulk polymer behavior may be controlled by the tailoring the construction of the molecular gradient interface.



Monday, April 8, 2013 10:30 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

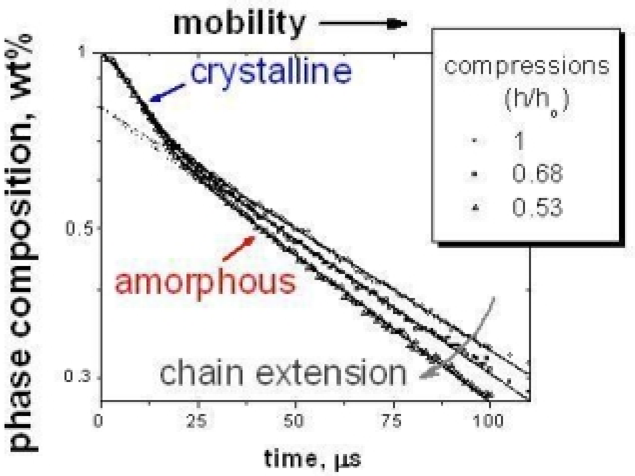
Location: Hilton Riverside

Room: Ste. C, Sec 18

125 - Effect of deformation on physical structures in polymers as studied by solid-state NMR

Victor M. Litvinov, *victor.litvinov@dsm.com, DSM Resolve, Geleen, The Netherlands*

Mechanical properties belong to one of the most important parameter of polymers largely determining many of their application areas. Much research has been devoted to understanding the mechanical properties. Despite these efforts, the deformation process in multi-phase materials is not well understood largely due to the lack of information about phenomena that occur at the molecular and nanometric length scales in different phases during deformation. Solid-state NMR methods offer very high selectivity to different phases/components in multi-phase polymers. Strain-induced phenomena in soft phases are of special interest since NMR is highly sensitive to even minor deformation-induced changes and results obtained are complimentary to those by X-ray studies. A significant number of NMR studies were mainly performed for polymers under a fixed strain and after strain-recovery. After a short review of these studies, the focus will be given to NMR studies described results obtained during deformation.

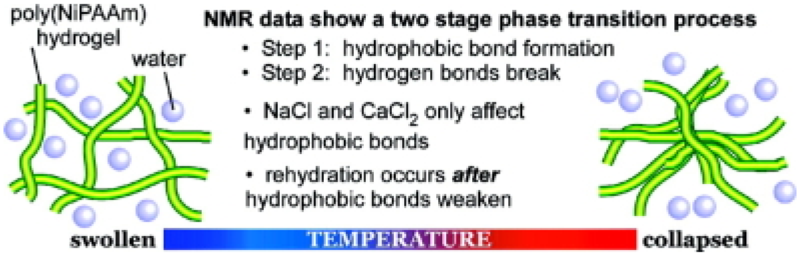


Monday, April 8, 2013 10:55 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

126 - Thermodynamics of temperature sensitive hydrogels from HRMAS NMR

Charles V. Rice, *rice@ou.edu, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, United States*

Poly(N-isopropylacrylamide) is water soluble and undergo a temperature-induced phase transition to an insoluble form, governed by competing hydrophilic and hydrophobic forces. NMR studies provide missing information - the enthalpy and entropy contributions. Salts affect phase transition thermodynamics through a linear decrease in the LCST whereas the enthalpy and entropy do not display a linear dependence. Finally, signal intensity during the heating-cooling cycle shows substantial hysteresis from the need to break hydrophobic interactions before water can infiltrate the polymer matrix.



Monday, April 8, 2013 11:20 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

Location: Hilton Riverside

Room: Ste. C, Sec 18

127 - Templated chiral polymer architectures

Micahel McConney, Madeline Duning, Seth Cazell, Lalgudi Natarajan, Vincent Tondiglia, Timothy White, ***Timothy Bunning****, timothy.bunning@wpafb.af.mil. Materials and Manufacturing Directorate, Air Force Research Laboaratory, WPAFB, OH, United States*

Aligned cholesteric liquid crystal systems which exhibit dynamic selective reflection properties are explored. Templating a chiral ordered fluid with LC monomers and subsequent photopolymerization enables a swollen, ordered LC network which has the initial optical properties of the starting LC fluid. We explore the dynamic response of such a system as a function of numerous variables and explore the structure/property relationships introduced when using a series of different LC monomers. Films which exhibit reflection across the visible and NIR spectral regions can be formed with a variety of reflection notch contrasts and bandwidths.

Monday, April 8, 2013 08:00 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

128 - Functional organic materials based on polymer liquid crystalline networks

***Albertus P.H.J. Schenning**, a.p.h.j.schenning@tue.nl, Dirk J. Broer, Kees W.M. Bastiaansen. Department of Chemistry and Chemical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands*

Functional organic materials are of great interest for variety of applications. For precise functional properties, well-defined hierarchically ordered supramolecular materials are crucial. The self-assembly of liquid crystals has proven to be an extremely useful tool in the development well-defined nanostructured materials.[1] During my lecture, I will show the example of photopolymerizable hydrogen bonded and photochromic mesogens to demonstrate that a wide variety of functional materials can be made from a relative simple set of building blocks. Upon mixing these compounds with other reactive mesogens, nematic, chiral nematic, and smectic liquid crystalline materials can be formed that can be applied as actuators [2], sensors [3],and nanoporous membranes [4], respectively.

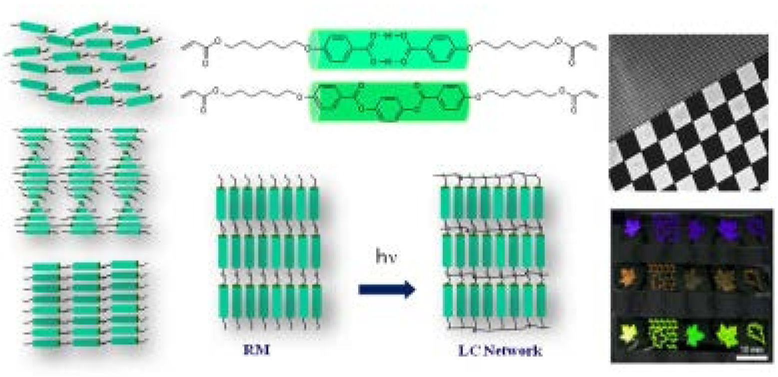


Figure 1. Schematic representation of a nematic, chiral nematic and smectic A LC phase (left side); the ability to create monodomain by alignment (bottom up) and to photopolymerize reactive mesogens to construct polymer materials (middle); the ability to photopattern and inkjet print these systems (top-down, right side).

References:

[1] D.J. Broer, C.M.W. Bastiaansen, M.G. Debije, A.P.H.J. Schenning, Angew. Chem. Int. Ed., 51 (2012) 7102.

[2] I.K. Shishmanova, C.W.M. Bastiaansen, A.P.H.J. Schenning, D.J. Broer Chem. Commun., 48 (2012) 4555.

[3] N. Herzer, H. Guneysu, D.J.D. Davies, D. Yildirim, A.R. Vaccaro, D.J. Broer, C.W.M. Bastiaansen A.P.H.J. Schenning, J. Am. Chem. Soc. *134*(2012) 7608.

[4] A.P.H.J. Schenning, Y. Gomez-Gonzalez, I. Shimanova, D.J. Broer, Liq. Cryst.38(2011) 1627.

Monday, April 8, 2013 08:30 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

129 - On patterning liquid crystal monomers into "perfect" geometric phase holograms

***Michael Escuti**, mjescuti@ncsu.edu, Department of Electrical & Computer Engineering, North Carolina State University, Raliegh, NC, United States*

Nematic liquid crystal (LC) monomers have an amazing ability to align according to surface alignment patterns, as originally developed for retarders in LC displays. More recently, smaller features (i.e., sometimes sub-micron) are being recorded holographically in order to create a new class of phase elements, which we call Geometric Phase Holograms (GPH). When these patterned birefringent elements are formed without LC disclinations or scattering, then nearly any arbitrary wavefront transformation can be embodied - and it will have nearly 100% efficiency in most cases. For example, a GP lens with ^{3} 99% of incident energy focused into a diffraction-limited spot, and the near 100% diffraction efficiency of GP prisms (i.e., more commonly known as polarization gratings). The key in almost all cases, however, to avoid LC defects. We recently reported on methods to record arbitrary and continuous alignment patterns in a photo-alignment polymer, with sub-micron resolution and 10s of cm in area.

In this talk, we study LC alignment at the limits of breakdown in these patterns. One interesting aspect is that in-plane alignment leads to only bend/splay deformations, while the broadband chiral out-of-plane structuring is solely a twist deformation. We report on how the ability of some(most?) photo-alignment polymers to record the time-average orientation of the illuminating polarized light allows for smoothly varying LC patterns and even the recording of multiple exposures. We explore the lower limits of LC alignment patterning, its implications for GPH applications and optics, and identify the most pressing materials-improvements needed.

Monday, April 8, 2013 09:00 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

130 - Color and intensity tuning in polymer stabilized cholesteric liquid crystals

Deng-Ke Yang, *dyang@kent.edu, Hussein Nemati, Rafael Zola. Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, United States*

We used polymer networks to stabilize the planar state in Cholesteric liquid crystals. Under externally applied electric fields, the layered helical structure is retained. We observed two competing modes: (1) the layer undulating while the liquid crystal remaining parallel to the layer, (2) liquid crystal reorienting to form conic helical structure while the layer remaining flat. The two modes depend on the aligning effect of the polymer network. With strong aligning polymer network, Mode 1 dominates and the color of the Cholesteric liquid crystal can be tuned. With weak aligning polymer network, Mode 2 dominates and the reflection intensity of the Cholesteric liquid crystal can be tuned.

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Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
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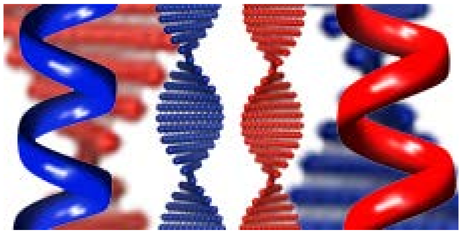
131 - Time-programmed helix inversion in phototunable liquid crystals

Sarah-Jane Aßhoff[1], *Supitchaya Iamsaard*[1], *Alessandro Bosco*[2], *Jeroen J.L.M. Cornelissen*[1], *Ben L. Feringa*[3], ***Nathalie Katsonis***[1], *n.h.katsonis@utwente.nl. (1) University of Twente, Enschede, The Netherlands, (2) Sincrotrone Trieste, Italy, (3) University of Groningen, Groningen, The Netherlands*

Doping liquid crystals with chiral molecular motors enables photocontrolling the period and handedness of the cholesteric helices which are formed. These systems hold great potential for applications, but controlling their rate of relaxation remains a challenge. Here, we show that relaxation of the cholesteric helix is fully determined by helix inversion of the dopants. As thermal helix inversion in molecular motors has been optimised, our results evidence that relaxation of phototunable cholesterics can be dramatically accelerated also.



Monday, April 8, 2013 09:50 AM

Liquid Crystals and Polymers (08:00 AM - 12:10 PM)

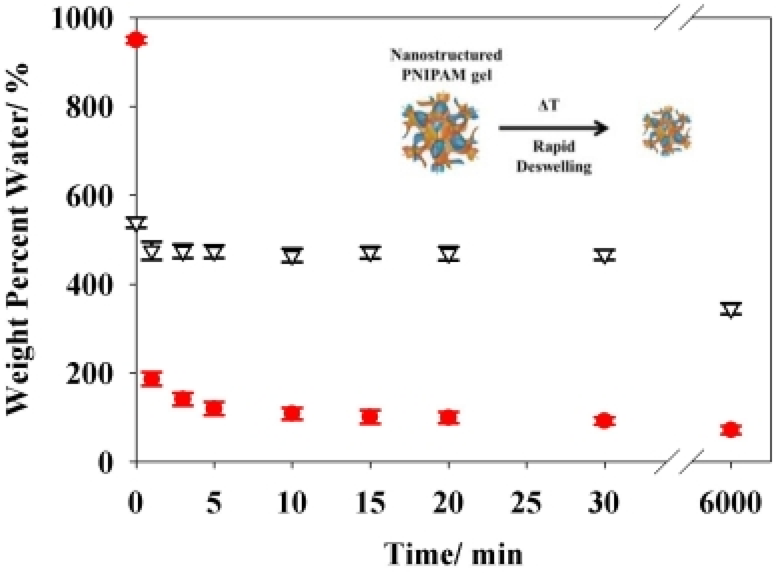
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

132 - Enhanced mechanical properties and stimuli response in nanostructured polymers templated in lyotropic liquid crystals

Bradley S. Forney, Kristan S. Worthington, ***Allan Guymon****, allan-guymon@uiowa.edu. Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa 52242, United States*

Stimuli-responsive polymers are a useful class of polymers that have far-reaching applications ranging from sensors to targeted drug-delivery systems. A major obstacle in many of these applications is the slow-response rate of stimuli-sensitive systems to changes in the external environment. For example, the temperature sensitive polymer poly(*N*-isopropylacrylamide) undergoes a reversible deswelling process when heated above a lower critical solution temperature (LCST) of 33 °C. Although traditional methods of generating a porous structure can dramatically increase the deswelling in PNIPAM systems, the compromised hydrogel structure typically leads to a mechanically weak gel and limits the functionality of the materials in real-world applications. Generating an ordered and nanometer size pore structure utilizing lyotropic liquid crystals (LLCs) as photopolymerization templates is a promising method of improving the transition kinetics of PNIPAM hydrogels without sacrificing the mechanical properties of the system often observed in traditional PNIPAM systems. In fact, a bicontinuous nanostructured gel has shown an astounding increase in the deswelling rate compared to a traditional PNIPAM hydrogel. Additionally, the LLC templating method allows incorporation of toughening agents such as multifunctional siloxane monomers into the network without sacrificing the swelling properties typically associated with the addition of crosslinking hydrophobic moieties. The nanostructured polymer network as directed by the LLC template provides a promising method of improving the transition kinetics and mechanical properties of stimuli-sensitive systems for use in a growing number of advanced applications.



Monday, April 8, 2013 10:30 AM

Liquid Crystals and Polymers (08:00 AM - 12:10 PM)

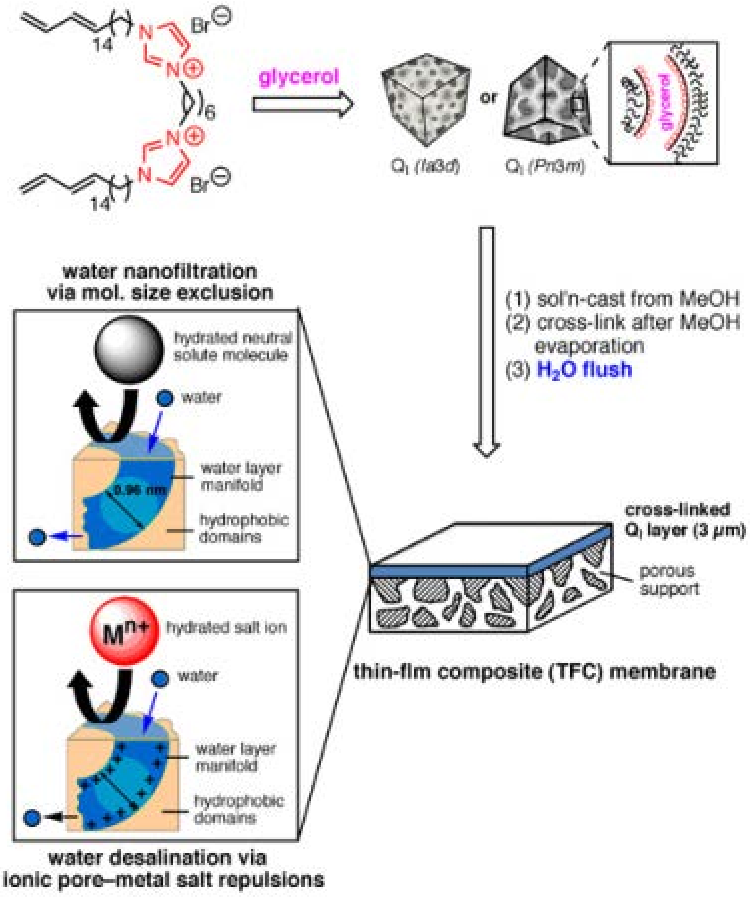
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

133 - Design of non-aqueous lyotropic liquid crystal monomer systems for the tuning of bicontinuous cubic networks in molecular separation applications

Douglas L Gin[1,2]*, douglas.gin@colorado.edu, Brian R Wiesenauer*[1]*, Blaine M Carter*[2]*, Richard D Noble*[2]*. (1) Dept. of Chemistry & Biochemistry, University of Colorado, Boulder, CO 80309-0215, United States, (2) Dept. of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424, United States*

Recently, we found that ordered, 3D-nanoporous, cross-linked lyotropic (i.e., surfactant) liquid crystal (LLC) polymers with a type I bicontinuous cubic (Q_I) structure can be prepared from a new imidazolium-based gemini LLC monomer **1** . The larger, softer, cationic headgroups on monomer **1** allow Q_I phase formation with several polar organic solvents instead of water. By using glycerol instead of more volatile water as the LLC-phase-forming solvent, it was possible to solution-cast thin-film composite (TFC) Q_I polymer membranes for the first time. After photo-cross-linking and pre-filtration to replace the glycerol in the LLC nanopores with water, TFC membranes with uniform, ca. 0.96 nm annular pores for water purification/desalination were obtained that operate by molecular sieving and charge repulsion effects. Herein, we present preliminary results on several new strategies for potentially tuning the Q_I nanopore size and incorporating new functional/responsive groups in the pores. These new approaches include copolymerization of **1** with other LLC monomers and modification of the glycerol liquid component of these new non-aqueous Q_I-phase monomer systems. The relative merits and technical challenges of these new approaches will be discussed.

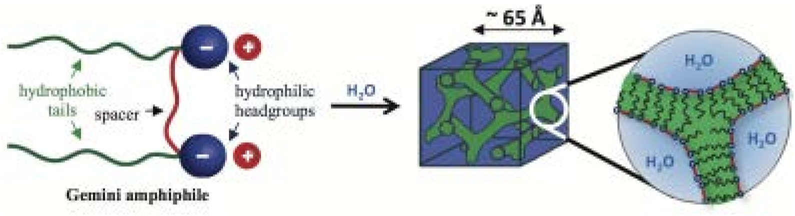


Monday, April 8, 2013 11:00 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

134 - Nanostructured membrane materials from gemini dicarboxylate surfactant lyotropic liquid crystal self-assembly

Gregory P. Sorenson, ***Mahesh K. Mahanthappa***, *mahesh@chem.wisc.edu. Department of Chemistry, University of Wisconsin–Madison, Madison, WI 53706, United States*

Aqueous lyotropic liquid crystal (LLC) self-assembly offers a route for generating functional ultrafiltration membranes with uniform nanoscale pores having well-defined tortuosities, which are lined with well-defined pore wall functionalities. We have developed a modular molecular platform of polymerizable gemini dicarboxylate surfactants, which self-assemble into aqueous LLC gyroid phases. We demonstrate the photocrosslinking of these non-covalent assemblies with unprecedented retention of the gyroid morphology. The selectivities of these materials in molecular filtrations will be discussed.



Monday, April 8, 2013 11:30 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
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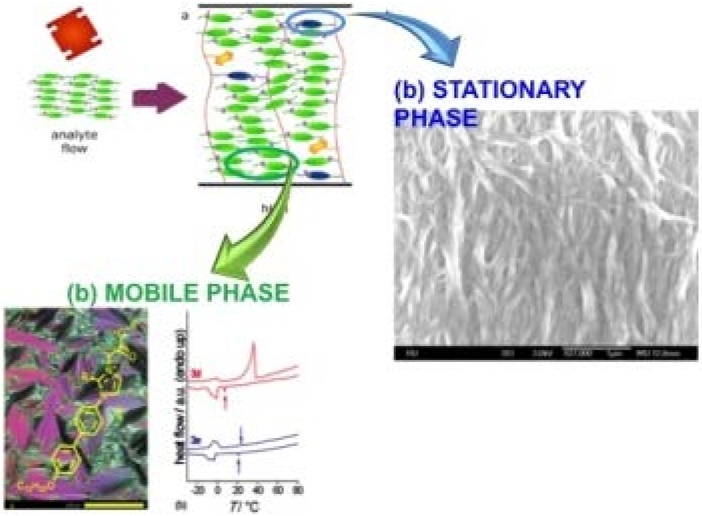
Room: Ste. B, Sec 7/10

135 - Toward 3D biosensors based on liquid-crystals

Alexandra Alvarez Fernandez, *lexalfer@gmail.com, Paul Kouwer. Molecular Materials, Radboud University Nijmegen, Nijmegen, Gelderland 6525 AJ, The Netherlands*

Liquid-crystals (LC) are suitable materials for sensing applications.

We propose a new 3D biosensor platform composed of **(a)** ***Stationary phase*** : a thin, porous film of aligned LC **(b)** ***LC mobile phase*** : aligned by **(a)** . Anything entrapped inside the network will distort it, decreasing birefringence.



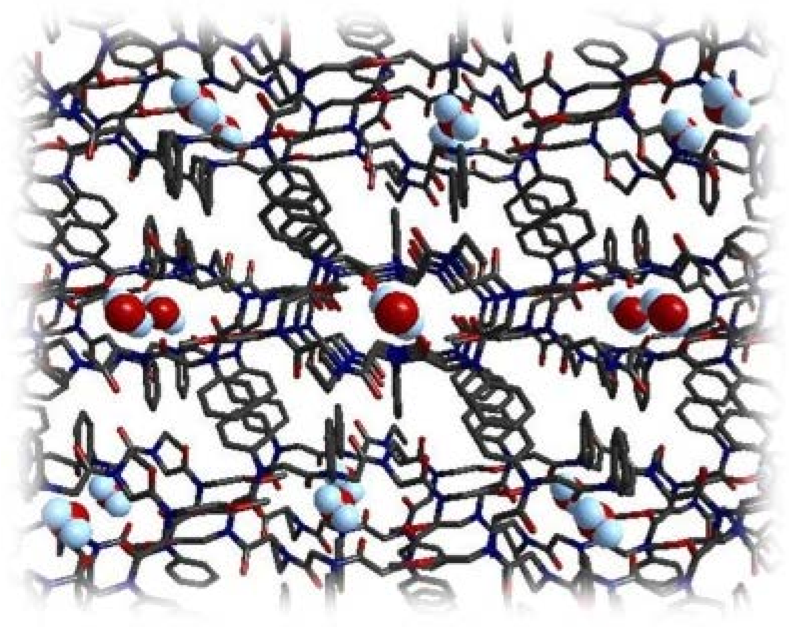
We present as **(b)** a new generation of functional room-temperature ionic-LC with displaying birefringence. For integration of the sensor into a microfluidic device, the scope of **(a)** as alignment tool and its mechanical support were investigated.

Monday, April 8, 2013 11:50 AM
Liquid Crystals and Polymers (08:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

136 - All wet: Peptoid oligomers as antifreeze agents and nanotube wells

Kent Kirshenbaum, *kent@nyu.edu, Department of Chemistry, New York University, New York, New York 10003, United States*

N-substituted glycine peptoids are a versatile and chemically diverse family of sequence-specific oligomers. Recent studies have explored conformational control of peptoids to enable the mimicry of biomolecular structure and function. We have identified peptoid oligomers as dual-action antifreeze agents that mimic the activity of natural antifreeze proteins. We also describe a peptoid macrocycle that forms supramolecular nanotubes in the solid state. The peptoids reversibly accommodate and release water molecules from central channels formed by the macrocycles in the crystalline array via a single-crystal-to-single-crystal transformation.



Monday, April 8, 2013 08:30 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

137 - Polypeptide nanoparticles for ocular drug delivery

Neil R. Cameron, *n.r.cameron@durham.ac.uk, Department of Chemistry & Biophysical Sciences Institute, Durham University, Durham, United Kingdom*

Peptide-based nanomaterials are attractive vehicles for drug delivery due to their inherent functionality, biodegradability and potential biocompatibility. In this presentation, the preparation of a variety of nanostructures from self-assembling amphiphilic block copolypeptides will be described. The polymers are prepared by controlled ring-opening polymerization of N-carboxyanhydrides. In aqueous solution these self-assemble into a variety of nanostructures depending on polymer architecture and assembly conditions. Initial drug loading and release studies as well as results of biocompatibility assays will be presented.

Monday, April 8, 2013 09:00 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

138 - Polymeric NF-kB inhibitors inhibit drug resistance in colon cancer stem cells and deliver chemotherapeutics in vivo

Niren Murthy, *nmurthy@berkeley.edu, Department of Bioengineering, University of California, Berkeley, CA 94704, United States*

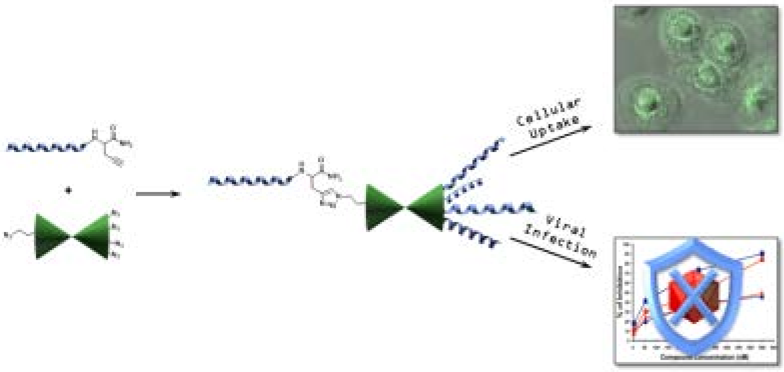
A central challenge in oncology is the development of therapies that eradicate cancer stem cells (CSCs). CSCs' innate drug resistance is a result of their slow self-replication and constitutive activation of nuclear factor-kB (NF-kB), which results in the expression of numerous genes that block current therapies. To overcome the drug-resistance mechanisms of CSCs, we developed nanoparticles that simultaneously deliver chemotherapeutics and an NF-kB inhibitor to tumors for extended periods of time, and thus efficiently kill both CSCs and bulk tumor cells. To deliver therapeutic quantities of a clinically viable NF-kB inhibitor to tumors, the matrix of our nanoparticle is composed of a polymeric prodrug of the NF-kB inhibitor CAPE (pCAPE). Thus, upon hydrolysis, our nanoparticles, termed CAPE nanoparticles (CNPs), degrade into compounds that inhibit NF-kB activation in CSCs and thus render them defenseless to co-delivered chemotherapeutics encapsulated within the particles.

Monday, April 8, 2013 09:20 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

139 - Peptide-functionalized dendrimers for biomedical applications

Tom P. Carberry, *tom.carberry@nyu.edu, Marcus Weck. Department of Chemistry, New York Univerity, New York, NY 10003, United States*

Poly(amide) based dendrimers exhibiting multiple copies of a membrane-interacting peptide sequence at the termini were synthesized through a modular synthesis. The peptide, derived from the Herpes Simplex Virus type 1 fusion proteins, allows the peptidodendrimer to penetrate into the cellular matrix mainly through a non-active translocation mechanism, whereas unfunctionalized dendrimers are excluded from translocation. Furthermore, the viral-derived peptides render the peptidodendrimer an effective antiviral agent. Preliminary designs of peptidodendrimer based therapeutics from our groups will also be presented.



Monday, April 8, 2013 09:40 AM

Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)

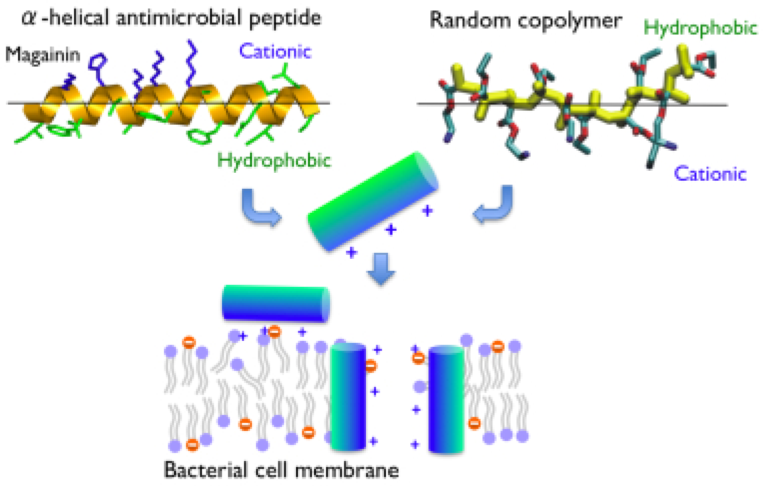
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

140 - Amphiphilic polymer structures and architectures for antimicrobial materials

Kenichi Kuroda, *kkuroda@umich.edu, Biologic and Materials Sciences, University of Michigan School of Dentistry, Ann Arbor, MI 48109, United States*

The emergence of antibiotic resistant bacteria or “superbugs” is rapidly the available treatment options. These new superbugs require newer antimicrobials which can overcome the existing or emerging resistance mechanisms of bacteria. This study focuses on new strategies to develop amphiphilic polymers as antimicrobial agents. These polymers are designed using cationic, amphiphilic structures and architectures as molecular frameworks to mimic the antimicrobial mechanism of host-defense peptides (HDPs) in the innate immune system. Our laboratory has developed cationic, amphiphilic random methacrylate copolymers as synthetic mimics of HDPs. The copolymers inhibited growth of a broad spectrum of bacteria including antibiotic-resistant *strains* without adverse toxicity to human cells. These polymers exert antimicrobial activity by disrupting bacterial cell membranes, in contrast to conventional antibiotics. We also prepared new amphiphilic di-block copolymers with cationic and hydrophobic blocks. The block copolymers showed selective activity to bacteria over human cells, and are much less hemolytic than their random copolymer counterparts. The di-block copolymer chains likely form single molecular micelles, in which the hydrophobic block aggregates and forms core domains in water, wrapped by the cationic polymer chain. This structure curtains the hydrophobic domains and prevents non-specific binding of polymers to human cells. These results suggest that both amphiphilic polymer structures and architectures play important roles in their antimicrobial mechanism.

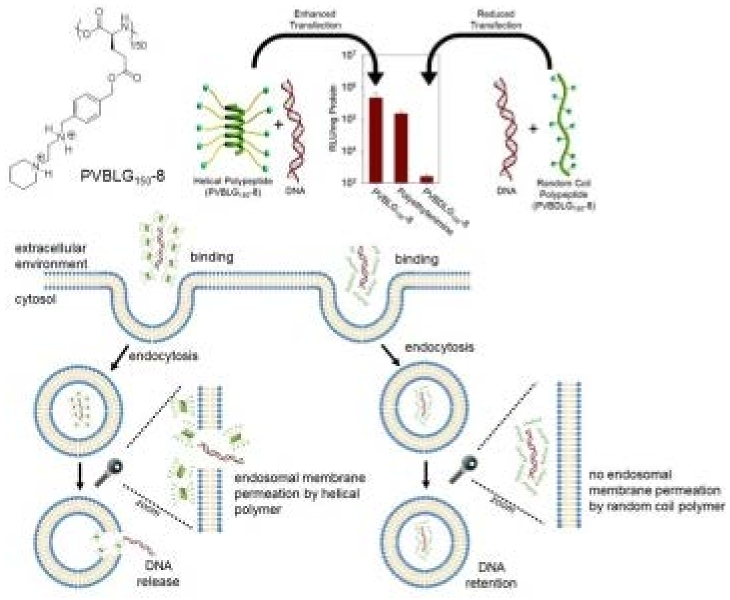


Monday, April 8, 2013 10:15 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

141 - Helical, cationic polypeptide for gene delivery

Lichen Yin, Hua Lu, Haoyu Tang, Nathan Gabrielson, Nan Zheng, Kyung Hoon Kim, Ziyuan Song, Catherine Yao, ***Jianjun Cheng****, jianjunc@illinois.edu. Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

Poly(g-(4-vinylbenzyl)-$_{L}$-glutamate) (PVBLG) served as a bioactive and reactive template for the generation of a library of cationic a-helical polypeptides for gene delivery. The top performing polymer, poly(g-4-(((2-(piperidin-1-yl)ethyl)amino)methyl)benzyl-L-glutamate) (PPEABLG or PVBLG-8), outperformed 25-kDa polyethylenimine by 12-fold. Preliminary data indicates that helicity of these cationic polypeptides is essential for their improved performance, with enhanced membrane disruption a likely source of their transfection efficiency.



Monday, April 8, 2013 10:45 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

142 - In vitro and in vivo evaluation of maleimide-modified liposome for drug delivery

Tianshu LI, *tianshuli@akane.waseda.jp, Shinji TAKEOKA. Department of Life Science and Medical Bioscience, Waseda University, Shinjuku-Ku, Tokyo 162-8480, Japan*

We developed a maleimide-modified liposome M-GGLG, which showed highly improved cellular uptake in all the cell lines tested.

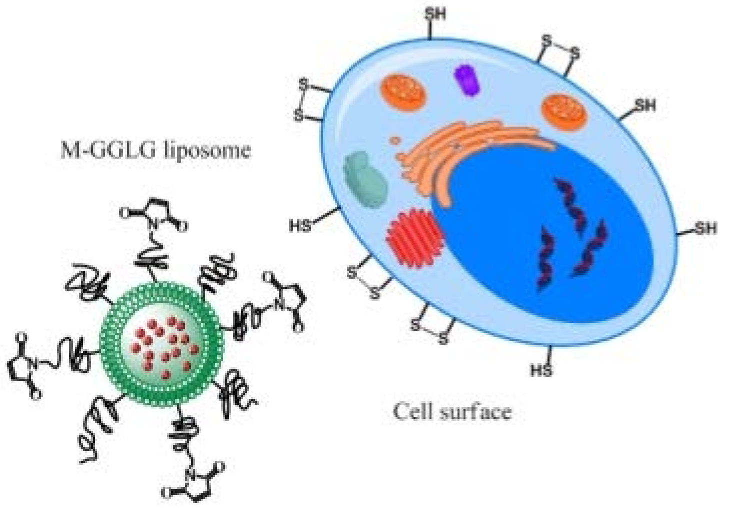


Fig.1. Structure of M-GGLG liposome. Maleimide is a thiol-reactive moiety that would have an interaction with cell membrane proteins.

After encapsulating Doxorubicin, the drug delivery efficiency was evaluated. M-GGLG-DOX had exhibited significantly increased anticancer effect than GGLG-DOX both *in vitro* and *in vivo*.

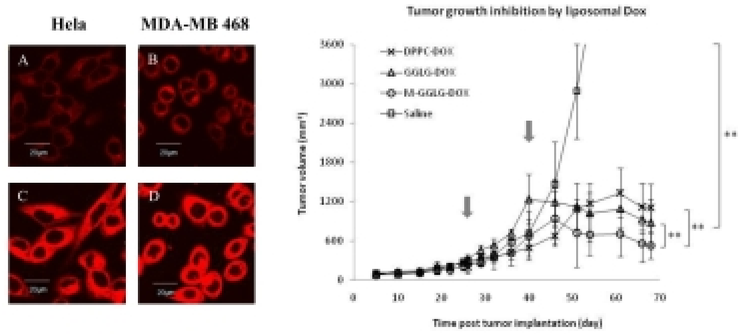


Fig.2. M-GGLG showed increased drug delivery efficiency *in vitro* and *in vivo*. (Left) Cellular uptake of GGLG- (A, B) and M-GGLG-DOX (C, D) in Hela and MDA-MB 468 cells. (Right) Tumor growth inhibition by s.c. injection of DOX-liposomes. Error bars mean ± S.D. n=4.

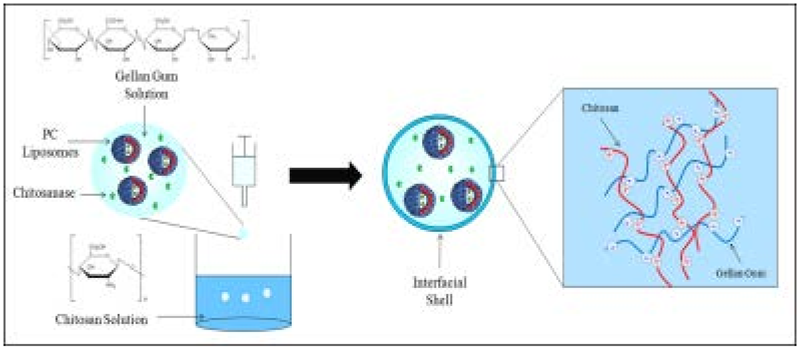
The advanced biological properties were considered as a contribution of the interaction between maleimide and thiols on cell surface. Therefore, we proposed that surface modification of liposome with maleimide might be a potent design for efficient drug delivery.

Monday, April 8, 2013 11:15 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

143 - Self-assembling/self-destructing: “Mothership” capsules for triggered release of vesicles

*Matthew B Dowling[2], Anand Bagal[1], Jaeho Lee[1], **Srinivasa R Raghavan**[1], sraghava@umd.edu. (1) Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States, (2) Fischell Department of Bioengineering, University of Maryland, College Park, Maryland 20742, United States*

Here, we explore a new class of hierarchical containers that are formed via single-step assembly, and at a later time, self-destruct due to their packaged contents. These containers are spherical capsules formed by electrostatic complexation of the anionic biopolymer, gellan gum with the cationic biopolymer, chitosan. We call these capsules “motherships”, as they are engineered to carry a payload of much smaller containers, i.e., nanoscale vesicles (“babyships”), within its lumen. By also packaging an enzyme, chitosanase, inside the capsule, we create “motherships” that self-destruct, releasing their payload of “babyships” into the external environment according to a pre-determined profile. The timescale for self-destruction can be engineered based on the internal concentration of enzyme. The “motherships” are stable when stored in a freeze-dried form and can be readily dispersed into buffer solutions at a later time, whereupon their “internal clock” for self-destruction is initiated. The above concept could be useful for the controlled release of a variety of payloads including drugs, biological therapeutics, cosmetics, or flavor ingredients.

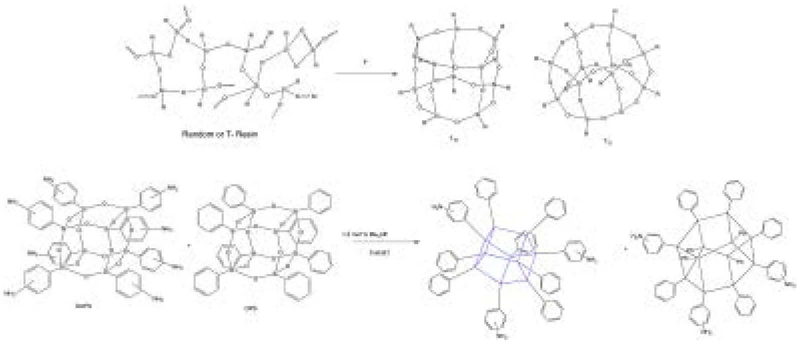


Monday, April 8, 2013 11:35 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

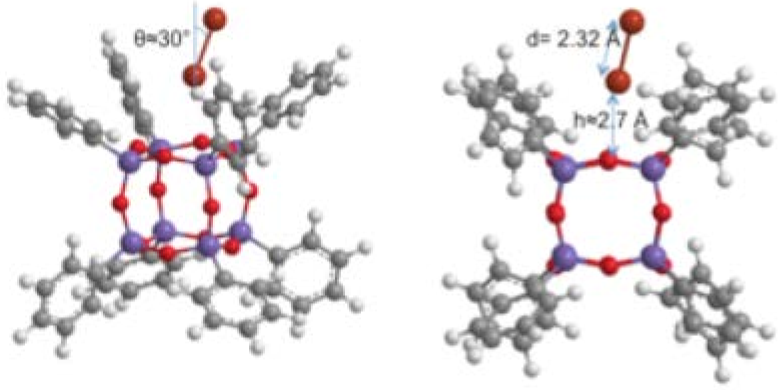
144 - F^- Catalytic rearrangements of silsesequioxanes (SQs) and analogs: New cage sizes and unusual reactive properties

__Richard M Laine__[1], talsdad@umich.edu, Joesph Furgal[2], Mozghan Bahrami[1], Hossein Hashemi[1], John Kieffer[1], Xiao Maier[1], Theodore Goodson[2]. (1) Macromolecular Science and Eng. and Department of MSE, University of Michigan, Ann Arbor, MI 48109-2136, United States, (2) Chemistry, University of Michigan, United States

We have been exploring the use of tBu_4NF as a means to transform either polymeric T resins or single functional group T_8 cages into mixed functional T_{10} and T_{12} SQs as illustrated in the two following reactions.



To this end, we have now developed simple, multigram routes to pure PhT_8, PhT_{10}- and PhT_{12}. The PhT_8 system offers cubic symmetry whereas the PhT_{10} system offers five fold symmetry and is therefore a very unusual molecule. In contrast, the PhT_{12} compound has no symmetry. We have also been able to identify and isolate still larger cages as will be discussed. The various cage sizes allow us to explore the effects of symmetry and size on a wide variety of properties. For example, the PhT_8 cage brominates almost exclusively in the ortho position. The PhT_{10} also brominates preferentially in the same position whereas the PhT_{12} is less selective.

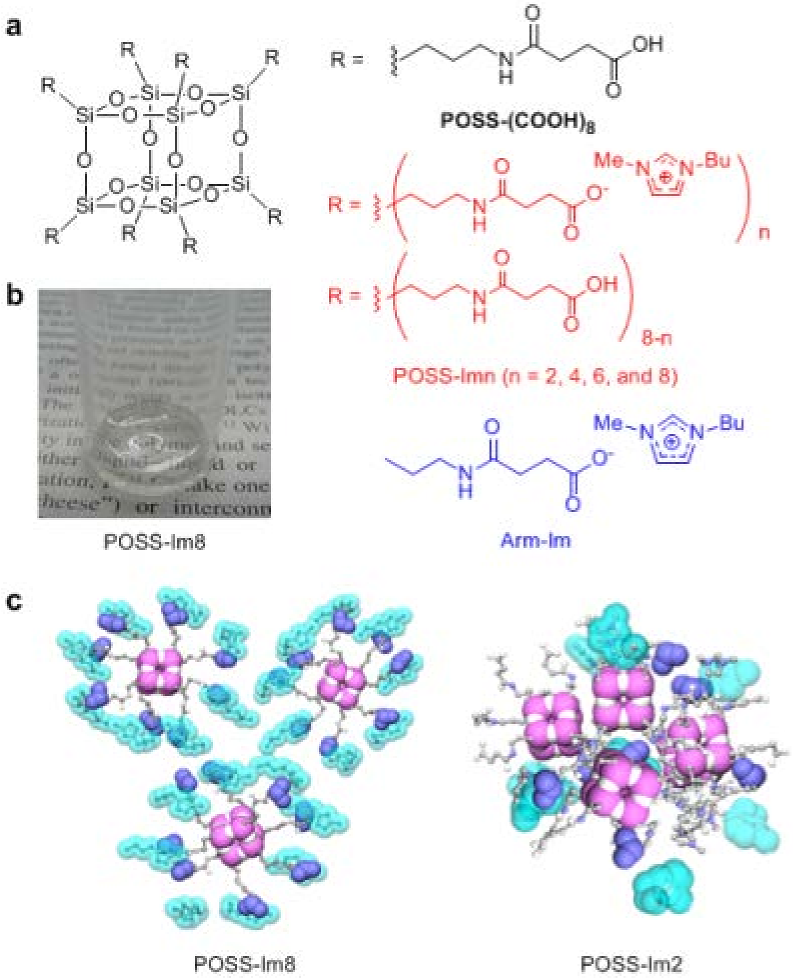


Monday, April 8, 2013 01:30 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

145 - POSS-based nanohybrid materials

Yoshiki Chujo, *chujo@chujo.synchem.kyoto-u.ac.jp, Kazuo Tanaka. Deapartment of Polymer Chemistry, Kyoto University, Kyoto, Kyoto 615-8510, Japan*

A typical polyhedral oligomeric silsesquioxane (POSS) molecule possesses a cubic rigid (T8) structure represented by the formula R8Si8O12, where the central inorganic core (Si8O12) is functionalized with organic moieties (R) at each of the eight vertices. The rigid silica cube shows significant high thermal and chemical stability. Moreover, POSS can form a highly-symmetrical and star-shaped structure. Thereby, unique characteristics distinctly different from planner molecules can be expected due to such structural features. Thus, the rigid polyhedral structures have received considerable attentions as a building block for constructing functional molecules and nanometric materials. Here in this paper, our recent works on advanced materials based on the functionalized POSS by the polar substituents are reviewed.

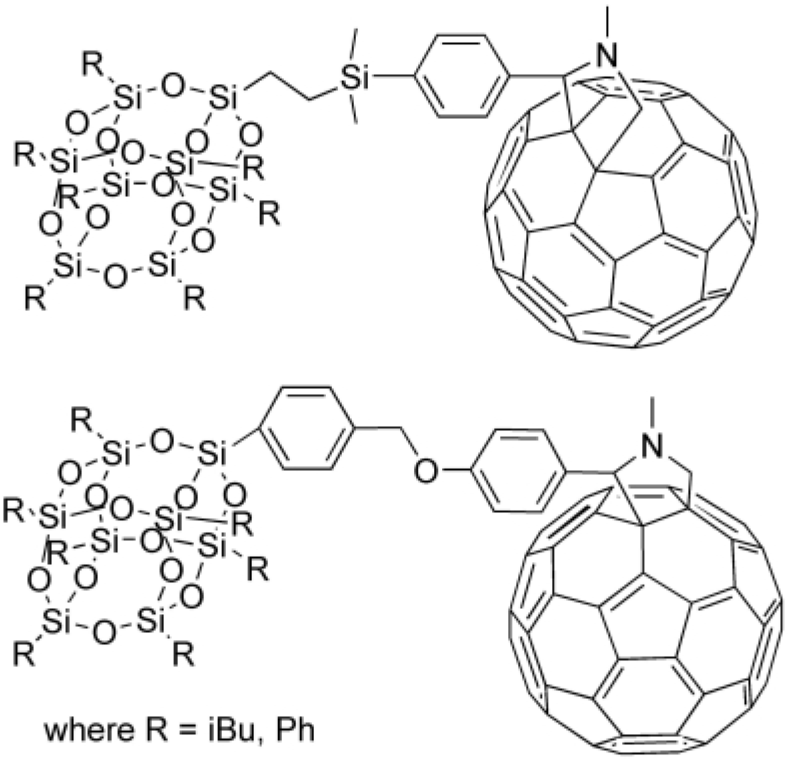


Monday, April 8, 2013 02:00 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

146 - Polyoligosilsesquioxane (POSS) based hybrid nanomateials: Functionality resulting in new directions

Janis G Matisons, *jmatisons@gelest.com, Research and Development, Gelest Inc, Morrisville, Pennsylvania 19067, United States*

The ideal aim of combining inorganic and organic materials is to achieve an optimum combination of the properties inherent to each material, which can then enhance the value of the hybrid nanomaterial in the end application. POSS nanocomposite materials, will be reviewed with some highlights taken from my last decade of synthetic preparations. Because they have unique, well-defined, and compact hybrid chemical structures with an inorganic silica-like core and organic functional groups bound to silicon, they have been widely used for preparing organic-inorganic hybrids for which the exact shape, size, and mechanical properties of the inorganic component are perfectly defined Recent work on both water soluble POSS inorganic-organic hybrid materials and POSS materials incorporating C60 functionality for optical limiting applications will be particularly highlighted.



Monday, April 8, 2013 02:30 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

147 - Analyzing structure-photophysical property pelationships of T8, T10, T12, and oligomeric stilbenevinyl silsesquioxanes

Joseph C Furgal[1], *furgaljc@umich.edu, Neranga Abeyasinghe*[1], *Jae Hwan Jung*[2], *Eongyu Yi*[3], *Theodore Goodson III*[1,2], *Richard M Laine*[2,3]. *(1) Department of Chemistry, University of Michigan Ann Arbor, Ann Arbor, Michigan 48109, United States, (2) Department of Macromolecular Science and Engineering, University of Michigan Ann Arbor, Ann Arbor, Michigan 48109, United States, (3) Department of Materials Science and Engineering, University of Michigan Ann Arbor, Ann Arbor, Michigan 48109, United States*

Silsesquioxane (SQ) materials are of considerable interest for hybrid photonic materials applications, due to high stability, high solubility, high functional group density, and potential 3-D excited state conjugation. Our goal is to establish structure-photophysical property relationships as a function of cage symmetry, size and substitution. Initial mapping studies explored $T_{10/12}$ mixed stilbenvinylSQs, of which unique photophysical properties were found in solution. Studies have been extended to the pure T_8, T_{10} and T_{12} cages and oligomers, with their solid-state analogs.

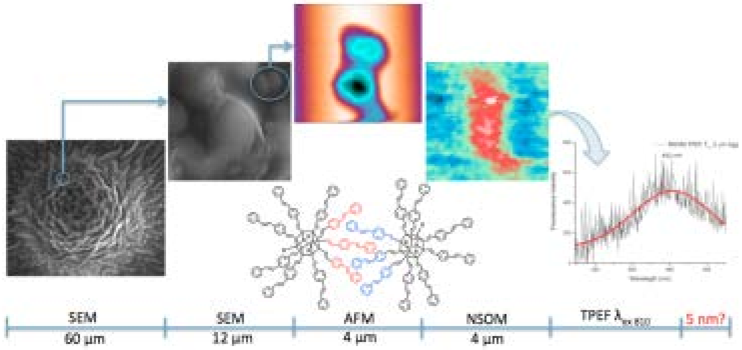


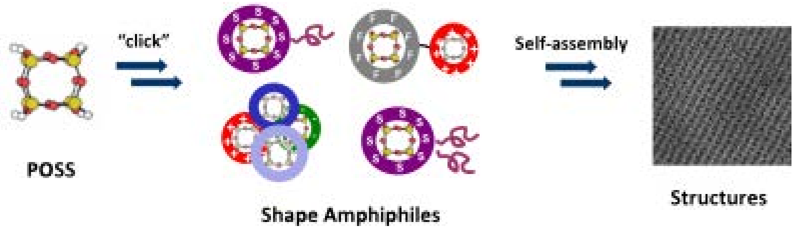
Figure 1. SEM, AFM, NSOM and TPEF-NSOM of T_{10} stilbenevinylSQ aggregates.

Monday, April 8, 2013 02:50 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

148 - Exploring POSS-based shape amphiphiles: “Click” synthesis and versatile self-assembly

***Wenbin Zhang**, wz8@uakron.edu, Xinfei Yu, I-Fan Hsieh, Yiwen Li, Xuehui Dong, Kan Yue, Mingjun Huang, Hao Liu, Jinlin He, Stephen Z. D. Cheng. Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 91107, United States*

Shape amphiphiles are hybrids constructed from building blocks of distinct shapes. Many model shape amphiphiles have been recently developed including molecular Janus particles, molecular nanoparticle clusters, and multi-headed and/or multi-tailed giant surfactants. The use of sequential click chemistry in combination with other efficient chemical transformations provides a modular, efficient, and robust approach for precision synthesis and their self-assembly reveals unique phase behavior and structures, promising a new platform for engineering structures with sub 10 nm feature sizes.



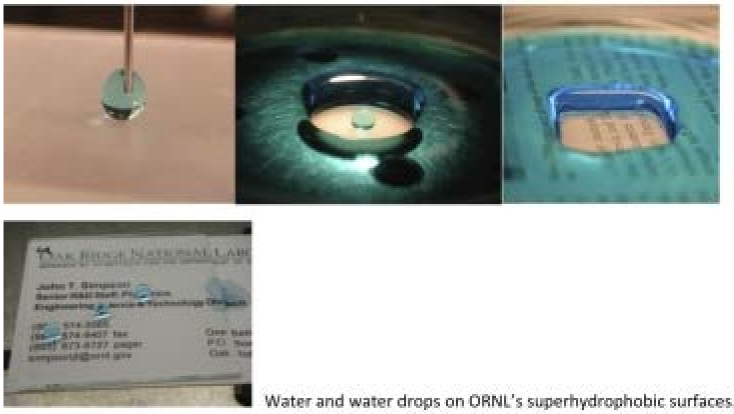
Monday, April 8, 2013 03:25 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

149 - ORNL's superhydrophobic (SH) technology

John T Simpson, *simpsonjt@ornl.gov, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6054, United States*

Researchers at the Department of Energy's Oak Ridge National Laboratory (ORNL) have developed a set of nanotextured amorphous silica-based materials, coatings, thin films, and surface treatments that are so water repellent that they have the ability to fundamentally change how liquid water interacts with surfaces and coatings. This talk will describe the nature and basics of superhydrophobicity, the history of ORNL's superhydrophobic research activities, our latest advancements in superhydrophobic optical quality and durability, and a discussion of possible commercial applications. Some examples of what will be discussed include: How ORNL created the world's most water repellant surface, how we went from small, expensive SH discs, to “dirt cheap” SH coatings and surface treatments, our clear SH coating development effort. And, I will show and explain the Moses Effect.

I will also discuss the following potential applications: Watercraft drag reduction; Anti-corrosion of equipment; Anti-biofouling of submerged sensors and equipment; Anti-icing on aircraft wings; and Keeping clothing completely dry and breathable in normally wet environments.



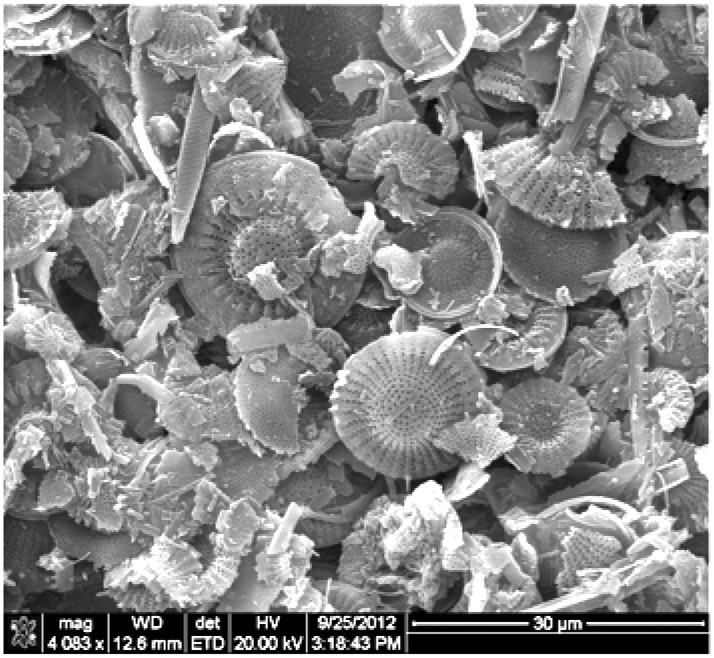
Water and water drops on ORNL's superhydrophobic surfaces.

Monday, April 8, 2013 03:45 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

150 - Development of hydrophobicity in silane-treated diatomaceous earth coatings

Frank D Blum, *fblum@okstate.edu, Helanka Perera, Bhishma Sedai, Bal K. Khatiwada, Hamid Mortazavian. Department of Chemistry, Oklahoma State U, Stillwater, OK 74078, United States*

The development of hydrophobic coatings from treated diatomaceous earth (DE) will be discussed in terms of the amounts of fluorosilane coupling agent on the surface and also the amount of treated-DE in the coating. The resulting coatings were probed by contact angle and scanning electron microscopy. It was found that for model DE-binder systems, the contact angle of the coating was independent of the polymer as long as the particle loading was greater than a minimum amount. It was also found that the DE seemed to go to the air interface as its fraction in the coating increased.



Monday, April 8, 2013 04:15 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: HEC C

151 - Programmable atom equivalents

***Chad A. Mirkin**, chadnano@northwestern.edu, Chemistry, Northwestern University, Evanston, IL 60208, United States*

Spherical nucleic acids (SNAs) are often comprised of an inorganic nanoparticle core functionalized with a densely-organized and highly-oriented nucleic acid shell. Aside from their uses in biomedicine, these unique materials can be utilized to generate nanoparticle superlattice assemblies with crystal structures never before seen in nature. SNAs are a new type of programmable atom equivalent. The strength and length of the DNA “bonds” can be adjusted by varying sequence and length; the properties of the nanoparticle “atom” equivalents can be adjusted by varying size, shape, and composition. Since DNA binding dictates assembly, it follows that any monodisperse nanoparticle that can be functionalized with a densely layer of DNA can be used as a building block. New developments towards creating a universal strategy to position any type of SNA into a wide variety of crystalline architectures will be discussed. This work has important implications in materials, optics, plasmonics, catalysis, and energy.

Monday, April 8, 2013 01:35 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

152 - Supramolecular self-assembly of small molecules in cellular environment

Yi Kuang, Yuan Gao, Xuewen Du, Fan Zhao, Junfeng Shi, Ning Zhou, Yibing Huang, ***Bing Xu****, bxu@brandeis.edu. Chemistry, Brandeis University, Waltham, MA 02454, United States*

Molecular self-assembly plays many critical roles in biology. Exhibiting important biological functions, from unfolding proteins to activating enzymes and to controlling cell fates, the assemblies of small molecules formed via supramolecular interactions, undoubtedly, are able to serve as functional molecular entities in cellular environment. Conventional biochemical and genetic methods are, however, inadequate to study the supramolecular assemblies of small molecules because they are not defined at the genetic level. We have developed the experimental strategies for controlling the formation and identifying the corresponding protein targets of the supramolecular assemblies of small molecules. In this talk, we discuss the emergent properties of the supramolecular assemblies of small molecules and report their potential applications in three closely related areas: anticancer nanomedicine, functional mimic of biomacromolecules, protein target identification.

Monday, April 8, 2013 02:10 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

153 - Advances in soft lithography for particle templating

Joseph M DeSimone, *desimone@unc.edu, Director, Frank Hawkins Kenan Institute of Private Enterprise, Chapel Hill, North Carolina 27599, United States, Department of Chemistry, Chancellor's Eminent Professor of Chemistry, Chapel Hill, NC 27599, United States, Department of Chemical Engineering at North Carolina State University, William R. Kenan Jr. Distinguished Professor of Chemical Engineering, Raleigh, NC, United States, Department of Chemistry, William R. Kenan Jr. Distinguished Professor of Chemistry, Chapel Hill, NC 27599, United States*

Nanotechnology has the potential to provide critical improvements and innovation in both life science and material science research. Progress in nanotechnology has been limited by challenges associated with controlling particle size, shape, deformability, chemical composition, uniformity, cell targeting and the ability to tune and control the release of known amounts of cargo. Particle Replication in Non-Wetting Templates (PRINT®) fabricates 'calibration quality' particles to assess the role of individual components in nanoparticle characteristics and behavior. PRINT is a continuous, high resolution molding technique that allows the fabrication of precisely defined nanoparticles with complete control over key particle attributes. The master templates are made using state-of-the-art technologies from the semiconductor industry which enables highly uniform populations of shape controlled particles to be fabricated. The top-down particle fabrication technique of PRINT enables the simultaneous and independent control over particle size (20 nm to >100micron), shape (filaments, cubes, cylinders, discs, toroidal), composition(organic/inorganic, solid/porous), cargo(hydrophilic or hydrophobic therapeutics, biologics, oligonucleotides, siRNA, imaging agents, sensors, imaging agents), modulus(stiff, deformable), and surface chemistries (targeting peptides, antibodies, aptamers, cation/anion exchange, stealth PEG chains. PRINT is a novel method for molding shape-specific particles at the nanometer to micrometer scale that has direct applications in life sciences and material science research.

Monday, April 8, 2013 02:45 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

154 - Development of 2D and 3D functional molecular architectures through dynamic covalent chemistry

Wei Zhang, *wei.zhang@colorado.edu, Yinghua Jin, Chenxi Zhang, Qi Wang, Kenji Okochi. Chemistry and Biochemistry, University of Colorado Boulder, Boulder, CO 80309, United States*

Dynamic covalent chemistry (DCC) has attracted tremendous research interest, particularly in the past decade, due to its great power in highly efficient synthesis of complex molecular architectures from simple small molecule precursors. This presentation will focus on the efficient synthesis of shape-persistent, structure-tunable 2-D hetero-sequenced macrocycles as well as 3-D molecular cages via metathesis reactions. These well-defined discrete molecules have shown great potential in a variety of important applications, such as carbon capture, fullerene separation, biomedical diagnostics, etc. These results illustrate how the thermodynamically controlled DCC can be utilized to construct target-specific nanomaterials and enable their practical applications.

Monday, April 8, 2013 03:35 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

155 - Water based polymer assembly for nanostructured bioresponsive cancer delivery systems

Paula T. Hammond, *hammond@mit.edu, Department of Chemical Engineering and Koch Institute of Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

It is possible to use layer-by-layer (LbL) assembly of polyelectrolytes as a means of generating delivery systems that target tumors and exhibit responsiveness to the tumor microenvironment to enhance cel uptake. It is possible to design nanoparticles that consist of several nanolayers wrapped around a core encapsulating material; we demonstrate that nucleic acids can be incorporated in the outer layers to enable delivery of single or multi-component drug schedules. We can use native polysaccharides as a means of targeting while maintaining effective stealth properties in the blood stream. Finally, we have also demonstrated the use of an RNA synthesis method known as rolling circle transcription (RCT) to produce extremely long strands of RNA for cellular delivery - a form of polymeric RNAi - and yield active siRNA strands at significant doses, as shown in an animal model. As the RNA strand is synthesized, it folds into a very dense, sponge-like sphere containing up to half a million copies of the same RNA sequence, which can be packed into a single nanoparticle for delivery. These poly-RNAi systems are unique approaches to the generation of RNAi that generates its own delivery vehicles, allowing release of RNAi in much more potent and less toxic conditions, thus opening up the therapeutic window for *in vivo* efficacy.

Monday, April 8, 2013 04:10 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

156 - Chemisitry and application of ketene functionalized polymers

Frank A Leibfarth, *Frank.Leibfarth@gmail.com*, *Craig J Hawker*. *Materials Research Laboratory, Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106, United States*

We introduce the versatile reactivity of ketenes to polymer chemistry. New materials synthesized take advantage of Meldrum's acid as both a synthetic building block and a thermolytic precursor to dialkyl ketenes. The inherent property of the ketene functional group provides crosslinking *via* dimerization, acts as a reactive chemical handle *via* addition, or both. To date, this Meldrum's acid-based system has provided opportunities in a number of advanced applications, including the surface chemical patterning of substrates, controlled crosslinking of commodity polyolefins, surface neutralization of block copolymer lithography substrates, and fabrication of mechanically robust, solvent-stable nanostructured materials. The facile access to Meldrum's acid containing polymers and the well-developed chemistry of ketenes assure that this methodology will be a powerful tool for chemists, materials scientists, and engineers in the future.

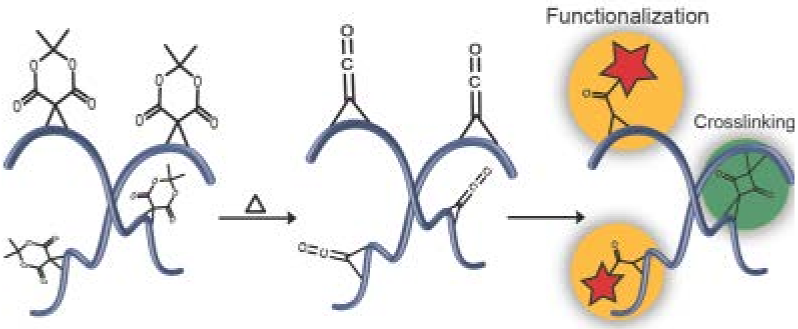


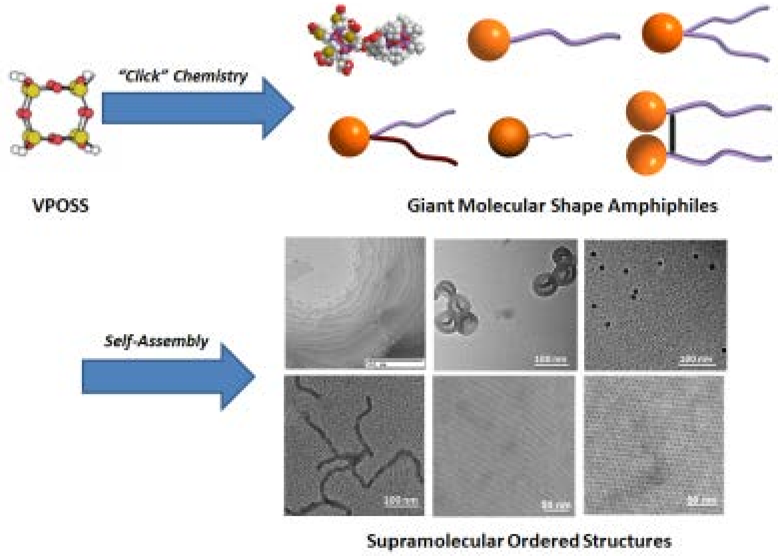
Figure 1. Generating crosslinked and functionalized polymer systems through our ketene-based methodology

Monday, April 8, 2013 01:30 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

157 - Giant molecular shape amphiphiles based-on polyhedral oligomeric silsesquioxanes: Molecular design, click synthesis, and self assembly

Yiwen Li, *yl48@zips.uakron.edu, Stephen Cheng. Department of Polymer Science, The University of Akron, Akron, Oh 44325, United States*

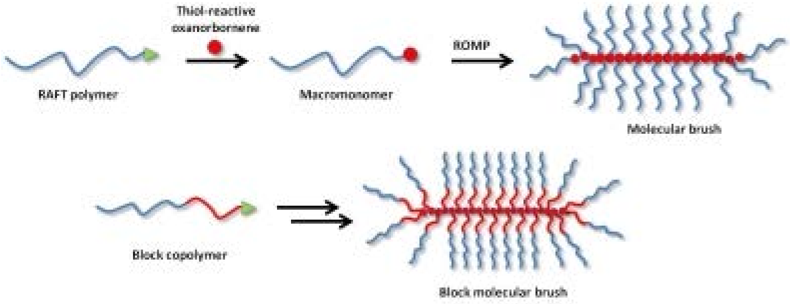
Recently, a new class of amphiphiles with both of shape and interaction incommensurate (named “shape amphiphiles”) has been proposed. It has been found that shape amphiphiles could self-assemble into diverse hierarchical structures, similar to those observed in small molecular surfactant and block copolymer systems; yet this class of amphiphiles possesses distinct differences with various molecular shape, symmetries, and topologies. My current research focuses on the Polyhedral Oligomeric Silsesquioxanes (POSS)-based giant molecular shape amphiphiles. For example, functionalized POSS cages with different surface chemistry and size were employed to construct molecular Janus particles with various symmetry breakings. These particles could self-organize into hierarchically ordered structures in bulk. Another illustrating example is a series of novel giant surfactants, lipids and geimin surfactants possessing a hydrophilic POSS head and polymer or alkyl chain tails. Diverse architectures of those materials have been constructed and their self-assembly processes in solution and bulk state have been discussed.



Monday, April 8, 2013 01:55 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

158 - Versatile brush architectures for siRNA delivery via controlled polymerization/click chemistry

Brooks A Abel[1], *brooks.abel@eagles.usm.edu, Charles L McCormick*[1,2]. *(1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States, (2) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406, United States*



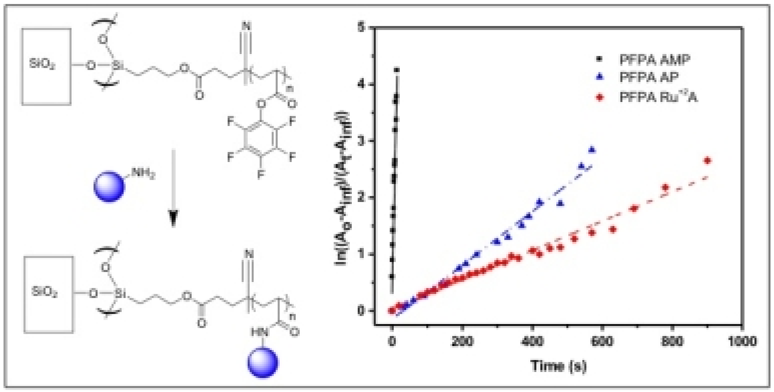
We report the preparation of macromonomers via post-polymerization modification of polymers produced by reversible addition-fragmentation chain transfer (RAFT) polymerization with thiol-reactive oxanorbornenes. Subsequent polymerization of oxanorbornene-functional macromonomers by ring opening metathesis polymerization (ROMP) affords the corresponding molecular brushes in a controlled fashion. This versatile route facilitates use of “off-the-shelf” styrene-, acrylamide-, and acrylate-based RAFT polymers prepared under conditions specific to the monomer-type (e.g. polymerization in aqueous or organic media) for convenient synthesis of a variety of molecular brush polymers. Furthermore, end group transformation of RAFT polymers using methanethiosulfonate-functional oxanorbornenes results in molecular brush polymers possessing side chains linked to the brush backbone via disulfide linkages, the latter serving as *in-situ* trigger sites for drug delivery. Future work focuses on molecular brushes specifically prepared for the targeted delivery of siRNA to cancer cells.

Monday, April 8, 2013 02:20 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

159 - Generation of complex surfaces through postpolymerization functionalization of surface-bound polymers with an orthogonal, self-sorting click reaction

Rachelle M Arnold, *arnoldrm@uga.edu, Gareth Sheppard, Jason Locklin. Department of Chemistry, University of Georgia, Athens, GA 30602, United States*

One effective method for adding complex functionality to a polymeric interface is through postpolymerization modification. Click reactions are ideal for the functionalization of surface-bound polymers and can be used to tune interfacial properties. Activated ester-containing monomers are commonly used for click reactions, as they reach high conversion, have simple reaction conditions, and do not produce harmful byproducts. In this work, the aminolysis kinetics between two active ester polymer brush platforms, poly(4-pentafluorophenyl acrylate) (poly(PFPA)) and poly(*N*-hydroxysuccinimide-4-vinyl benzoate) (poly(NHS4VB)), were compared. UV-vis was used to monitor the aminolysis of both brush platforms with 1-aminomethylpyrene (AMP), 1-aminopyrene (AP), and Ru(bpy)$_2$(phen-5-NH$_2$)(PF$_6$) (Ru^{2+}A). The pseudo-first-order rate constant (*k*¢) of poly(PFPA) modified with AMP, AP, and Ru^{2+}A were 2.46 × 10^{-1}, 5.11 × 10^{-3}, and 2.59 × 10^{-3} s^{-1}, respectively, while poly(NHS4VB) only reacted with the alkyl amine, albeit at a slower rate constant, *k*¢ of 3.49 × 10^{-3} s^{-1}, compared to poly(PFPA) with AMP. PFPA was then used for the generation of a patterned surface. PFPA was photopolymerized in the presence of a shadow mask, and a TMS-protected alkyne derivative of styrene was photopolymerized to backfill the areas that were protected by the TEM grid. A one-pot, self-sorting copper catalyzed azide-alkyne/aminolysis reaction was then used to functionalize the surface with two different dyes. Fluorescence microscope images showed distinct spatial control over the sequential polymerizations, with little cross-contamination.

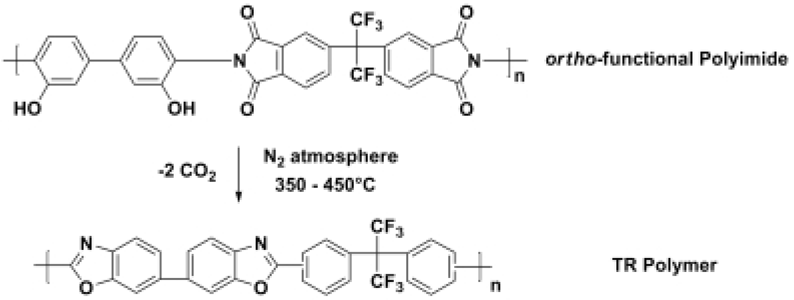


Monday, April 8, 2013 02:45 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

160 - Synthesis, characterization, and transport properties of thermally rearranged polyimides for gas separations

Zachary P. Smith[1], *zachary@che.utexas.edu, David F. Sanders*[1]*, Benny D. Freeman*[1]*, Donald R. Paul*[1]*, Ruilan Guo*[2]*, James E. McGrath*[3]*. (1) Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78758, United States, (2) Department of Chemical and Biomolecular Engineering, Notre Dame, South Bend, IN 46556-5637, United States, (3) Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States*

Thermally rearranged (TR) polymers are polybenzoxazoles derived from a thermally-induced decarboxylation reaction of *ortho*-functional polyimides:



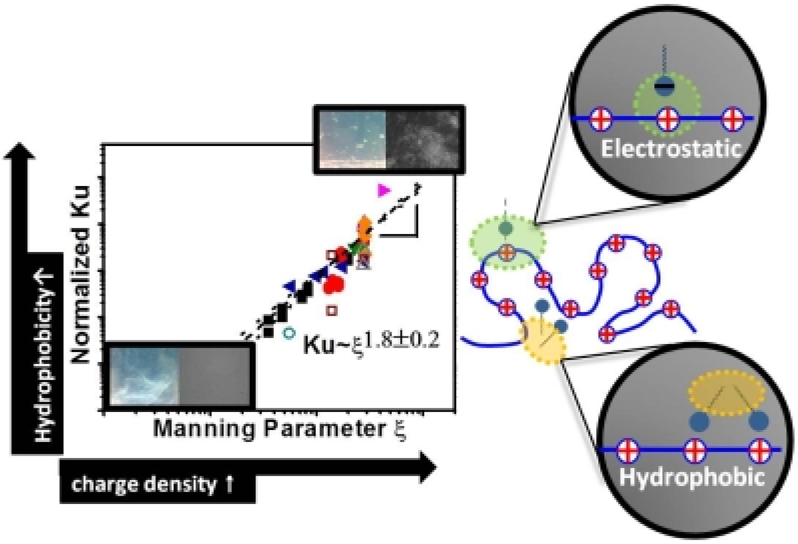
These TR polymers have very high combinations of permeability and selectivity for a number of gas separations including CO_2/CH_4 and C_2H_4/C_2H_6. To investigate the effect of conversion on transport properties, a series of TR polymer films were synthesized, characterized, and tested for H_2, N_2, O_2, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 permeability. Increasing conversion increases permeability with minimal losses in selectivity.

Monday, April 8, 2013 03:25 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

161 - Coacervation in model oppositely charged polyelectrolyte/surfactant mixtures: Effects of cationic polymer charge density and alkyl chain surfactant hydrophobicity

Dongcui Li[1], *dongcui@udel.edu, Beth Schubert*[2], *Norman J. Wagner*[1]. *(1) Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States, (2) The Procter & Gamble Company, Cincinnati, OH 45252, United States*

Coacervation in mixture of polyelectrolytes and surfactants with opposite charge is common in nature and is also technologically important for applied research including food, cosmetics and pharmaceutics. To better understand the complexation behavior of these systems, we have investigated a systematic variation of model mixtures, to assess the significance of polymer's charge density and surfactant chain's hydrophobicity, holding as many of the auxiliary properties constant. The goal is a quantitative link between molecular interactions, phase behavior, microstructure and coacervate rheological performance. To achieve this, we combined experimental techniques for thermodynamic measurements with methods for microstructure characterizations, and rheology at different structural levels. A model for surfactant binding onto the polymer enables a semi-empirical quantification of the polyelectrolyte/surfactant association behavior, where a master binding behavior was identified in the frame work of the Satake-Yang binding parameters. The interactions are governed by both electrostatic and hydrophobic interactions, with relative importance depending on the polymer's charge density and surfactant alkyl chain's hydrophobicity. The proposed semi-empirical free energy equation with the given contributions of both the charge density as well the surfactant hydrophobicity, provides us with an engineering map describing the self-assembly behavior in coacervation systems. Finally, along with the structural and rheological characterizations, it is shown that increasing the polymer's charge density and surfactant chain's hydrophobicity lead to dramatic changes in coacervate microstructure, which also corresponds to the greater shear and elastic moduli.

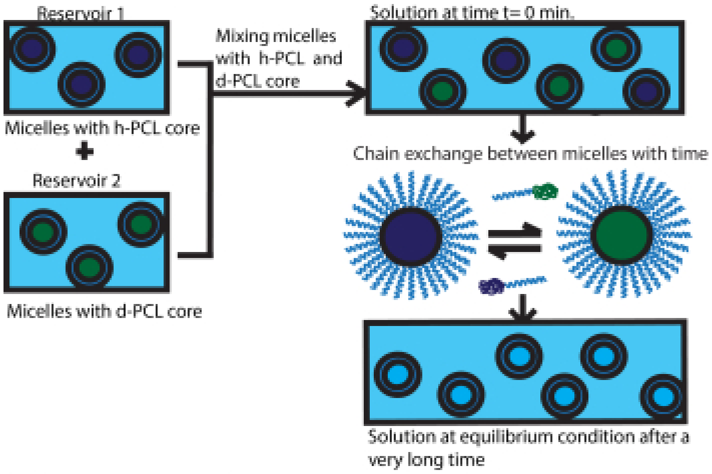


Monday, April 8, 2013 03:50 PM
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

162 - Dynamic processes in diblock copolymer micelles with a semi-crystalline core

Avantika Singh, *asingh15@uh.edu, Maria D. Marquez, Megan L. Robertson. Department of Chemical And Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States*

The impact of core crystallization on the chain exchange kinetics in polymeric micelles is being investigated. Micelles containing diblock copolymers of poly(ethylene oxide) and poly(e-caprolactone) are compared with a structurally similar amorphous analogue. Time resolved-small angle neutron scattering and pulse field gradient NMR are employed to probe single chain exchange and the free unimer concentration, respectively. Fluorescence resonance energy transfer is used to determine the residence time of an encapsulated dye in the micelle core, a model for drug delivery.



Schematic representation of a time resolved-small angle neutron scattering experiment.

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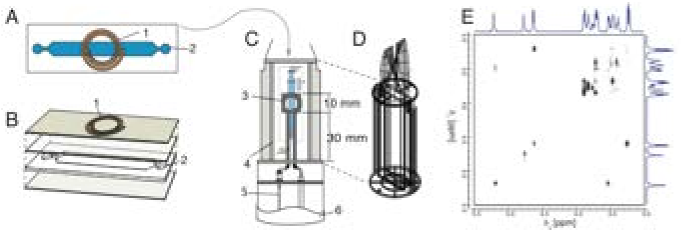
Excellence in Graduate Polymer Research (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

163 - Integration of high-resolution NMR into lab-on-a-chip devices for the study of complex systems

Marcel Utz[1], *marcel.utz@soton.ac.uk, Herbert Ryan*[2], *Graeme Finch*[1]*. (1) School of Chemistry, University of Southampton, Southampton, United Kingdom, (2) Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia VA 22904, United States*

Lab-on-a-chip devices (LoC) offer detailed control over colloidal systems, complex reaction networks, cells, and small organisms. Integration of NMR spectroscopy into LoC is attractive, but challenging in terms of sensitivity and resolution. We have recently shown that highly resolved spectra can be obtained from LoC by integration of a passive radiofrequency resonator, along with careful design of the fluidic network to avoid susceptibility broadening. The approach offers new opportunities, including the incorporation of hyperpolarisation techniques into LOC NMR devices.

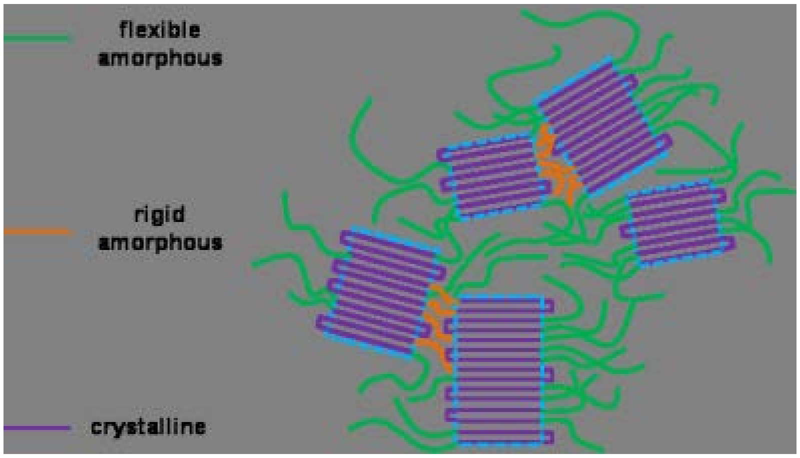


Monday, April 8, 2013 01:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

164 - Insights into molecular packing of semicrystalline P3HT by variable temperature ^{1}H relaxation and ^{13}C solid-state NMR measurements

Ryan Nieuwendaal*, ryann@nist.gov, Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8541, United States*

Despite its prevalent use in organic electronics, a generally agreed upon model of crystallization of high molecular weight, highly regioregular (> 98%) poly-3-hexylthiophene (P3HT) has not arisen due to its complex, semicrystalline nature. P3HT chains have been proposed to form in a number of crystalline motifs, and a multitude of solid-solid phase transitions have been reported that have been tied to either thiophene main chain or the hexyl side chain motions. Furthermore, a number of mesophases have been proposed for P3HT, but a definitive assignment has been elusive. In this presentation, I will discuss the results of ^{1}H and ^{13}C variable temperature NMR relaxation experiments on P3HT films that were prepared as a function of drying rate and post-processing conditions. Results of powder x-ray diffraction, optical absorption, and differential scanning calorimetry measurements will be supported by solid-state NMR spectra in order to comment on the local packing of chains both inside and outside the crystal.

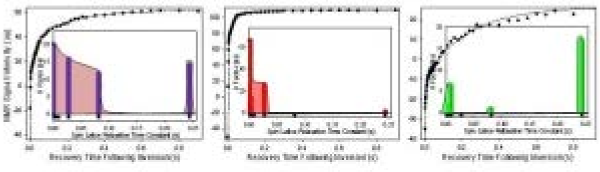


Monday, April 8, 2013 01:55 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

165 - New NMR techniques for measuring relaxation-time distributions in polymer blends and shale materials

Lingyu Chi, Rex E. Gerald, ***Klaus Woelk****, woelk@mst.edu. Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409-0010, United States*

^{1}H-NMR inversion-recovery and spin-echo relaxation-times are valuable indicators for material properties such as atomic environment and mobility. Relaxation-time distributions can be used to interpret the properties of heterogeneous materials such as polymer blends or shale materials. While 3D relaxation-time-weighted maps from magnetic resonance imaging (MRI) are limited to inhomogeneities larger than the MRI spatial resolution, special techniques are needed to exploit those below the MRI resolution. We have developed techniques to accurately extract relaxation-time distributions from mixtures of known relaxivities. Several combinations of up to nine control samples were measured in a low-field NMR probe and the resulting complex inversion-recovery curves fitted to a series of weighted exponential terms. By combining different numbers and kinds of control samples, various multimodal or skewed distributions could be mimicked. The interpretation of these distributions for different shale samples and an extension to spin-spin relaxation-time distributions is currently under investigation. By positioning our samples in very inhomogeneous regions of the magnetic field to increase the FID decay, we have observed improvements in our T_2 analyses of control samples.

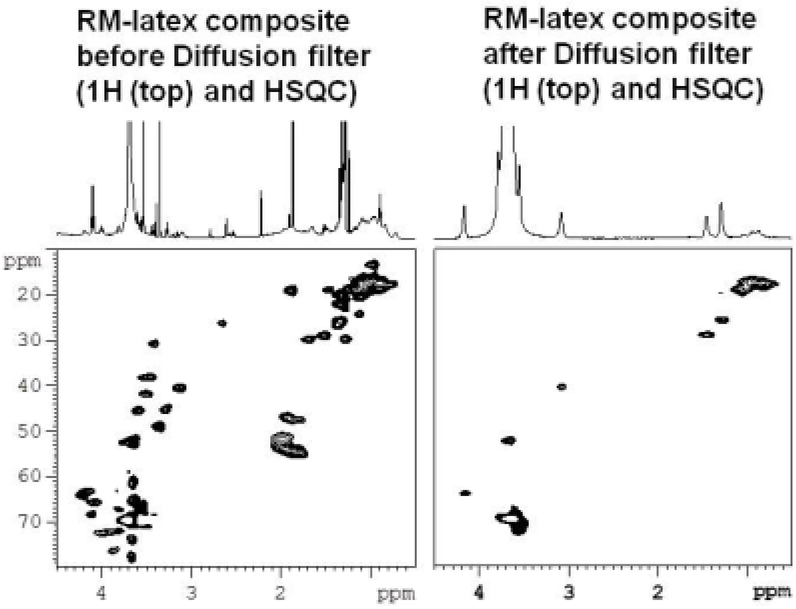


Monday, April 8, 2013 02:20 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

166 - Molecular level studies of HEUR rheology modifiers (RM) and latex particles interactions: PFGNMR study

Kebede Beshah, *KBeshah@dow.com, Aslin Izmitli, John Rabasco, Jim Bohling, Suzan Fitzwater, Ant Vandyk. The Dow Chemical Company, Spring House, PA 19477, United States*

Pulsed field gradient NMR (PFGNMR) permit signal editing of emulsion polymers that enables the detection of low level components of high Mw species such as RMs in the aqueous phase in the presence of ubiquitous water soluble species of emulsion polymers. We have extended diffusion filtered methods to 2D NMR experiments that have significantly aided the signal identification and assignment in complex emulsion polymers. In this study, it provides an unprecedented access to signals of hydrophobe end groups and urethane linkers of rheology modifiers in RM-latex composites in-situ. We have also been able to probe these interactions as a function of latex surface hydrophilicity. The approach is robust enough to enable us construct adsorption isotherms of a composite of any HEUR molecule with any latex of commercial grade without any special treatment. Our observation has lead to a new model of RM-latex interaction that sheds light on the elusive mechanism of high shear viscosity of RM-latex composites. Its implication to shear thinning rheology of RM-latex composites will be discussed.



Monday, April 8, 2013 03:00 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

167 - Synthesis and characterization of well-defined PEG networks by click-chemistry

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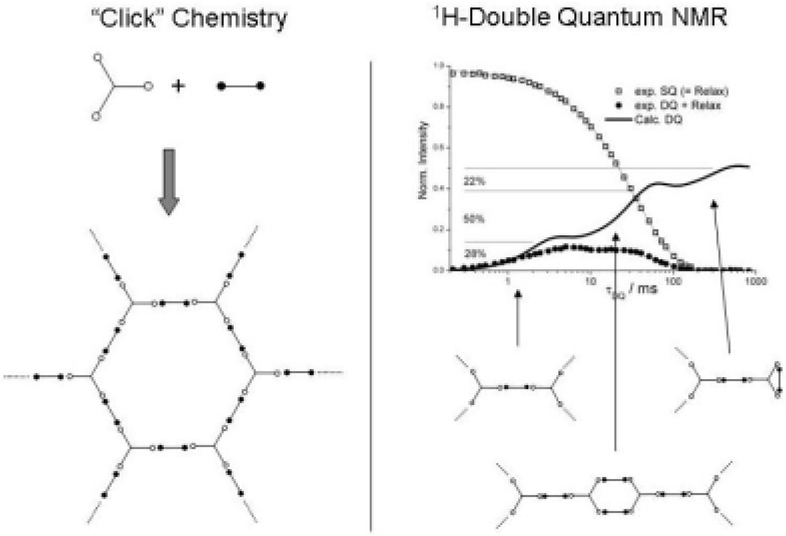
We present synthesis and characterization of well defined poly(ethylene glycol) networks that have been synthesized by using Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, also known as “click” reaction. Two types of PEG network structures were produced by: (i) linking two three-arm star PEG oligomers together and (ii) connecting three-arm PEG star units with various linear PEG oligomers of different molar masses. Both approaches ideally should result in well-defined three-functional networks. The conversion of the precursors and the formation of networks were studied by ^{13}C-MAS-NMR and FTIR spectroscopy. Network defects like multiple links and dangling ends were quantified by ^{1}H-Double Quantum (DQ) NMR spectroscopy. The samples will be used to study crystallization in polymer networks. Preliminary DSC experiments found a decrease of the tendency to crystallize occurred in PEG chains confined in networks compared to the precursor polymer chains, as expected.

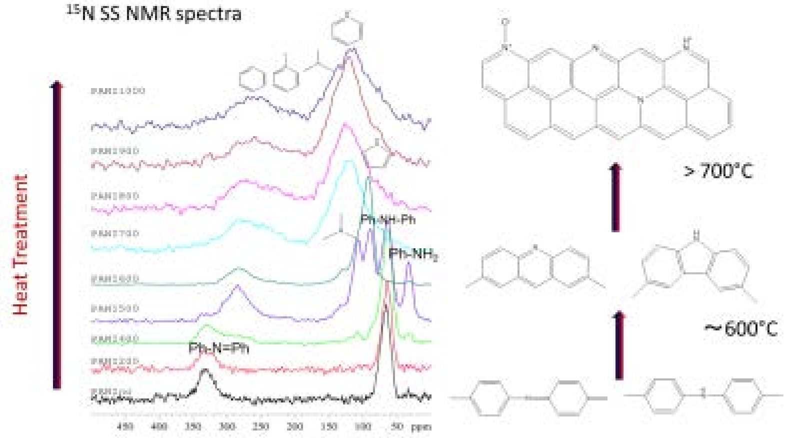


Monday, April 8, 2013 03:25 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

168 - Solid state NMR study of carbonization process of polyaniline

Shigeki Kuroki, *kuroki.s.aa@m.titech.ac.jp, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 1528552, Japan*

^{15}N labelled polyaniline (PANI) is heat treated at several different temperatures from 200 to 1000 °C in a nitrogen atmosphere. The carbonization process of PANI is determined by using solid state(SS) ^{13}C and ^{15}N NMR method. Further, in an attempt to accurate assignment of experimentally observed ^{15}N NMR chemical shift, theoretical nitrogen shielding is calculated employing ab initio MO calculations. . The SS NMR results imply that the reconstruction of polymer backbone occurs in the temperature range of 400 to 600 °C and the nitrogen of Phe-NH-Phe amino group change to the pyrrolic or tertiary nitrogen and the imine nitrogen change to pyridinic nitrogen. Further the heat-treatment above 700 °C leads to that the amount of five-membered ring containing nitrogen atom (pyrrolic) decreases and that of six-membered ring containing nitrogen atom (pyridinic, pyridine-oxide and pridinium) increases.



Monday, April 8, 2013 03:50 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:15 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

169 - Nanostructured liquid crystals exhibiting photonic and ionic functions

Takashi Kato, *kato@chiral.t.u-tokyo.ac.jp, Department of Chemistry and Biotechnology, University of Tokyo, Tokyo, Japan*

We have been developing new generation of liquid-crystalline (LC) materials. Use of dynamic properties and self-assembled nanostructures of liquid crystals has led to the formation of ion-, photo-, and electro-active materials as well as stimuli-responsive and sensing materials (1-4). Nanostructured liquid crystals such as smectic, columnar, micellar cubic, and bicontinuous cubic phases are important for such functionalizaition because they exhibit well-organized nanometer-scale segregated structures. Design of molecular shape and molecular block structures are key factors for the materials design. Control of intermolecular interactions such as hydrogen bonding, ionic, and dipole interactions is also important. We report here two types of nanostructured functional liquid crystals: stimuli-responsive luminescent liquid crystals (2) and ionic liquid crystals that transport ions and molecules (3,4). Luminescent liquid crystals that respond to mechanical stimuli have been developed. They change their luminescent colors by phase transitions induced my mechanical stimuli. For ionic liquid crystals, efficient and selective transportation is achieved by using self-organized 3D, 2D, and 1D ion channels. For example, 3D ionic network channels are formed by self-assembly of ammonium and phosphonium ionic LC molecules (3). They show efficient ion-conductive properties due to interconnected 3D networks. The fixation of these structures in the solid polymer films are achieved by in-situ polymerization of reactive liquid-crystalline molecules (3). This LC-based membrane is also used for water treatment (4).

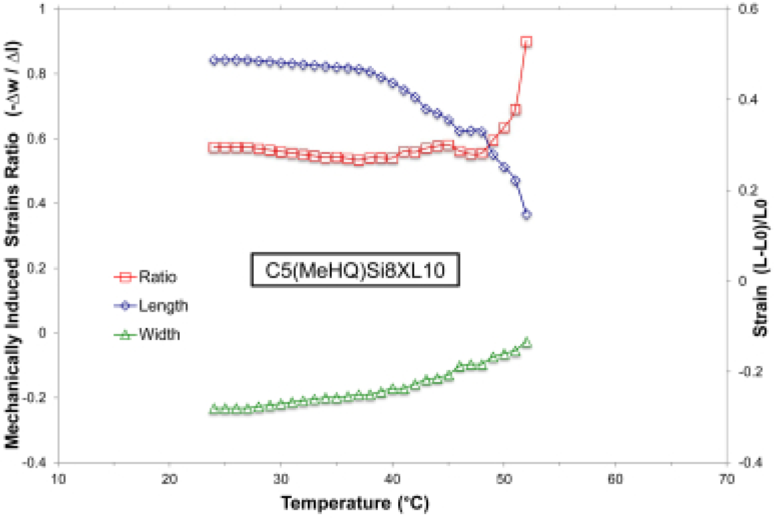
References: [ol][li]1. Kato, T. Science, 2002, 295, 2414; Kato, T. Angew. Chem. Int. Ed., 2010, 49, 7847.[/li][li]2. Sagara, Y.; Kato, T. Nature Chem., 2009, 1, 605; Angew. Chem., 2011, 50, 9128.[/li][li]3. Ichikawa, T. et al. J. Am. Chem. Soc., 2011, 133, 2163-2169; Ichikawa, T. et al. J. Am. Chem. Soc., 2012, 134, 2634.[/li][li]4. Henmi. T. et al. Adv. Mater., 2012, 24, 2238. [/li][/ol]

Monday, April 8, 2013 01:30 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

170 - Thermal strain recovery in liquid crystalline elastomers

Anselm C Griffin, *anselm.griffin@mse.gatech.edu, Tyne M Dutzer, Coley P Rahn. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, United States*

Uniaxial stretching of a polydomain liquid crystalline (SmC) network film produces a monodomain structure that can, after removal of load, retain a significant level of the imposed strain. This strain can be recovered by heating the films. We will present thermally activated strain recovery experiments that reveal a two stage recovery for one material



and a complex isothermal recovery process in another film. Nanoscale mechanistic interpretations will be offered for these observations.

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Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

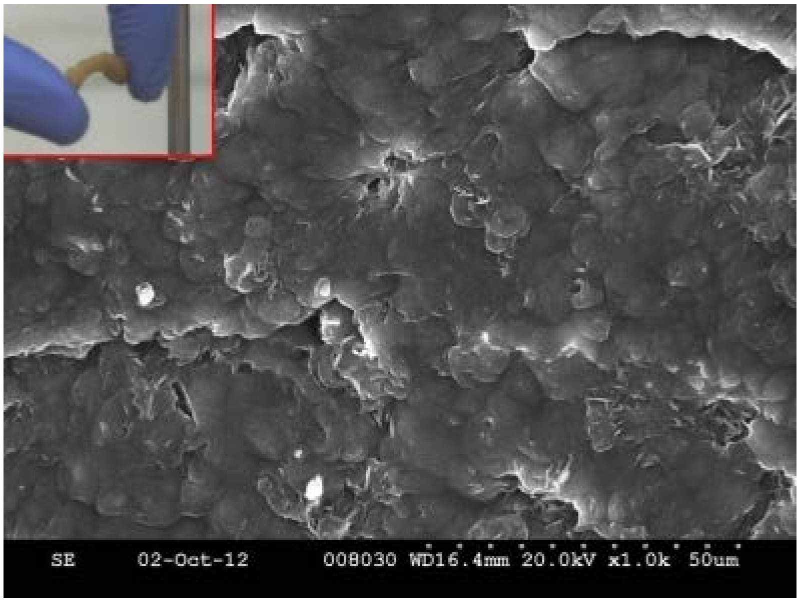
171 - Biodegradable and biocompatible side chain liquid crystal elastomers: Synthesis, characterization, and cellular response of e-caprolactone-based scaffolds

Abdollah Neshat[1], Anshul Sharma[1], Tory Stankovich[1,3], Alek Nielsen[1,3], Torsten Hegmann[1,4], ***Elda Hegmann**[1,2],* *ehegmann@kent.edu. (1) Liquid Crystal Institute, Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio 44240, United States, (2) Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44240, United States, (3) Department of Biological Sciences, Kent State University, Kent, Ohio 44240, United States, (4) Department of Chemistry & Department of Pharmacology and Ther, University of Manitoba, Winnipeg, Manitoba R3T2N2, Canada*

The combination of cells with polymeric scaffolds is a promising strategy for engineering tissues and cellular delivery. Most of these materials are engineered so they could provide support, adherence and growth of cells under physiological conditions. Once *in vivo*, scaffolds should retain their structural integrity and biomechanical strength for a long period of time.

We have successfully synthesized series of side chain liquid crystal *e*-caprolactone-based elastomers modified with cholesterol liquid crystal units to enhance mechanical properties and promote stimuli-responsive surface properties for cell attachment. The new *e*-caprolactone based elastomers are being used as viable candidates for tissue regeneration to which cells can attach, differentiate and proliferate.

We will provide morphological and structural information on the synthesized biopolymeric scaffolds, discuss the macroscopic physical behavior of the elastomers, and focus on interactions between the liquid crystalline scaffolds with cells depending on applied external stresses/stimuli.

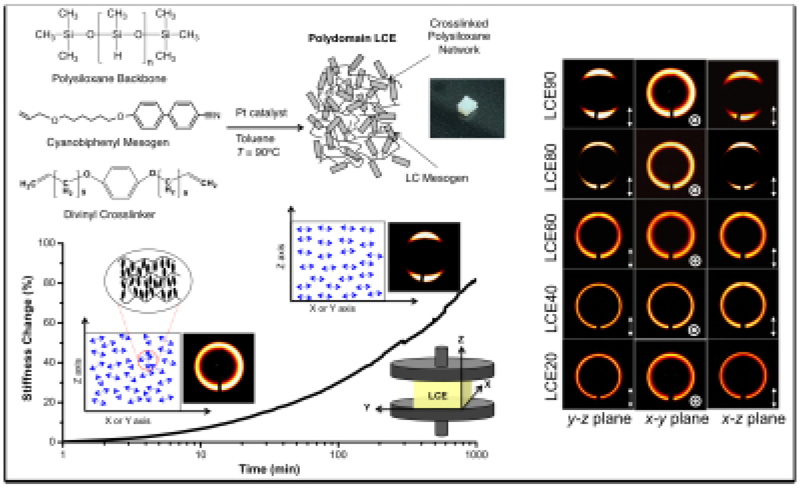


Monday, April 8, 2013 02:20 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

172 - Dynamic self-strengthening in liquid crystal elastomers

Aditya Agrawal[1], *aa21@rice.edu, Alin Cristian Chipara*[2], *Yousif Shamoo*[3], *Prabir K. Patra*[4], *Pulickel M. Ajayan*[2], *Walter G. Chapman*[1], *Rafael Verduzco*[1]. *(1) Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States, (2) Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, United States, (3) Department of Biochemistry and Cell Biology, Rice University, Houston, Texas 77005, United States, (4) Departments of Biomedical Engineering and Mechanical Engineering, University of Bridgeport, Bridgeport, CT 06604, United States*

Herein, we report that liquid crystal elastomers dramatically increase in stiffness by up to 90 % under low-amplitude, repetitive (dynamic) compression. Such stiffening behavior is common in biological tissues but rare in synthetic elastomers. Through combination of 2D-WAXD, dynamic mechanical analysis and polarizing optical microscopy, we demonstrate that stiffness increase is directly influenced by the liquid crystal content of elastomers, the presence of a nematic liquid crystal phase and the use of a dynamic as opposed to static deformation.



Monday, April 8, 2013 02:40 PM

Liquid Crystals and Polymers (01:30 PM - 04:45 PM)

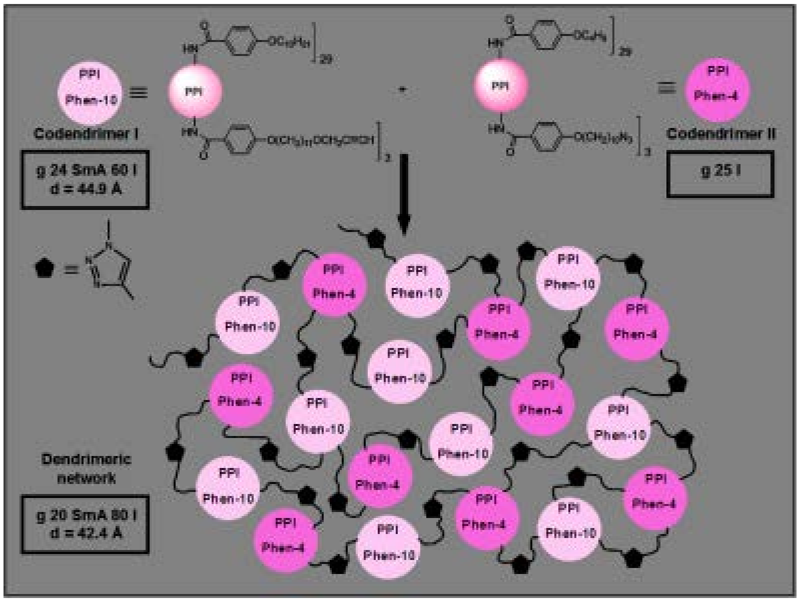
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

173 - New liquid crystalline dendrimeric networks: A surprisingly high versatile type of materials

Jose L. Serrano, *joseluis@unizar.es, Ana Omenat, Ramon Cervera-Procas. Department of Organic Chemistry-ICMA-INA, University of Zaragoza-CSIC, Zaragoza, Zaragoza 50009, Spain*

We report on the preparation and characterization of a number of liquid crystalline (LC) dendrimeric networks, which have been designed to show diverse physical properties in addition to their mesomorphism. The networks have been prepared by the cross-linking of LC dendrimers by *click Chemistry* reactions.



The most relevant results obtained show that they behave as LC elastomers, that they are able to afford microstructured organogels, which may be swollen with a variety of organic solvents and may encapsulate dyes reversibly.

Monday, April 8, 2013 03:15 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

174 - All-aromatic liquid crystal thermosets: A new family high performance polymers

Theo J. Dingemans[1], *t.j.dingemans@tudelft.nl, Edward Samulski*[2]. *(1) Aerospace Engineering, Delft University of Technology, Delft, Zuid Holland 2629HS, The Netherlands, (2) Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States*

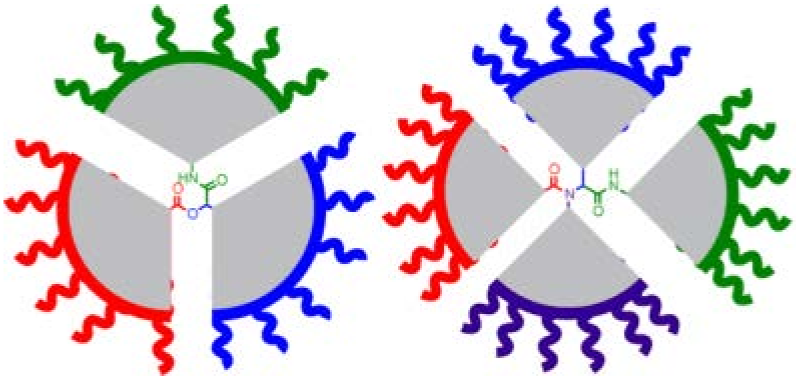
In order to meet the demand for new structural and solvent resistant polymers for aerospace composites, we are exploring new families of all-aromatic main-chain thermotropic liquid crystal thermosetting polymers (LCTs). We have synthesized reactive ester-based macromonomers, based on affordable monomers such as terephthalic acid, hydroquinone and 4-hydroxybenzoic acid, with Mn= 1000, 5000, and 9000 g/mol. All macromonomers were end-capped with phenylethynyl and could be melt-processed and cured between 350-400 ^{o}C. The fully cured polymers show high glass-transition temperatures (190-400 ^{o}C), and exhibit high storage moduli at elevated temperatures (2-4 GPa at 300 ^{o}C). The macromonomers exhibit low melt viscosities and are therefore easy to process in complex articles such as fiber-reinforced composites using a variety of composite processing tools. Our results show that LCTs offer improved processing characteristics and improved (thermo)mechanical properties over current state-of-the-art high-performance aerospace polymers such as PPS, PEKK and PEEK.

Monday, April 8, 2013 03:45 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

175 - Toward polyphilic liquid crystalline dendrimers based on multiblock dendrimers

Jonathan G. Rudick, *jon.rudick@stonybrook.edu, Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, United States*

Self-organization of amphiphilic dendrons and dendrimers balances thermodynamic incompatibility of the immiscible blocks with the shape of the dendritic architecture. Elucidation of the mechanisms by which dendrons and dendrimers self-organize in bulk has uncovered novel liquid crystalline mesophases. Increasing the number of immiscible blocks adds to the complexity of how the polyphilic molecules organize in bulk, which has been explored with for both low-molecular weight liquid crystals and block copolymers. This presentation will discuss our the successful synthesis of dendrimers composed of three and four different blocks, as well as our progress toward polyphilic liquid crystalline dendrimers based on these new architectures.

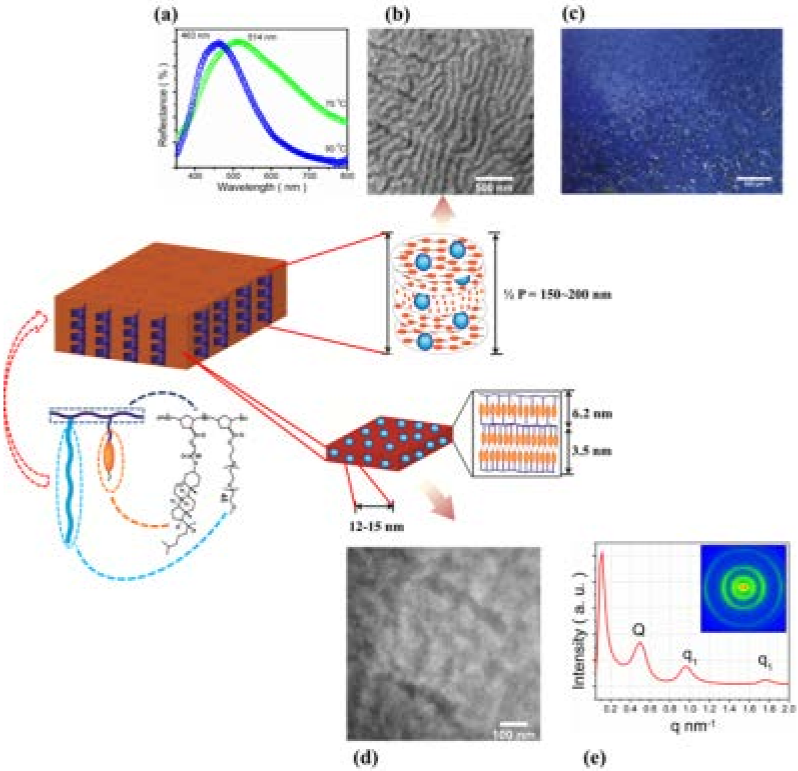


Monday, April 8, 2013 04:05 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

176 - Design of advanced functional material for photonic application by exploiting side-chain liquid crystalline brush copolymers

Prashant Deshmukh[1], *prashant.deshmukh@uconn.edu, Sukkyun Ahn*[2], *Manesh Gopinadhan*[3], *Chinedum O Osuji*[3], *Rajeswari M Kasi*[1,2]. *(1) Department of Chemistry, University of Connecticut, Storrs, CT 06269, United States, (2) Polymer Program, Institute of Material Science, University of Connecitcut, Storrs, CT 06269, United States, (3) Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520, United States*

Here we investigate a series of side-chain liquid-crystalline copolymer brushes which form self-assembled hierarchical structure on multiple length scale. These copolymers are prepared two different functionalized norbornenes comprising cholesteryl ester and poly(ethylene glycol) monomethyl ether (MPEG) as side-chain, respectively. Thermal transitions including glass transition (T_g), liquid-crystalline clearing transition (T_{cl}) and melting temperature (T_m) are determined by differential scanning calorimetry (DSC). Self-assembled hierarchical structures in the melt state are explored by small-angle and wide-angle X-ray scattering. This copolymer self-assembles into multi-level hierarchical order, consisting of (1) smectic LC layers in 3-7 nm, (2) microphase segregated PEG side-chain in 10-12 nm and (3) periodicities from helical structure (cholesteric phase) in = 150-200 nm. Our approach to create a multi-level hierarchical material will serve as a guide to designing bio-mimicking advanced functional materials.



Multi-level hierarchical structure obtained by quenching LCRCB78 from cholesteric mesophase (a) UV-Vis data selective light reflection (b) fingerprint cholesteric texture TEM (c) oily streak cholesteric texture POM (d) Microphase segregated PEG spherical domain (e) SAXS diagram showing peak for microphase segregation and liquid crystal smectic order

Monday, April 8, 2013 04:25 PM
Liquid Crystals and Polymers (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

177 - Bioinspired molecular sequestering in the stem cell microenvironment

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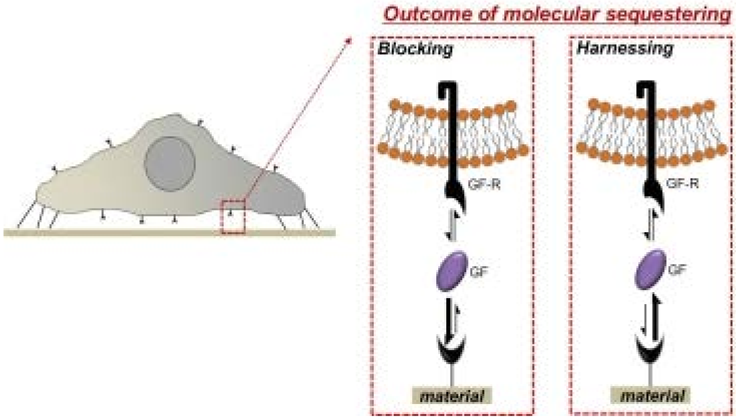
The extracellular matrix (ECM) plays a critical role in stem cell behaviors ranging from cell adhesion to lineage-specific differentiation. However, the influence of the ECM on stem cell behavior is often difficult to study in traditional cell culture, as the extracellular microenvironment in cell culture is often complex and poorly defined. This challenge is particularly relevant to molecular sequestering, a common mechanism by which the ECM locally regulates soluble growth factor concentrations. We have hypothesized that chemically well-defined cell culture environments can be used to study the influence of ECM-mimicking (or “bioinspired”) ligands on stem cell behavior. Bioinspired ligands have included growth factor sequestering ligands, proteoglycan sequestering ligands, and cell adhesion ligands. Our results demonstrate that bioinspired ligands can control diverse stem cell behaviors, including adhesion, proliferation, migration, phenotypic transformation, and lineage-specific differentiation. In addition, the context in which specific ligands are presented to stem cells critically influences molecular sequestering and associated cell behavioral responses. Importantly, the use of chemically well-defined biomaterials in these studies helps to eliminate the confounding factor of random, non-specific biomolecule adsorption, and enables identification of molecular sequestering as a key mediators of stem cell behavior. Recent studies in this area have focused on harnessing endogenous growth factors to amplify specific stem cell behaviors, and using biomaterials to knock out the activity of specific growth factors in stem cell culture.

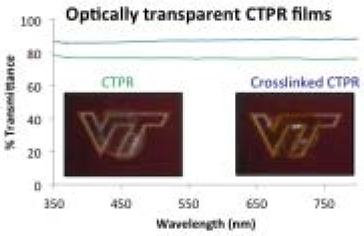


Monday, April 8, 2013 01:30 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

178 - Repeat-proteins arrays for protein-polymer hybrid materials with tunable properties

***Tijana Z. Grove**, tijana.grove@vt.edu, Nathan Carter. Department of Chemistry, Virginia Tech, Blacksburg, VA 24060, United States*

Bio-hybrid materials with tailored morphology and mechanical properties show promise for a wide range of applications in energy, biotechnology, and medicine. The Concensus sequence Tetratricopeptide Repeat protein (CTPR) comprised of 20 tandem repeats self-assemble into uniformly birefringent films. Covalently cross-linking the CTPR arrays with a bi-functional photoactive polyethylene glycol gives rise to networks whose properties depend on the length of the cross-linking polymer and the cross-link density. Here we report morphology, and thermal and mechanical properties of these materials.

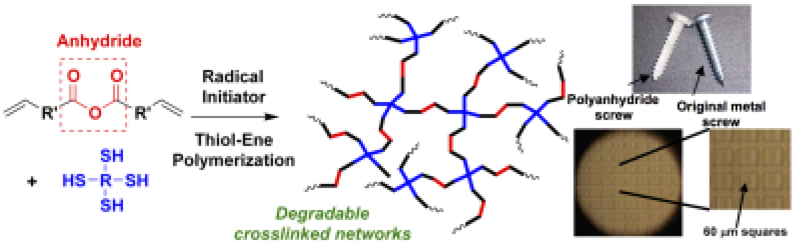


Monday, April 8, 2013 02:00 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

179 - Polyanhydride network polymers by thiol-ene polymerization: Potential macro- and microscopic therapeutic delivery devices

Devon A. Shipp, *dshipp@clarkson.edu, Katie L. Poetz, Nicole A. Traphagen, Brittany Snyder, Qin Lou. Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, NY 13699-5810, United States*

We have recently discovered that thiol-ene chemistry, a step-growth mechanism of polymerization, can be applied to make polyanhydrides that are elastomeric, photocurable and have controllable degradation rates, starting from only several hours. These may fulfil the need for new biocompatible and biodegradable materials for medical use, for example, in drug delivery, therapeutic devices and gene therapy/delivery. We have shown that these polanhydrides undergo surface erosion, maintaining their mechanical integrity during degradation and exhibit a gradual loss in size. In this paper we show that these thiol-ene based polyanhydrides show first-order pharmacokinetics over the majority of their degradation profile. Furthermore, they can be utilized in lithographic applications, opening up many possibilities in terms of making micro- and nano-sized therapeutic delivery devices.



Monday, April 8, 2013 02:20 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

180 - Self-assembly of cell scaffolds with hierarchically organized topographic guidance cues

Jason J Benkoski[1], *jason.benkoski@jhuapl.edu, Melanie L Morris*[1]*, Asmi Panigrahi*[1]*, Michael C Gross*[1]*, Ryan M Deacon*[1]*, Yun-An Chen*[2]*, Justin Morrissette-McAlmon*[2]*, Warren L Grayson*[2]*. (1) Research and Exploratory Development Department, JHU Applied Physics Laboratory, Laurel, MD 20723, United States, (2) Department of Biomedical Engineering, The Johns Hopkins University, Baltimore, MD 21287, United States*

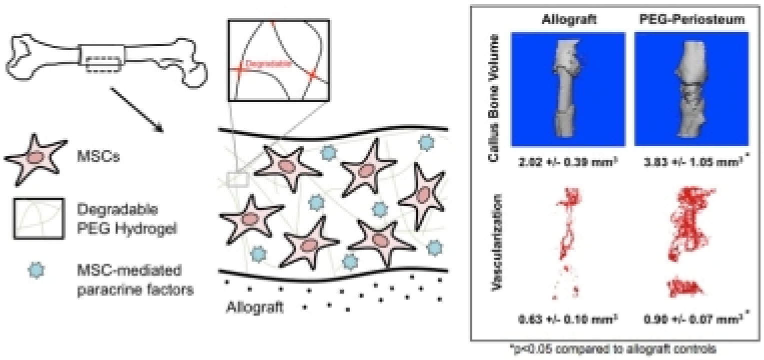
Our improved understanding of the relationship between mechanics and biochemistry at the molecular level increasingly suggests an additional mechanical basis for the hierarchical organization of living systems. Seen in this light, the hierarchical organization of the extracellular matrix may supply the blueprint for mechanoregulation across multiple length scales. Herein we present the self-assembly of hierarchically structured cell scaffolds and subsequent seeding with adipose-derived stem cells (ASCs). Our unique platform consists of a photocurable polydimethylsiloxane-diacrylate and water. Surfactants sculpt the monomer into the desired shape, and UV light solidifies the structure. Hierarchical organization is controlled through the superposition of three distinct instabilities: spontaneous emulsification, dewetting, and Rayleigh-Taylor instability. 3-D optical profilometry quantifies these effects through the fractal dimension, surface roughness, and other parameters. Finally, we demonstrate systematic control of these three processes, and hence, the hierarchical structure, by adjusting four system variables: surfactant type, surfactant concentration, processing time, and film thickness.

Monday, April 8, 2013 02:40 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

181 - Promoting allograft healing and remodeling by tissue engineering the periosteum

Michael D. Hoffman[1,2], *Chao Xie*[2,3], ***Danielle S. W. Benoit***[1,2,3], *benoit@bme.rochester.edu. (1) Department of Biomedical Engineering, University of Rochester, Rochester, NY 14627, United States, (2) Center for Musculoskeletal Research, University of Rochester Medical Center, Rochester, NY 14627, United States, (3) Department of Orthopaedics, University of Rochester, Rochester, NY 14627, United States*

Allografts remain the clinical gold standard for treatment of massive bone defects but exhibit minimal engraftment and a 60%, 10-year post implantation failure rate due to microcrack propagation and fibrotic non-unions. In contrast, autografts completely heal, mediated by the periosteum, a thin layer of tissue housing periosteal cells (PCs) with similar proliferative and differentiation capacities as mesenchymal stem cells (MSCs). Growing evidence suggests that periosteum-mediated autograft healing is due to PC paracrine factor release as PCs persist at autografts for only ~3 weeks during healing and do not contribute to new tissue formation. Herein, we demonstrate that hydrolytically degradable poly(ethylene glycol) (PEG) hydrogels designed to mediate MSC transplantation to and persistence at the allograft surface can mimic PC mediated autograft healing. Using a murine segmental defect model, periosteum mimetic-coated allografts exhibit a 1.4-fold increase in host-mediate vascularization and a 1.9-fold increase in callus bone formation as compared to allograft only controls (Figure 1).

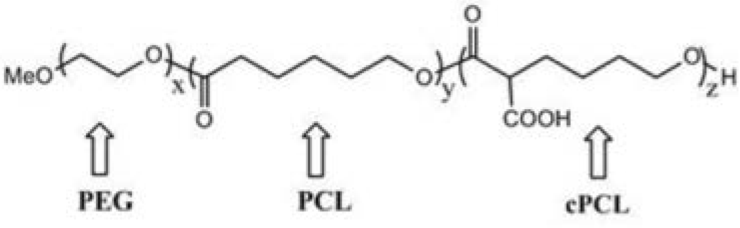


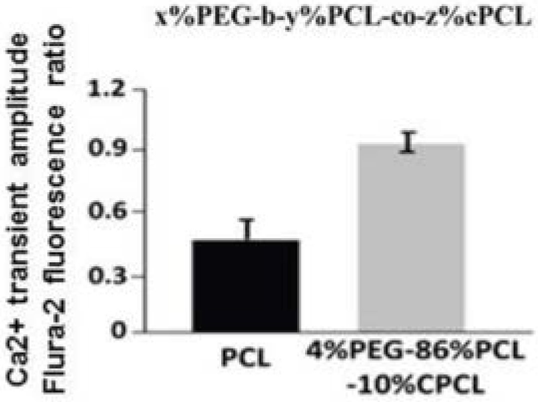
Monday, April 8, 2013 03:15 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

182 - Modular design of combinatorial polymers for differentiation and delivery of stem cells towards cardiac therapy

Hak-Joon Sung, *hak-joon.sung@vanderbilt.edu, Department of Biomedical Engineering, Vanderbilt University, Nashville, TN 37235, United States*

A new class of combinatorial polymers has been developed and utilized in combination with stem cell and bioreactor technologies for regeneration of infarcted heart. To provide tunable properties of polymer scaffolds, poly(e-caprolactone) (**PCL**), poly(ethylene glycol) (**PEG**), and carboxyl PCL (**cPCL**) were copolymerized at varying molar ratios and identified as **_x_%PEG-_y_%PCL-_z_%CPCL** (*x, y, z*: individual mole percentage). These polymers were fabricated to fiber mesh scaffolds through electrospinning. These scaffolds were loaded to a bioreactor in which cyclic strain and electric field stimulation can be programmed in a user-specified manner. Also an injectable, biodegradable scaffold was developed using the same library of polymers and tested for stem cell delivery in a rodent model of myocardial infarction (MI). The new class of combinatorial polymer library controlled mechanical and chemical properties for efficient differentiation of adult stem cells. The unique thermomechanical properties of copolymers were successfully tuned through compositional alternation to enable injectability.





Monday, April 8, 2013 03:45 PM

Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)

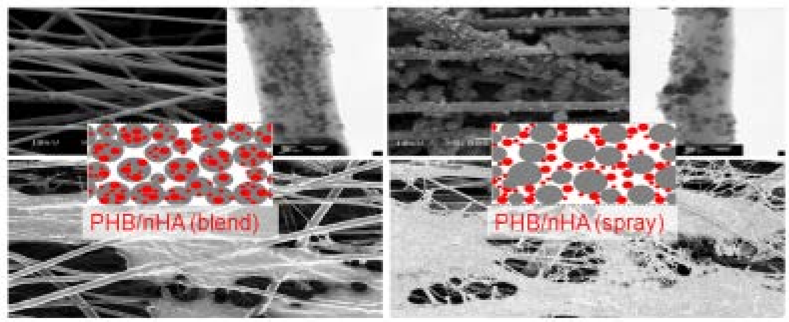
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

183 - Novel nanofibrous biomaterials based on electrospun poly(3-hydroxybutyrate) and electrosprayed hydroxyapatite

Daniel Grande[1], *grande@icmpe.cnrs.fr, Julien Ramier*[1], *Estelle Renard*[1], *Valérie Langlois*[1], *Olya Stoilova*[2], *Nevena Manolova*[2], *Iliya Rashkov*[2], *Patricia Albanese*[3]. *(1) Institut de Chimie et des Matériaux Paris-Est, Thiais, FR 94320, France, (2) Institute of Polymers, Sofia, BG 1113, Bulgaria, (3) Laboratoire "Croissance, Réparation et Régénération Tissulaires", Créteil, FR 94010, France*

The electrospinning technique coupled with the electrospraying process provides a straightforward and versatile tandem approach to novel nanofibrous biomaterials with structural, mechanical, and biological properties potentially suitable for bone tissue regeneration. In this comparative investigation, three different types of poly(3-hydroxybutyrate) (PHB)-based scaffolds were engineered, namely neat PHB mats, PHB nanofibers with incorporated hydroxyapatite nanoparticles (nHA) within their structure, as well as PHB nanofibers with electrosprayed nHA deposited on their surface.



Monday, April 8, 2013 04:15 PM

Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)

Location: Hilton Riverside

Room: Ste. C, Sec 13/16

184 - Use of FTIR imaging and scanning electron microscopy to analyze the effects of degradation on a resorbable polyester biomaterial

Jeremy J Harris, *jeremy.harris@secantmedical.com, Peter Gabriele. Department of Emerging Technologies, Secant Medical, Inc., Perkasie, PA 18944, United States*

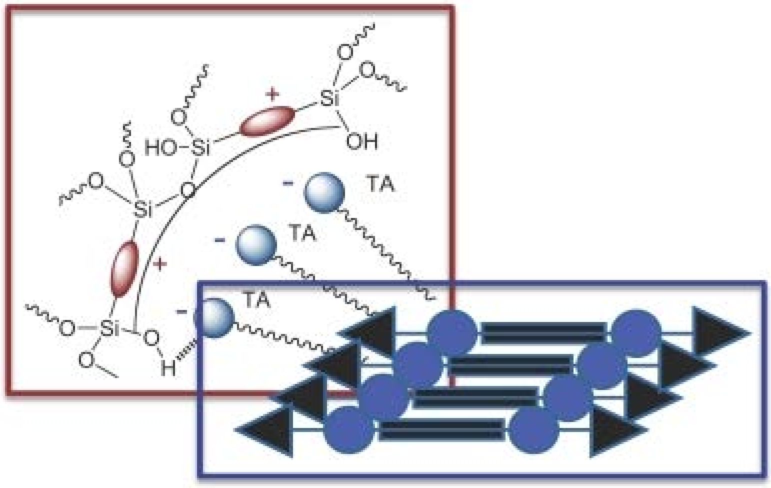
Degradation and cellular proliferation properties are critical parameters in the design of new biomaterials. Poly(glycerol sebacate) (PGS) has attracted significant interest as a resorbable polymer for tissue engineering due to its ease of synthesis and biocompatibility. Previous studies have shown that PGS degrades by surface erosion; however, the degradation effects on surface chemistry and ultimately cell proliferation are not known. FTIR imaging microscopy is a powerful technique for analyzing the spatial distribution of surface functionality of materials and was used to analyze the surface chemistry of PGS as a function of degradation. In addition to surface functionality, topography plays a significant role in cell proliferation and was monitored with SEM and correlated to the surface functionality map. Lastly, the chain length of the diacid used in the polycondensation was examined to determine the effects on polymer degradation and surface functionality and morphology.

Monday, April 8, 2013 04:35 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

185 - Self-organised organosilicas: Recent results in the structuration of the pores and of the organic substructures

Joël JE Moreau, *joel.moreau@enscm.fr, ICG AM2N CNRS UMR 5253, Ecole Nationale Supérieure de Chimie Montpellier, MONTPELLIER, France 34296 cedex 5, France*

The combination of organic and inorganic substructures in organosilicas offers unique possibilities for designing new synthetic routes to nanostructured hybrid materials. We will report our recent results on the nano structuring of porous or bulk hybrid silicas, by taking advantage of the self-organisation properties of the organic moieties within the materials. The control of the pore structure of organosilicas was obtained upon reinforcing the interactions between the molecular precursor and the ionic surfactant during the materials synthesis. Owing to the presence of organic cationic species in the precursor molecule, it allowed the synthesis of organosilicas containing ionic substructures or masked organic functional groups showing pore structure with hexagonal symmetry. By controlling the stacking of the organic substructures, we also generated nanostructured and micro-structured materials with tuned optical and electro-optical properties. It allows a one step preparation of nanostructured and micropatterned thin films from a single informed molecular precursor.

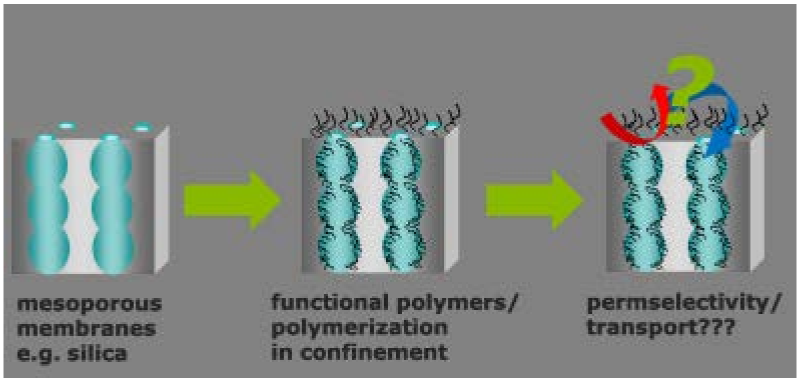


Tuesday, April 9, 2013 08:30 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

186 - Manipulation of permselectivity in mesoporous silica-polymerhybrid thin films

Annette Brunsen[1]*, brunsen@cellulose.tu-darmstadt.de, Galo J. J. A. Soler-Illia*[2,3]*, Omar Azzaroni*[3,4]*. (1) Department of Macromolecular Chemistry, Technical University Darmstadt, Darmstadt, Hessen 64287, Germany, (2) Gerencia Química, Comisión Nacional de Energía Atómica (CNEA), Buenos Aires, Buenos Aires, Argentina, (3) Consejo Nacional de Investigaciones Científicas y Tècnicas (CONICET), Buenos Aires, Buenos Aires, Argentina, (4) Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química, Facultad de Ciencias, Exactas, Universidad Nacional de La Plata, La Plata, Argentina*

Nanostructured hybrid films allow the combination of different functionalities at nanometer scale. With a good choice of building blocks, and a controlled assembly, it is possible to prepare sol-gel processed, mesoporous films with precisely defined and tunable structural and chemical functions. Subsequent incorporation of stimuli-responsive polymer brushes enables control over the film properties, such as permselectivity. Charge-controlled switching of permselectivity for example can be performed with pH-, and ion-responsive polymer brushes, attached inside and on the outer surface of mesoporous silica films.

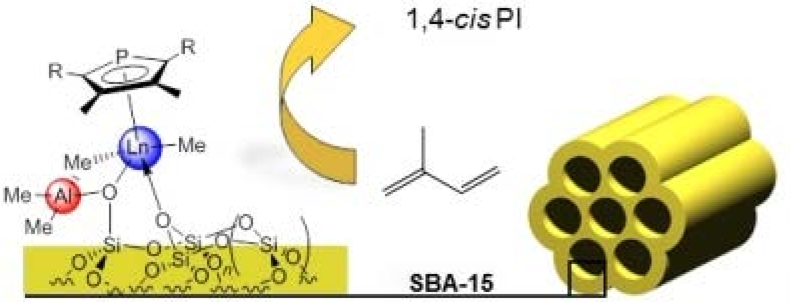


Tuesday, April 9, 2013 09:00 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

187 - Nanostructured catalysts via smart grafting

Reiner Anwander[1], *reiner.anwander@uni-tuebingen.de, Yucang Liang*[1], *Erwan Le Roux*[2], *Clemens Zapilko*[2], *Thomas Deschner*[2], *Sonja König*[1], *Tatiana Spallek*[1]. *(1) Department of Chemistry, University of Tübingen, Tübingen, Germany, (2) Department of Chemistry, University of Bergen, Bergen, Norway*

Periodic mesoporous silicas (PMSs) and periodic mesoporous organosilicas (PMOs) are high-surface-area materials, which are currently investigated as catalyst supports both in industry and academia. While size- or shape-selective reactions are a unique and formidable phenomenon occurring in zeolitic materials (pore diameter pseudo *s*urface *o*rgano*m*etallic *c*hemistry (*p*SOMC)- as an efficient strategy for tailoring the meso-, micro-, and local environment of various PMS/PMO materials. Such *p*SOMC can be exploited for the generation of catalytically active nanostructured inorganic-metalorganic hybrid materials. This presentation will focus on various aspects of silylamide- and tetramethylaluminate-based *p*SOMC as well as size selectivity.

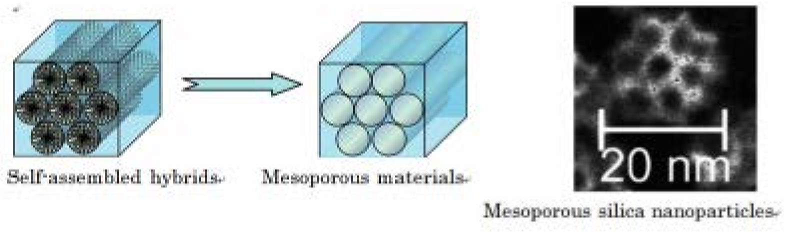


Tuesday, April 9, 2013 09:30 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

188 - Role of hybrid materials in the preparation of functional porous materials

Kazuyuki Kuroda, *kuroda@waseda.jp, Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan*

Functional porous materials can be prepared from inorganic-organic hybrid materials in many cases. In particular, mesoporous materials possess unique characteristics, such as uniform pore size, ordered arrangement of mesopores, large pore volume, etc. Because mesoporous materials are compositionally, structurally, and morphologically tuned, there are many potential applications in various fields including separation, catalysis, nanocomposite formation, medicine, electronics, optics, etc. The preparation of porous materials, in particular mesoporous materials, will be presented from the viewpoint of design of functionalities. Functionalities depending on the composition, structure, and porosity will be discussed in relation to the role of hybrid materials design. Morphological control of mesoporous materials is important for applications and thin films with unidirectional arrangement of straight mesopores will be important for future device applications. These are also very dependent on the design of hybrid materials.



Tuesday, April 9, 2013 10:15 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

189 - Hybrid ice-release coatings: New polyoxetane fluorous elastomers, new laboratory test, new theory

Kenneth J Wynne, *kjwynne@vcu.edu, Souvik Chakrabarty, Wei Zhang, Chenyu Wang. Department of Chemical and Life Science Engineering, Virginia Commonwealtlh University, Richmond, VA 23284, United States*

Minimizing adhesion of ice has been the subject of extensive studies for applications such aircraft wings and power transmission wires, while a growing interest concerns coatings for wind turbine blades. This paper reports new, transparent ice-release hybrid coatings that incorporate fluorous polyoxetane soft blocks and consist of urethane, urea and siliceous components.

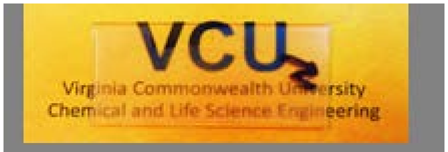


Figure 1. Coating image

Unexpectedly, these coatings undergo compositionally dependent vertical phase segregation into nanosurface, mesosurface, and bulk domains. Using a combination of ATR-IR spectroscopy, TM-AFM, dynamic contact angles and laboratory ice-removal tests, results are presented that provide insight into low peak removal forces and removal energies. A new theory is described to account for easy release.

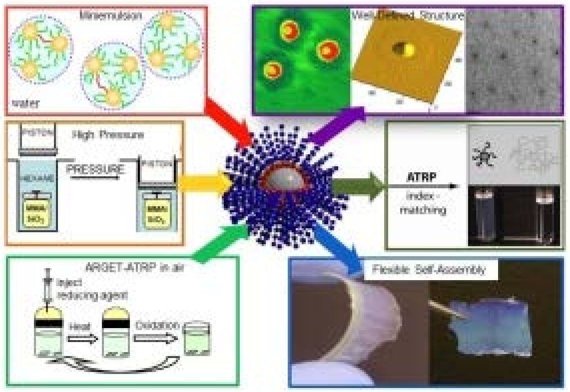
[1] The authors thank the National Science Foundation (DMR-0802452 and DMR-1206259) for generous support of this research.

Tuesday, April 9, 2013 10:45 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

190 - Nanostructured functional hybrid materials by ATRP

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu, Chin Ming Hui, Hongchen Dong, Satyajeet Ojha, Jihoon Choi, Joanna Pietrasik, Michael R. Bockstaller. Carnegie Mellon, Pittsburgh, PA 15213, United States*

Solid inorganic surfaces modified with polymeric materials can impart novel and enhanced properties. These features have fueled both academic and industrial interest in polymer nanocomposites during the past twenty years. However, the development of new materials with predetermined properties requires control over material functionality and nanostructure. Recently, surface modifications by various ATRP (atom transfer radical polymerization) techniques have been developed to control the nanostructures. For example, ARGET-ATRP allowed hybrid materials to be synthesized in the presence of limited amount of air and high pressure-ATRP allowed achievement of high molecular weight with well-defined structure and good amount of functionality. These new advanced techniques have been used to develop hybrid nanostructures for various applications.



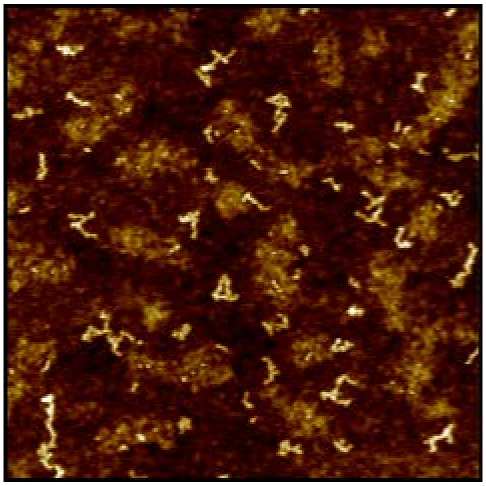
Tuesday, April 9, 2013 11:15 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

191 - Improved mechanical and corrosion properties of hybrid thin films based on epoxidized acrylic copolymers loaded with silica particles

Farid Khelifa, *farid.khelifa@umons.ac.be, Marie-Eve Druart, Youssef Habibi, Freddy Benard, Philippe Leclère, Marjorie Olivier, Philippe Dubois. Departement of Research in Science and Engineering of Materials, University of Mons, Mons, Mons 7000, Belgium*

Automotive and aeronautic industries require good corrosion protection combined with good mechanical reinforcement of aluminum substrates due to severe conditions of use. Polymeric films and more particularly hybrid ones based on organic matrices filled with inorganic particles have been applied to solid substrates for decorative, protective, and functional purposes. They present many advantages since they combine the properties of the organic phase such as flexibility, good processibility and those of the inorganic phase such as mechanical strength, scratch resistance, thermal stability, etc.

The aim of the present work is to synthesize through sol-gel approach new hybrid polymeric nanocomposites to be used as coating materials. An acrylic-based polymer was prepared by free-radical copolymerization in which silica nanoparticles were incorporated by *in situ* acid hydrolysis. Subsequent photo-crosslinking is performed in order to enhance mechanical properties of such coating. The morphology, chemical, thermal, mechanical properties and corrosion resistance of thin films applied on aluminum alloys were assessed by atomic force microscopy (AFM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), and electrochemical impedance spectroscopy (EIS).



Tuesday, April 9, 2013 11:35 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

192 - Silica with aggregated glycopolymers encapsulated and removed: Future energy saving technologies?

Mark J. MacLachlan, *mmaclach@chem.ubc.ca, Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada*

Reflective coatings that can be applied to windows have the potential to control the amount of light entering buildings and cars, and thus to reduce the amount of air conditioning utilized. We have recently discovered a new family of silica-based materials that have photonic properties. (Figure 1 shows a photo of an iridescent mesoporous silica film.) Templated by cellulose, these mesoporous materials can selectively reflect light of a given wavelength. The reflection can be tuned across the spectrum, from the IR to the UV regions, by simple modifications to the synthesis. In this talk, I will describe our recent efforts to construct new mesoporous photonic materials using cellulose as a template.

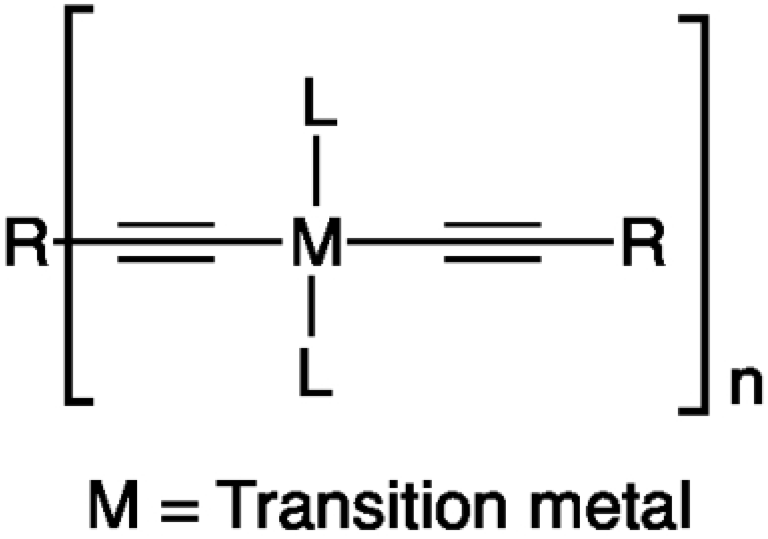
Figure 1. Photograph of iridescent mesoporous silica with a drop of water added.

Tuesday, April 9, 2013 08:35 AM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
Location: Hilton Riverside
Room: HEC C

193 - Toward novel phosphorescent materials

Koushik Venkatesan, *venkatesan.koushik@aci.uzh.ch, Institute of Inorganic Chemistry, University of Zürich, Zurich, Zurich CH-8057, Switzerland*

Metal complexes displaying room temperature phosphorescence have been well investigated for their application in phosphorescence organic light-emitting devices (PhOLED). Solution processible materials exhibiting rich phosphorescent properties based on the design and incorporation of novel ligands into metal complexes have been developed. Design principle, electronic and photophysical aspects of these materials will be discussed in detail.

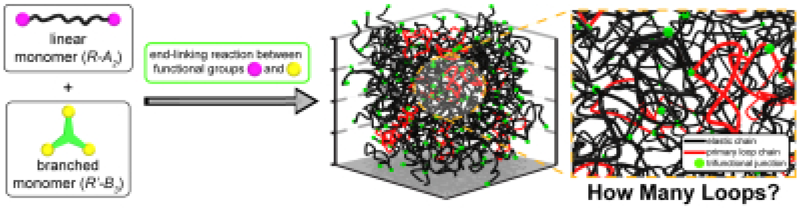


Tuesday, April 9, 2013 09:10 AM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
Location: Hilton Riverside
Room: HEC C

194 - Counting primary loops in polymer networks

*Huaxing Zhou[1], Jiyeon Woo[1], Alexandra M. Cok[1], Muzhou Wang[2], Bradley D. Olsen[2], **Jeremiah A. Johnson**[1], jaj2109@mit.edu. (1) Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (2) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Though the structures and properties of end-linked polymer networks have attracted theoretical and experimental interest for nearly a century, a direct method for quantification of cyclic, primary loop junctions in real materials has remained elusive. This presentation will discuss our efforts towards development of a general methodology for quantification of cyclic network imperfections. A new class of responsive polymer networks constructed via Diels-Alder cycloaddition between a multi-functional tetrazine derivative and norbornene-telechelic polyethylene(glycol) (PEG) is described. These materials decompose in response to a chemical stimulus to yield a tractable set of degradation products whose ratios are defined by the numbers of primary loops and unreacted chains in the parent network. We use these materials to probe classical questions in end-linking polymerization chemistry. The concepts and techniques presented here are broadly applicable to the characterization of fundamental structures of end-linked polymers and other complex macromolecular architectures.



Tuesday, April 9, 2013 09:45 AM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
Location: Hilton Riverside
Room: HEC C

195 - Chemistry of some intriguing organoboron materials

Shigehiro Yamaguchi, *yamaguchi@chem.nagoya-u.ac.jp, Department of Chemistry, Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan*

Incorporation of main group elements into p-conjugated skeletons is a powerful strategy to develop new optoelectronic organic materials with unusual properties. Among various main group elements, group 13 boron is particularly useful. One of the key issues in the molecular designs for boron-containing materials are how to make best use of a vacant p orbital of boron atom and how to stabilize inherently unstable Lewis-acidic organoboron materials. A general strategy for the stabilization is to sterically protect the boron moiety. Most of the organoboron materials so far reported employed at least one or two bulky aryl groups on the boron atom. However, their steric bulkiness sometimes gives rise to a detrimental effect on the solid-state properties that relies on the intermolecular interaction, such as charge carrier transporting properties. We now introduce a new idea for the stabilization of tri-coordinated boron-containing p skeletons, which is “stabilization based on structural restriction.” On the basis of this concept, we have synthesized a series of fully planarized triarylboranes, including boron-doped nanograhenes. These compounds showed intriguing features, such as high stability, red-shifted fluorescence with interesting dynamic behavior in the excited state, interesting crystal structures, and plane-to-bowl structural changes upon capture of a fluoride ion.

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ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
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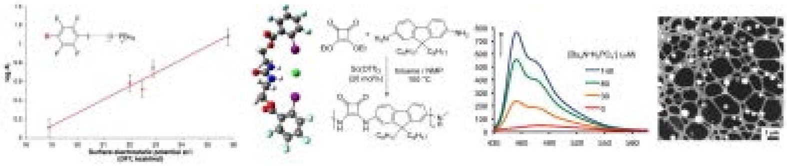
196 - Noncovalent interactions: Fundamental studies and new applications

Mark S. Taylor, *mtaylor@chem.utoronto.ca, Department of Chemistry, University of Toronto, Toronto, ON M5S 3H6, Canada*

Two aspects of our research targeting new applications of molecular recognition phenomena will be discussed:

-Halogen bonding interactions in solution. Interactions between electrophilic halogens and Lewis bases have generated much interest, with applications in crystal engineering, materials science and medicinal chemistry. Solution-phase thermodynamics and demonstrations of high-affinity molecular recognition will be described.

- Anion-responsive poly(squaramides). Polyamides composed of 3,4-diaminocyclobutene-1,2-dione moieties display a selective fluorescence response to dihydrogenphosphate in competitive media. Complementary techniques support a mechanism involving cooperative aggregation upon anion binding.



Tuesday, April 9, 2013 11:10 AM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
Location: Hilton Riverside
Room: HEC C

197 - Chiral polymer-derived microcapsules as new chiral reactors

Mindy Levine, *mindy.levine@gmail.com, Patrick Marks. Department of Chemistry, University of Rhode Island, Kingston, RI 02881, United States*

Reported herein is the fabrication of covalently linked chiral microcapsules as new supramolecular organic catalysts. The microcapsules are fabricated from chiral cationic polyamines, which are in turn synthesized from the cationic polymerization of chiral oxazolines. Capsules are formed from the polymers using covalent linkers via the amino groups to generate spherical chiral microcapsules. Once formed, the capsules can be used as catalysts for a number of organic reactions, including a Michael reaction and a transamination reaction (in combination with an organic co-factor).

Tuesday, April 9, 2013 11:45 AM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (08:30 AM - 12:20 PM)
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Room: HEC C

198 - Molecular ordering and macroscale mobility: Design concepts for polymer based semiconductors

*Boyi Fu[1], Nabil Kleinhenz[3], Dalsu Choi[1], Karthik Nayani[2], Jung Ok Park[2], Mohan Srinivasarao[2], **Elsa Reichmanis**[1], ereichmanis@chbe.gatech.edu. (1) School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States, (2) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States, (3) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States*

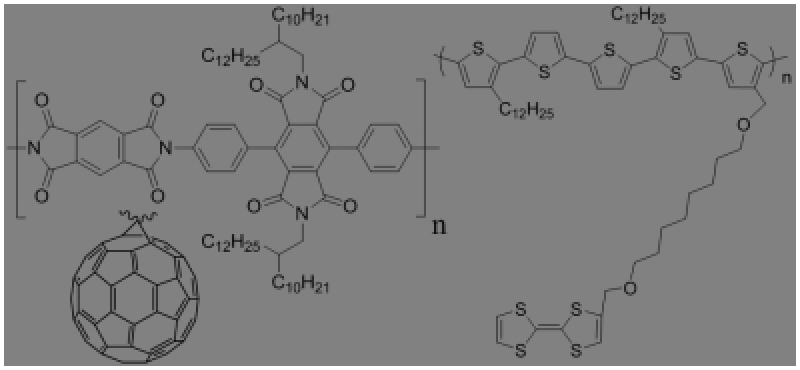
The performance of devices fabricated using polymeric semiconductors is critically dependent upon alignment of the semiconductor at the nano- through macro-scales. Significant structure-process-property relationships that allow for enhancement of long-range order will be described. A lyotropic liquid crystalline (LC) phase in poly-(3-hexylthiophene) (P3HT) has been observed via solvent-evaporation induced self-assembly. *In-situ* polarized Raman spectroscopy was used to study the evolution of structure that eventually leads to a phase transition from an isotropic solution to an LC phase. These insights have further been applied to the design of an alternative, donor-acceptor (D-A) benzothiadiazole oligothiophene based copolymer material. For one family of copolymers, structural elements were found to provide for a span in hole mobility of approximately 3 orders of magnitude. Samples annealed at moderate temperatures exhibited mobilities approaching 1 cm^2/Vs. The insights obtained through these studies may allow for simple, controllable, and cost-effective methodologies for achieving high performance plastic electronic devices. (figure 1)

Tuesday, April 9, 2013 08:20 AM
Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

199 - Chargeable functionalities with semiconducting polymers: Sensing, energetics, and switching

Howard E. Katz, *hekatz@jhu.edu, Jasmine Sinha, Hoyoul Kong, Thomas J. Dawidczyk, Srinivas Kola. Department of Materials Science and Engineering and of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States*

This presentation focuses on the synergy between semiconducting polymers and additional components of the same polarity. While counterintuitive because these functional groups would quench ordinary charge transport, they provide additional activity not ordinarily seen in semiconducting polymers, such as enhanced mobility from the additives, turn-on (conduction increase) response to analytes useful for selective sensor arrays, and tunable Seebeck coefficients for the design of thermoelectric composites. Demonstration of these materials in nonvolatile transistors and photodetectors will also be discussed.



Tuesday, April 9, 2013 08:50 AM

Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)

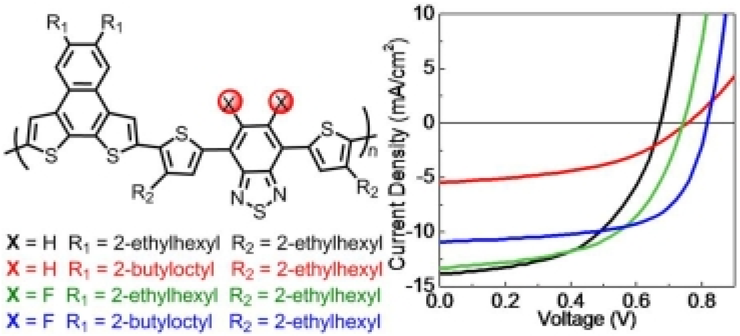
Location: Hilton Riverside

Room: Ste. C, Sec 15

200 - Disentangling the impact of side chains and fluorine substituents of conjugated donor polymers on the performance of bulk heterojunction solar cells

Wei You, *wyou@unc.edu, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, United States*

Side chains and fluorine substituents on conjugated polymers have shown significant impacts on the photovoltaic properties of polymer-based bulk heterojunction (BHJ) solar cells. We comprehensively investigate a series of conjugated polymers with an identical backbone but different combinations of side chains and F substituents. Devices based on the polymer with long bulky side chain and F substituent simultaneously exhibit large open circuit voltage, high short circuit current and good fill factor, leading to the highest efficiency up to 5.6%.



Tuesday, April 9, 2013 09:20 AM

Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)

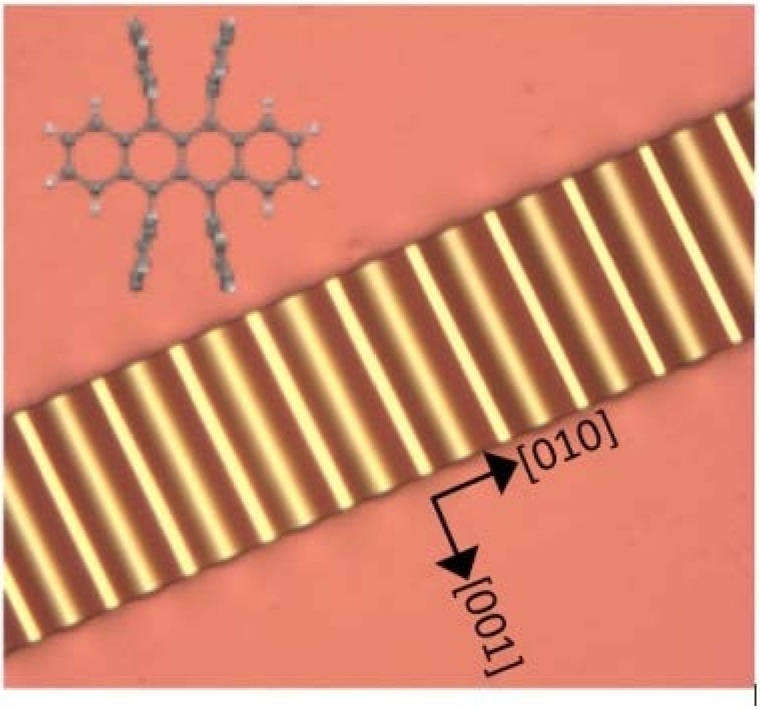
Location: Hilton Riverside

Room: Ste. C, Sec 15

201 - Decade of organic semiconductor single crystals

Alejandro L Briseno, *abriseno@mail.pse.umass.edu, Polymer Science & Engineering, University of Massachusetts, Amherst, MA 01003, United States*

Over the past 10 years, a tremendous amount of work has been published in the area of organic single crystals. The ability to extract the intrinsic charge transport properties from these molecular solids has enabled scientist to have a deeper understanding of the performance limitations in organic semiconductors. This symposium presentation will focus and honor Professor Zhenan Bao and her efforts on semiconductor crystals over the past several years. The first half of the presentation will highlight our collaborative work and the second half will focus on my independent research. Specifically, I will focus on new phenomana and applications of organic single crystals (Figure 1. Wrinkled rubrene crystal on PDMS) and also on interfacial crystallization- a new method of growing oriented vertical crystals for achieving the ideal architecture for organic solar cells. We employ graphene monolayer films as substrates for observing the evolution of growth and molecular orientation of organic semiconductor thin films. These interfaces offer a promising route towards understanding how to develop highly efficient photovoltaics, but also allow for fundamental structural studies to be carried out.



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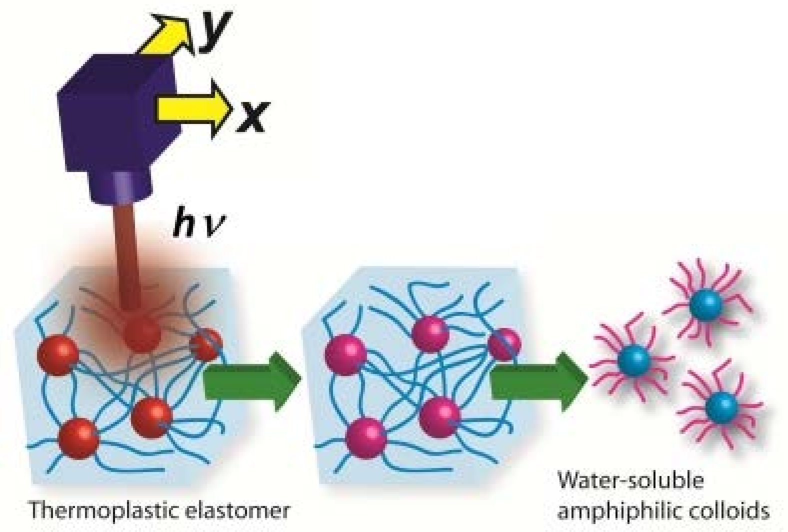
Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

202 - Multi-scale reconfigurable polymeric networks as dynamic medical materials

Christopher J Bettinger[1,2], *cbetting@andrew.cmu.edu, Suze Ninh*[1], *Congcong Zhu*[1]. *(1) Department of Materials Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (2) Department of Biomedical Engineering, Carnegie Mellon University, Pi, PA 15213, United States*

Next-generation medical materials that are designed to seamlessly integrate with the human body will benefit from the ability to reconfigure polymeric networks at multiple length scales. Here we report the synthesis and characterization of biodegradable elastomeric networks that can be reconfigured in response to heat and light. One example of this class of materials features reconfigurable chemistries for use in temporary shape-memory medical materials. Another class of material features a tri-block co-polymer configuration that can be reconfigured at the networks scale in response to light (See Figure). The applicability of these soft polymeric materials in biomedical devices will be discussed.



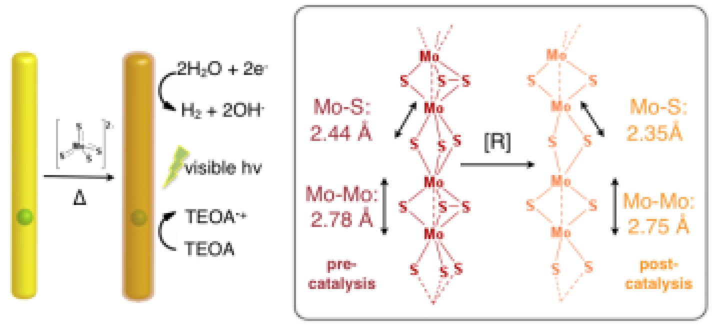
Tuesday, April 9, 2013 10:20 AM
Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

203 - Structural and electronic study of an amorphous MoS_3 hydrogen generation catalyst on a quantum controlled photosensitizer

Ming L Tang, *mltang@ucr.edu, Chemistry, University of California, Riverside, Riverside, CA 92521, United States*

This work is the first observation of MoS_3being active as a proton reducing catalyst. In addition, this is also the first empirical observation of a transition from full coordination (6) to under-coordination (4-5) of the Mo centers in molybdenum sulfide catalysts directly accompanied by a turn-on in catalytic acitivty. Under-coordination has been cited frequently as the cause of high activites for Mo based catalysts, yet has never been directly observed.

The research concentrates on the structure and catalytic properties of an amorphous molybdenum sulfide film with composition MoS_3. Using a simple thermal degradation of $[MoS_4](NH_4)_2$, we deposit a thin film of MoS_3 on a pseudo type-II nanoparticle heterostructure, which photosensitizes the molybdenum sulfide for proton reduction from water using a sacrifical hole acceptor. Our most active system shows good photocatalytic activity with an apparent quantum yield of 10% at 450 nm irradiation. Despite the amorphous nature of this thin film, we attain important structural information from X-ray absorption spectroscopy of samples, both pre- and post-catalysis. Our results show that an observed induction period prior to catalytic activity is accompanied by a decrease in the number coordinating atoms in the molybdenum coordination sphere.



Reduced MoS_3 is an active catalyst for H_2 evolution:

- Reduction of Mo center, ↓ in Mo coordination, Mo-S bond length

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Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
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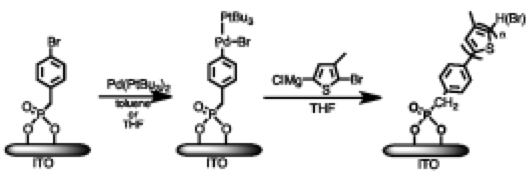
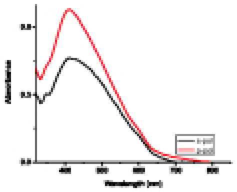
204 - Creating conjugated polymer brushes using surface initiated polymerization

Eric Huddleston, Jenna Bilbrey, Jing Gao, Anandi Roy, ***Jason Locklin****, jlocklin@uga.edu. Department of Chemistry, University of Georgia, Athens, GA 30602, United States*

Surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP) is a powerful technique for creating surface-bound conjugated polymer films. The mechanism of polymerization has been under intense investigation because of the promise this technique holds for the development of a diverse array of nanostructured systems in organic electronic devices. SI-KCTP remains rare in the literature due to the difficulty encountered with bulky monomers. In this talk, we will elaborate on recent work in our laboratory that yields further insight into the density and distribution of initiating sites on the surface using both Ni and Pd based initiators. Psuedo-first order rate constants were obtained through Grignard metathesis reactions with ferrocene-substituted thiophenes for both oxidative addition and transmetallation, and vary depending on the ligand/catalyst system used. Using optimized conditions, oriented thin films of various poly(thiophenes) and poly(phenylenes) were produced via SI-KCTP.





Tuesday, April 9, 2013 11:20 AM
Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

205 - Processing, morphology, and interfaces in organic electronic and redox active polymer-based devices

John R Reynolds*, reynolds@chemistry.gatech.edu, School of Chemistry and Biochemistry/Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*

Synthetic chemistry is the enabling science for organic electronic and redox active materials, while the processing methods employed provide control of the nature of electrode/material interfaces and the morphology of the active material itself. We will discuss electron-rich (donor type), electron-poor (acceptor type), and donor-acceptor polymers as electrochromic, charge transport and organic solar cell materials. We compare the use of spin-coating, slot-die coating and spray-coating in preparing materials and devices for field effect transistors, molecular- and polymer-based bulk heterojunction solar cells, along with electrochromic windows and displays. In some instances, the use of processing additives controls the rate with which a material morphology develops and can be instrumental in enhancing performance. High contrast electrochromic polymers are effectively processed to open morphology films using ultrasonic spray coating. Interface control in polymer solar cells, allow dithienosilole- and dithienogermole-based polymers cells to attain EQE's of ~70% from 400 to 700 nm and PCEs ranging from 7.0 to 8.5%.

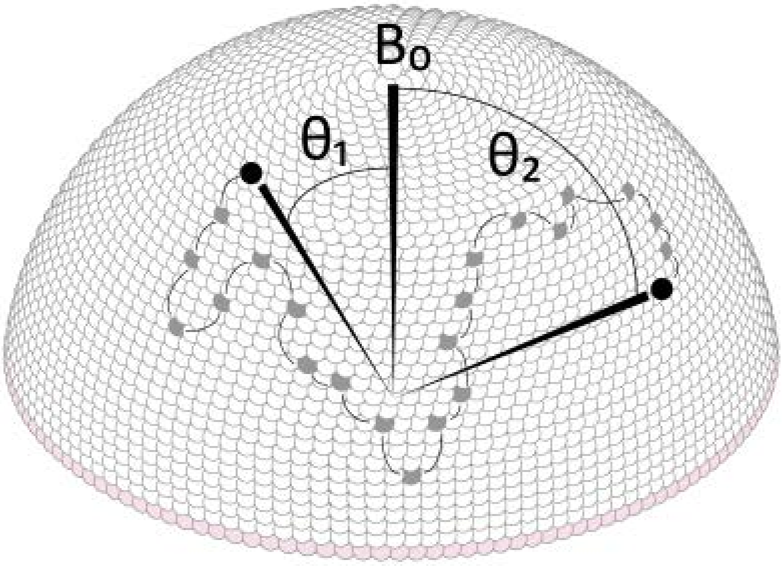
[figure 1]

Tuesday, April 9, 2013 11:50 AM
Carl S. Marvel Creative Polymer Chemistry Award (08:15 AM - 12:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

206 - NMR methods for measuring lateral diffusion in membranes

Peter M Macdonald, *pm.macdonald@utoronto.ca, Qasim Saleem, Angel Lai, Hannah H Morales. Department of Chemical and Physical Sciences, University of Toronto Missisauga, Mississauga, Ontario L5L 1C6, Canada*

Lateral diffusion is a fundamental property of biological membrane components, important for a host of biomembrane functions. Although long studied, novel aspects of the relationship between the structure of membrane components and their lateral diffusion properties continue to emerge. NMR-based lateral diffusion measurements are complicated by the spectral broadening arising from the slow anisotropic motions in membranes. Nevertheless, both pulsed field gradient (PFG) and exchange spectroscopy (EXSY) methods can be adapted to permit NMR measurements of lateral diffusion in membranes. These will be described in overview, but with particular emphasis on results from our laboratory using ^{1}H PFG NMR measurements in magnetically aligned bicelles, and ^{31}P CODEX (Centre-band-Only-Detection-of-Exchange) measurements in spherical phospholipid vesicles.



Tuesday, April 9, 2013 09:00 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)

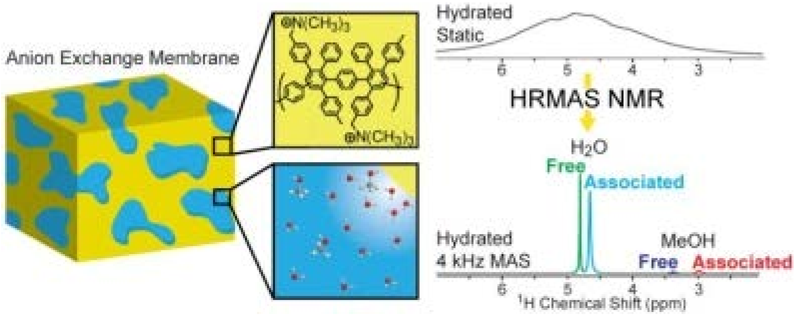
Location: Hilton Riverside

Room: Ste. C, Sec 18

207 - Opening the door on heterogeneous diffusion in polymer membranes using HRMAS NMR PFG

Todd M. Alam, *tmalam@sandia.gov, Department of Electronic, Optical and Nano Materials, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States*

Determination of local chemistry and transport properties in fuel cell membranes is crucial for predicting and optimizing performance. By combining High Resolution Magic Angle Spinning (HRMAS) NMR and Pulse Field Gradient (PFG) diffusion experiments it is demonstrated that different environments in alkaline fuel cell polymer membranes could be resolved. These HRMAS experiments clearly reveal the heterogeneous nature of solvent-membrane interactions and “open the door” to measuring local equilibrium constants, diffusion, and exchange rates in mixed solvent systems.

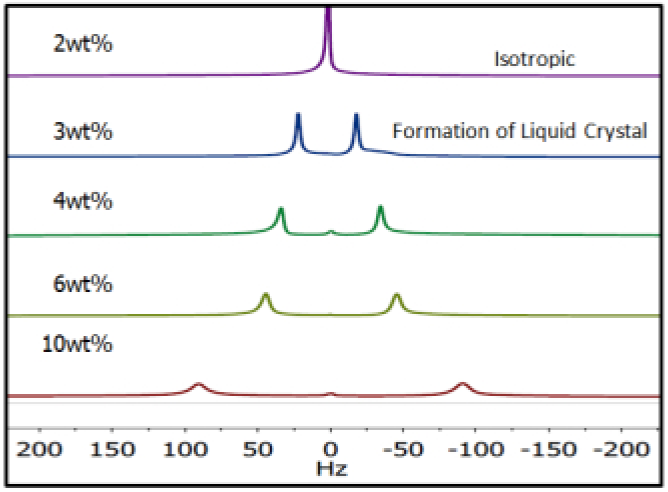


Tuesday, April 9, 2013 09:25 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

208 - Diffusion and realignment of a liquid crystalline ion conducting membrane

Ying Wang[1], *wying102@vt.edu, Jianwei Gao*[2], *Theo J Dingemans*[2], *Louis A Madsen*[1]. *(1) Department of Chemistry and Macromolecular Science and Engineering, Virginia Tech, Macromolecules and Interfaces Institute, Blacksburg, VA 24061, United States, (2) Department of Aerospace Engineering, Delft University of Technology, Delft, The Netherlands*

Sulfonated hydrocarbon ionomers represent promising candidates for applications in polymer electrolyte membrane (PEM) fuel cells and a range of other ion and water transport applications. Designing orientational alignment into these materials can significantly enhance transport properties in, e.g., the device-relevant through-plane direction. We are studying Poly(2,2'-disulfonybenzidine terephthalamide) (PBDT), which is a water soluble polymer with an aromatic backbone structure (for thermal, mechanical, and chemical stability) and sulfonated side groups (for ionic conductivity). PBDT forms a lyotropic liquid crystal in aqueous solution, and we are working toward PBDT membranes with highly aligned hydrophilic channels perpendicular to the membrane plane. We will present studies of diffusion anisotropy and long range orientational order of PBDT membranes using NMR diffusometry and ^{2}H NMR spectroscopy, conducted both after and during membrane casting. The figure shows ^{2}H NMR spectra as a function of PBDT solution concentration. The occurrence of peak splittings at ^{3} 3 wt % PBDT signifies an isotropic to nematic liquid crystal phase transition, as well as increasing long-range orientational order with PBDT concentration. Using this system, we seek to understand and finely optimize the performance of oriented membranes, thus promoting efficiency in fuel cells, batteries, and other conducting organic devices.



^{2}H NMR spectra for PBDT solutions vs. concentration. At ≥ 3 wt%, peak splittings occur, signifying a nematic liquid crystalline phase.

Tuesday, April 9, 2013 09:50 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)

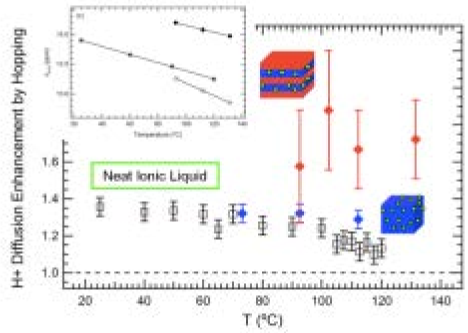
Location: Hilton Riverside

Room: Ste. C, Sec 18

209 - Effects of confinement on proton transport in block copolymers

Jeffrey A Reimer, *reimer@berkeley.edu, Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, CA 94720, United States*

NMR pulsed field gradient diffusion methods quantify proton transport in block copolymer membranes imbibed with ionic liquids. Combining the ionic liquid [Im][TFSI] with both P2VP and PS-b-P2VP has significant effects on ion aggregation and the proton transference number. The amount of proton hopping compared with vehicle diffusion is increased in the nanostructured membrane. High resolution proton MAS NMR suggests that confinement significantly affects for hydrogen bonding. This work is done jointly with Prof. Rachel Segalman, (former) PhD student Megan Hoarfrost, and (current) PhD student Velencia Witherspoon.

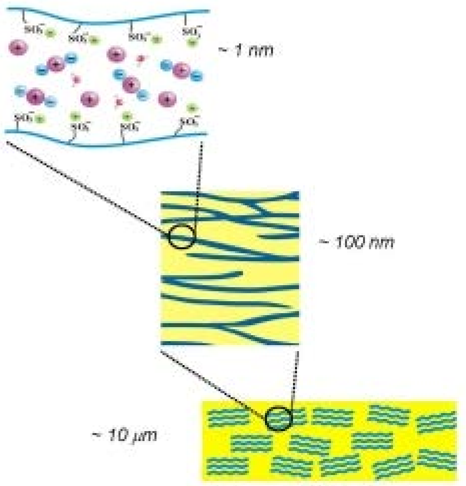


Tuesday, April 9, 2013 10:15 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

210 - Multiscale transport and collective interactions in ionic liquids and polymers: Vistas from gradient NMR

Louis A Madsen, *lmadsen@vt.edu, Jianbo Hou, Zhiyang Zhang, Mark D Lingwood, Ying Wang, Bryce E Kidd. Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061, United States*

Self-organized polymer membranes find uses encompassing reverse-osmosis, nanofiltration, gas separations, and fuel cells, and are at or approaching the lowest cost technology in these venues. Mobile species within these membranes (ions, water, alcohols, gases) move according to local molecular interactions as well as a hierarchy of structural morphologies that span sub-nm to > 10 mm in length scale. We draw on structural information from scattering and microscopy as well as on theories of porous media, electrolytic transport, and oriented matter, then combine these ideas with transport measurements using NMR. Pulsed-field-gradient (PFG) NMR can track chemically distinct moving species, and one can vary the measurement encoding time to uncover the polymer structures that influence diffusion. This talk will focus on how polymer alignment relates to transport in ionomers, as well as on restricted diffusion that is ion specific. On this last subject, we have probed diffusion over a wide range of diffusion lengths of ionic liquids absorbed into a perfluorosulfonate ionomer. Surprisingly, anions experience diffusive restrictions on the micron scale that are strongly temperature and hydration dependent, while cations experience no restrictions. These new fundamental insights will drive rational membrane materials and device design, and will enable new ionomer membrane applications.



Hierarchy of structure in a self-assembled ionomer membrane. Molecular, nano, and micro-scale structures and dynamics all critically influence bulk transport.

Tuesday, April 9, 2013 10:55 AM

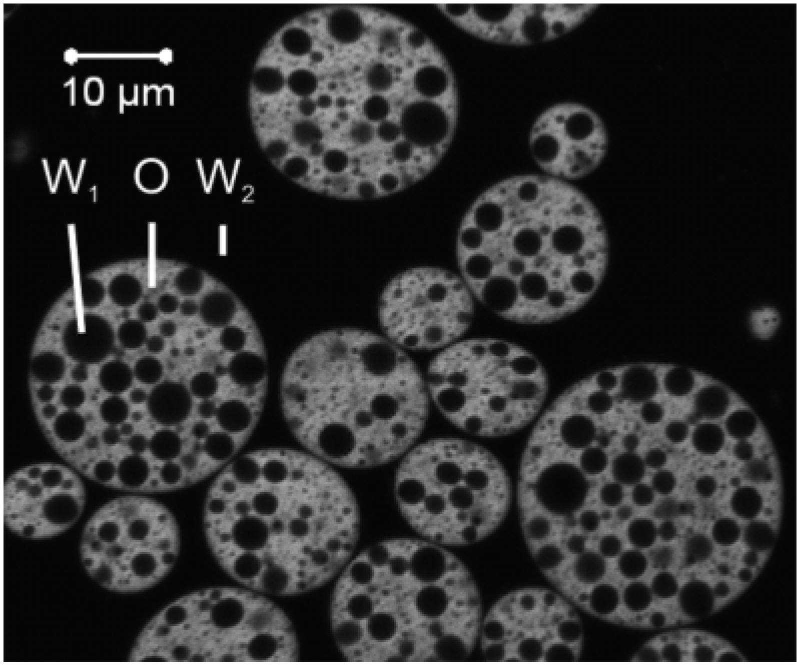
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)

Location: Hilton Riverside
Room: Ste. C, Sec 18

211 - Structure and molecular dynamics in (double-)emulsions by NMR

*R. Bernewitz, K. Köhler, H. P. Schuchmann, **G. Guthausen**, gisela.guthausen@kit.edu. IMVM/BVT, KIT, Karlsruhe, Germany*

Important questions in emulsion science are composition, release kinetics, and structure of multiple emulsions (Fig. 1).



In a quasi-continuous phase, an emulsion is dispersed, consisting of oil and an inner water phase. As these systems are often opaque and dilution additionally influences the system's equilibrium states, NMR is ex-ploited to give insight into geometrical structure as well as composition and molecular dynamics.

Structure can be addressed by PFG-NMR. Signals of the different phases can be dis-criminated either by chemical shift, relaxation or diffusion contrasts[1-5]. Apart from size distributions, influencing e.g. mouth feel, microbial and physical stability and shelf life stability, also composition is of interest, mainly in the context of process and product development. NMR spectros-copy can be exploited, also at low magnetic fields. Additional differentiation is found in terms of diffusion or relaxation fro double emulsions. Different schemes will be compared in this respect. Molecular dynamics is addressed by either PFG-STE NMR or spectroscopy in combination with paramagnetic relaxation enhancement.

References: [1] M. L. Johns et al., *Progr. NMR Spectroscopy* **2007** , *50*, 51. [2] X. Z. Guan et al., *EJLST* **2010** , *112*, 828. [3] R. Bernewitz et al., *Magn. Reson. Chem.* **2011** , *49*, S93. [4] J. P. M. van Duynhoven et al., *Magn. Reson. Chem.* **2002** , *40*, S51. [5] M. A. Voda et al., *Trends Food Sci. Technol.* **2009** , *20*, 533.

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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)
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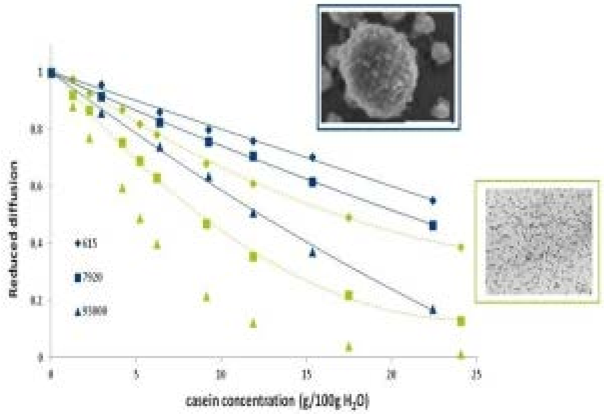
212 - Investigation of dairy colloids using PFG-NMR diffusion techniques

François Mariette, *francois.mariette@irstea.fr, UR TERE, Irstea, Rennes, France and Université européenne de Bretagne, Rennes, France*

Molecular transport is a key feature of food processes, particularly dairy processes. For example, the transformation of milk into cheese involves coagulation, draining, salting and ripening, in which water and solute diffusion are important parameters affecting the microbiological and sensorial properties of cheese. In milk, caseins represent around 80% of the total protein and are large colloidal particles called casein micelles. They are directly involved in the formation of dairy gels as they constitute the building blocks of the network These colloidal particles can be destabilized by addition of enzyme, by slow acidification, or by combinations of both. To improve our understanding of the microstructure, different PFG-NMR approaches have been carrying out in order to answer to the following question i) how the water diffusion coefficient is affected by the casein concentration and gel microstructure ii) How the casein micelle and gel structure modify the diffusion of probe polymer



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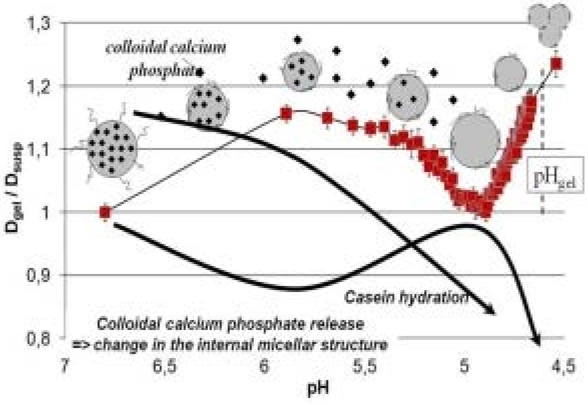

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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 12:10 PM)

Location: Hilton Riverside

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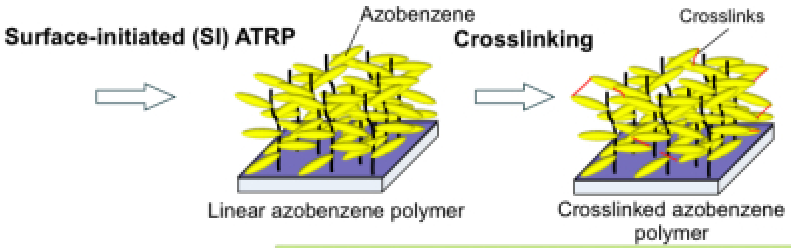
213 - Fabrication of photomobile polymer materials with a bilayer structure and their photoresponsive behavior

Tomiki Ikeda, *tikeda@tamacc.chuo-u.ac.jp, Research & Development Initiative, Chuo University, Tokyo, Japan*

Photomobile polymer materials with a bilayer structure have been prepared by a variety of methods, including electron beam irradiation of azobenzene liquid crystalline (LC) polymers coated on a polymer substrate and azobenzene LC polymer brushes grown on a flexible polymer film by surface-initiated ATRP, followed by a crosslinking reaction. We then evaluated their physical properties and photoresponsive behavior upon exposure to UV and vis light. We observed that these materials show high fatigue resistance even by irradiation with UV light.



Tuesday, April 9, 2013 08:00 AM
Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

214 - Wireless mechanical adaptivity: Photomechanical effects in azobenzene-functionalized polymeric materials

***Timothy J White**[1], timothy.white2@wpafb.af.mil, Michael E McConney[1,2], Kyung Min Lee[1,2]. (1) Materials and Manufacturing Directorate, Air Force Research Laboratory, United States, (2) Azimuth Corporation, United States*

Employing light to direct functional responses in photoresponsive polymeric materials and composites is potentially advantageous as it is wireless and extremely rapid. Furthermore, the intensity, phase, and polarization of light can be easily modulated into complex spatial patterns with holography (intensity or polarization) or masking (intensity or phase). Deriving from these foundational properties of light, photoresponsive macromolecular systems exhibit exceeding potential to yield rapid and highly engineered macroscopic as well as spatially selectable mechanically adaptive responses useful as soft actuators or topographical surfaces in aerospace, automotive, and biomedical applications. This talk will discuss our recent work generating both shape fixing (shape memory) and shape restoring (elastic) responses in a variety of photoresponsive polymeric materials. Particular emphasis will be placed on the generation of topographical features in liquid crystalline polymer networks.

Tuesday, April 9, 2013 08:30 AM
Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
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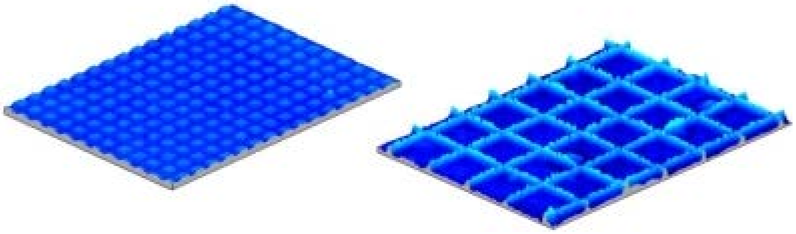
Room: Ste. B, Sec 7/10

215 - Switchable and permanent surface topographies formed in chiral nematic media

Danqing Liu[1,2], *d.liu1@tue.nl, Cees W.M. Bastiaansen*[1], *Jaap den Toonder*[2], ***Dirk Broer***[1], *d.broer@tue.nl. (1) Department of Chemical Engineering & Chemistry, Group Functional Organic Materials & Devices (SFD), Eindhoven, The Netherlands, (2) Department of Mechanical Engineering, Materials Technology, The Netherlands*

The formation of surfaces with well-controlled non-flat topologies is of relevance for many applications.Here we present a more general method to form surface protrusions in a non-patterned chiral-nematic film by localized exposure. We demonstrate that by adjustment of composition and curing conditions one can either make an elastic film that forms dynamic protrusions that disappear as soon as the exposure stops or deformable films that have permanent surface relief that do not disappear even after a heating treatment.

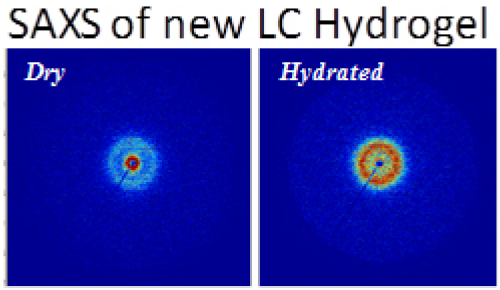


Tuesday, April 9, 2013 09:00 AM
Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

216 - Synthesis and characterization of a thiol-ene based liquid crystalline hydrogel

*Amir Torbati, **Patrick T Mather**, ptmather@syr.edu. Department of Biomedical and Chemical Engineering and Syracuse Biomaterials Institute, Syracuse University, Syracuse, NY 13244, United States*

In contrast to biological gels, synthetic hydrogels are generally amorphous and possess no particular ordered structure, limiting their functionality in biological environments. To address this, we have synthesized a series of main-chain liquid crystalline hydrogels (LCGs) utilizing thiol-ene chemistry. Three distinct thermal transitions were evident: glass, melt, and isotropization, and the materials exhibited shape memory properties with heat and water triggering of shape change. Wide- and small-angle X-ray scattering studies were utilized to investigate liquid crystalline structure in both dry and hydrated states. The WAXS results indicated that the usual lamellar structure of one of the constituent phases becomes disordered upon sample is hydration (Figure 1(a)). SAXS results indicated long-range ordering of a smectic phase in the hydrated state (Figure 1(b)). These characteristics open up a range of applications for biomedical devices that exploit the unique combination of order, hydrated softness, and shape memory mechanical action.



Tuesday, April 9, 2013 09:20 AM
Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
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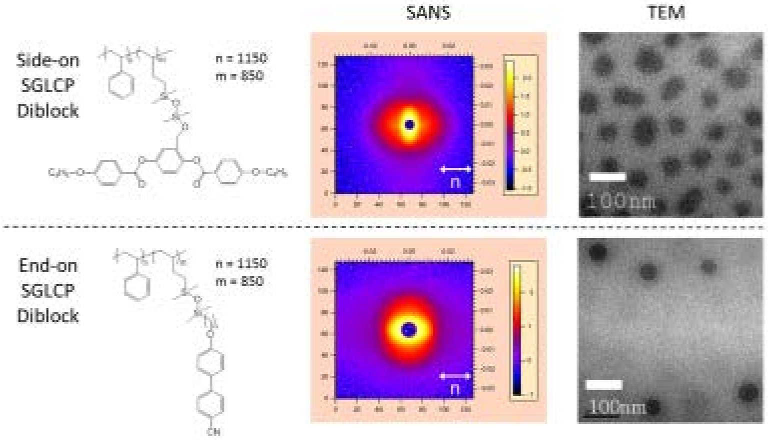
217 - Self-assembly of coil-liquid crystal (LC) diblocks in LC solvent: Hierarchies of anisotropies

Julia A Kornfield, *jak@cheme.caltech.edu, Rohan Hule, Zuleikha Kurji, Paul Pirogovsky. Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

Spontaneous anisotropy in the local chain conformation of Side-Group Liquid Crystalline Polymers (SGLCPs) drives the formation of anisotropic self-assembled microstructures of diblock copolymers consisting of an SGLCP block and a random coil block when dissolved in a small molecule LC, as observed by SANS and TEM. A physically-inspired, segment-based model allows us to predict scattering profiles for different proposed arrangements of the block copolymers within the microstructure. Predicted scattering patterns, spanning the range from the overall assembly (>100nm) to the intrachain scale (5-100nm), are compared with the observed scattering profiles to discriminate between different possible self-assembled structures.



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Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
Location: Hilton Riverside
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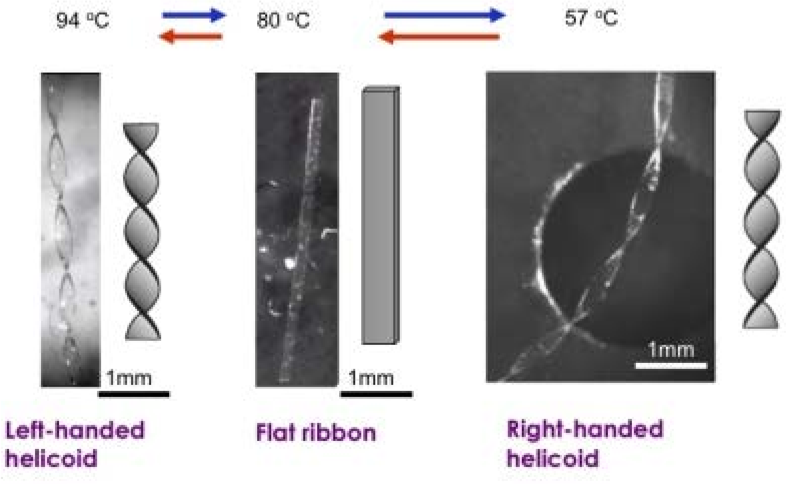
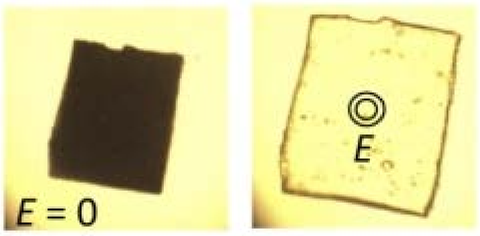
218 - Stimulus response properties of nematic elastomers with various director configurations

Kenji Urayama, *urayama@rheogate.polym.kyoto-u.ac.jp, Department of Materials Chemistry, Kyoto University, Kyoto, Japan*

The nematic elastomer (NE) ribbons with twist orientation form helicoidal shape and the helical pitch strongly depends on temperature including the reversal of handedness (*PNAS*, 2011). The polydomain NEs which are originally made in the high-temperature isotropic state (IGPNE) undergo the polydomain-to-monodomain transtion by a markedly small magnitude of mechanical work (*Macromolecules*, 2009; *Macromol. Chem. Phys.*, 2012). The IGPNEs exhibit a larger degree of electromechanical effect than the ferroelectric LC elastomers reported ealier (*Soft Matter*, 2011).





Tuesday, April 9, 2013 10:15 AM

Liquid Crystals and Polymers (08:00 AM - 11:35 AM)

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219 - Photodeformable crosslinked liquid crystal polymers and light-driven soft actuators

***Yanlei Yu**, ylyu@fudan.edu.cn, Department of Materials Science, Fudan University, China*

Crosslinked liquid crystal polymers (CLCPs) have recently attracted more and more attention because they exhibit such unique properties as elasticity, anisotropy, stimuli-responsiveness, and molecular cooperation effect.It has been reported that the CLCP films exhibited anisotropic contraction by heat because of the liquid crystal (LC)-isotropic thermal phase transition, accompanied by the cooperative effect of LC molecules and the strong correlation between the conformation of polymer chains and the alignment of mesogens. By incorporating azobenzene groups into the CLCPs, large deformations such as contraction and bending have been induced by light due to the photoisomerization of the azobenzene chromophores.Since light is an ideal stimulus for it can be localized (in time and space), selective, nondamaging, and allows for remote activation and remote delivery of energy to a system, photodeformable CLCPs present an interesting opportunity to realize soft actuators in microscope applications. Full-light-driven plastic motors, oscillators, microrobots, microvalves and micropumps have thus been fabricated from the CLCPs. Recently several thermo- and photo-responsive flexible micro actuators have further been assembled from the CLCPs using such advanced techniques as soft lithography, microfluidic, and photomask technology. In this work, a two-dimensional (2D) micro-array with a micro-sized period (~1 mm) was first fabricated from an azobenzene CLCP with replica molding technology. It was found that the reflection spectra of the micro-array showed the switchable behavior when irradiated with UV and visible light alternately. This phenomenon is ascribed to the change in the order of the periodic structure of the micro-array, resulted from the photoinduced deformation of the azobenzene CLCP. Furthermore, we prepared a micro-arrayed CLCP film from an optimized azobenzene precursor and polydimethylsiloxane-soft-template-based secondary replication. Regulated by alternating irradiation of UV-visible light (365 nm/530 nm), the micro-arrayed film showed an ideal quick (<1 min) and reversible switch of superhydrophobic adhesion.

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Liquid Crystals and Polymers (08:00 AM - 11:35 AM)
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220 - 3D mechanical deformations of azobenzene functionalized liquid crystalline polymer networks

Jeong Jae Wie[1,2], *wie@udel.edu, Kyung Min Lee*[1,2], *Brandon M Lynch*[3], *Timothy J White*[1]. *(1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio 45433, United States, (2) Azimuth Corporation, Dayton, Ohio 45432, United States, (3) Department of Chemistry, Wright State University, Dayton, Ohio 45435, United States*

Azobenzene-functionalized liquid crystal polymer networks (azo-LCN) have been well-known to convert light energy stimulus into mechanical work. Employing twisted nematic (TN) geometry, we investigated photomechanical responses of azo-LCN upon exposure to linearly polarized 442 nm irradiation. The TN azo-LCN exhibited large scale photodirected out-of-plane mechanical deformation. (i.e, coiling). Out-of-plane deformation is beneficial to form 3-dimensional structures, which is essential to design complex architectures. Low intensity laser irradiation provided isolation of the photomechanical phenomenon from photothermal contributions observed upon exposure to higher intensities.

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221 - Flash NanoPrecipitation enables the production of nanoparticle drug cocktails and multivalent targeted nanoparticles for imaging and drug delivery

Robert K Prud'homme, *prudhomm@princeton.edu, Chemical and Biological Engineering, Princeton University, Princeton, NJ 08540, United States*

We have developed a block-copolymer-directed, kinetically-controlled self-assembly process called Flash NanoPrecipitation (FNP) to produce 50-400 nm nanoparticles. The process involves controlling micromixing to effect supersaturations as high as 10,000 in 1.5 ms, and then controlling nucleation and growth rates to match block copolymer assembly rates. The rapid assembly enables the encapsulation of multiple drugs and imaging agents into the same nanoparticle, and the production of multivalent targeted nanoparticles. **[figure 1]** We will give examples of nanoparticle assembly and focus on targeting and imaging applications. Imaging using long wavelength fluorphores, MRI contrast agents, and SPEC agents will be presented. An example of TB treatment combining multiple drugs and targeting made is a single step process shows the versatility of the FNP assembly. The FNP process enables the production of nanoparticle libraries with variable ligand density. Examples of small molecule (mannose for TB), folate ligand, and antibody targeting will be presented. For the mannose targeted nanoparticles we show a maximum ligand density for uptake into macrophages, and a reduce uptake beyond this maxium value. Finally, the rules for block copolymer selection on circulation time will be addressed.

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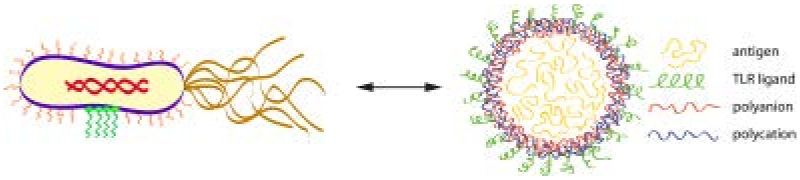
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

222 - Bio-mimicking synthetic vaccines via layer-by-layer self-assembly of polyelectrolytes, inorganic carbonates, proteins, and nucleic acids

Bruno G De Geest, *br.degeest@ugent.be, Stefaan De Koker. Department of Pharmaceutics, Ghent University, Ghent, Belgium*

Microbes interact with the immune system by activating immune cells through specific biological cues termed 'danger associated molecular patterns' (DAMPs). When sensing these signals, antigen presenting cells will process microbial proteins and initiate an adaptive immune response. Here we design a bio-mimic of the microbial structure by assembling alternating layers of oppositely charged polypeptides and polysaccharides onto protein loaded calcium carbonate microparticles. Removal of the calcium carbonate templates yields capsules with protein suspended in their hollow void. Surface-functionalization with DAMPS is achieved again through electrostatic self-assembly with a oligonucleotide based Toll-like receptor agonist. The thus obtained bio-mimics are evaluated as vaccine carriers in a battery of immunological assays and shown to confer protective immunity in vivo models for cancer immunotherapy and influenza vaccination.



Tuesday, April 9, 2013 09:00 AM
Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
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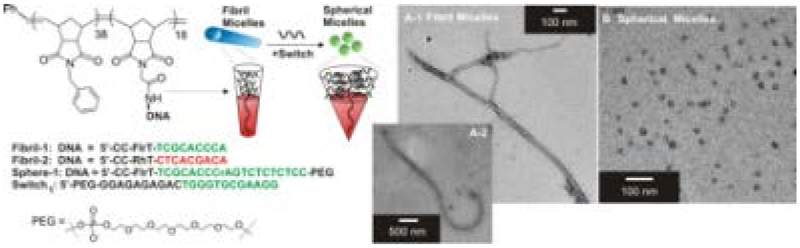
223 - Programming phamacokinetics in vivo via remotely controlled switching of nanoparticle size and shape

Miao-Ping Chien, *m1chien@ucsd.edu, Nathan Gianneschi. Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, United States*

It has been shown that the pharmacokinetic profile of otherwise similar particles can depend to a large degree on their size and shape (morphology). This has tremendous implications for drug delivery and diagnostic vehicles designed to have particular blood cicrulation half-lives and specific targeting characteristics, which are inherently important properties in the science of small molecule and nanoscale drug design. We were intrigued by the possibility that one may be able to manipulate the pharmacokinetics of a material in the blood stream of a living organism if one were able to dramatically ulter the morphology of the material via some stimulus either endogenous or exogenous. Here, we utilize programmed morphology switches to modulate the blood circulation half-life of a nanomaterial post-injection in vivo. In addition to differential circulation times and tissue accumulation depending on morphology, we demonstrate that a fibril-to-spherical micelle morphology switch can be used to modulate cell-uptake rates in murine macrophages in vitro. We have demonstrated spatiotemporal control *in vivo*allowing unprecendented control over blood circulation, clearance and tissue accumulation of an injected material.These results have broad implications for the design of nanoscale materials in drug delivery and diagnostics applications where tunable pharmacokinetics could play a role in enhanced targeting and clearance.



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Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
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224 - Miniemulsion template synthesis of well-defined cross-linked polymeric nanomaterials for biomedical delivery

*Chih-Kuang Chen, Yukun Li, Qing Wang, Yun Yu, Jiong Zou, **Chong Cheng**, ccheng8@buffalo.edu. Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States*

Miniemulsion template synthesis has afforded a variety of well-defined polymeric nanomaterials through highly efficient cross-linking processes. Particularly, the strategic combination of UV-induced thiol-ene click cross-linking with transparent miniemulsion templates yielded well-defined nanomaterials within 30 minutes. These biodegradable nanoparticles and nanocapsules can be used as scaffolds for drug and gene delivery. Moreover, crystallization strategy was developed to dramatically increase the kinetic stability of miniemulsion templates, resulting in novel polyelectrolyte nanocapsules with monolayer-thick shells.

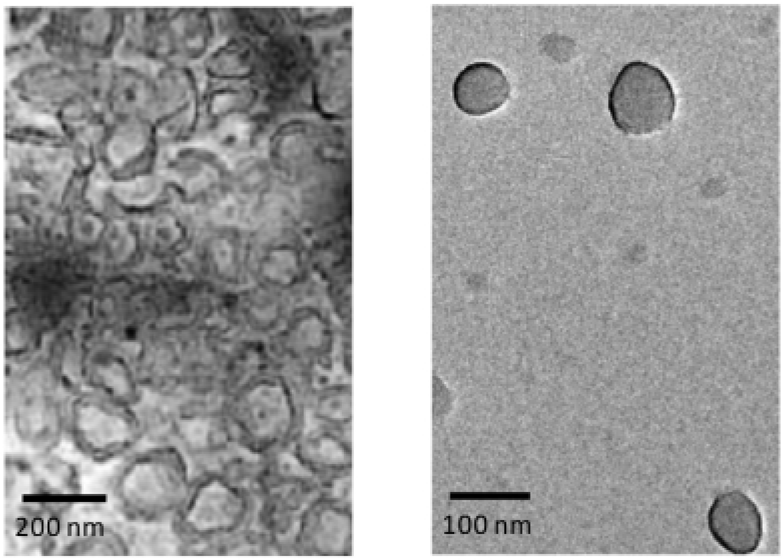

Figure 1. TEM images of nanocapsules

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225 - Self-assembling coacervate controls the release of proteins: From design to in vivo functionality

Yadong Wang, *yaw20@pitt.edu, Department of Bioengineering, University of Pittsburgh, Pittsburgh, PA 15261, United States*

Clinical translation of growth factor therapies faces multiples challenges; the most significant is how to maintain bioactivity. My lab uses heparin and a biocompatible polycation to form an injectable coacervate that preserves the bioactivities of heparin-binding proteins including many growth factors. This design is inspired by the ternary structure of fibroblast growth factor-2 (FGF2), heparin and FGF receptor. The effectiveness of the coacervate delivery system is demonstrated using multiple growth factors in multiple animal models. The coacervate provides spatial and temporal control of the release of heparin-binding proteins. Here I will discuss three applications: angiogenesis, skin wound healing, and cardiac repair post- infarction. Promising data in large animals suggests the potential of clinical translation.

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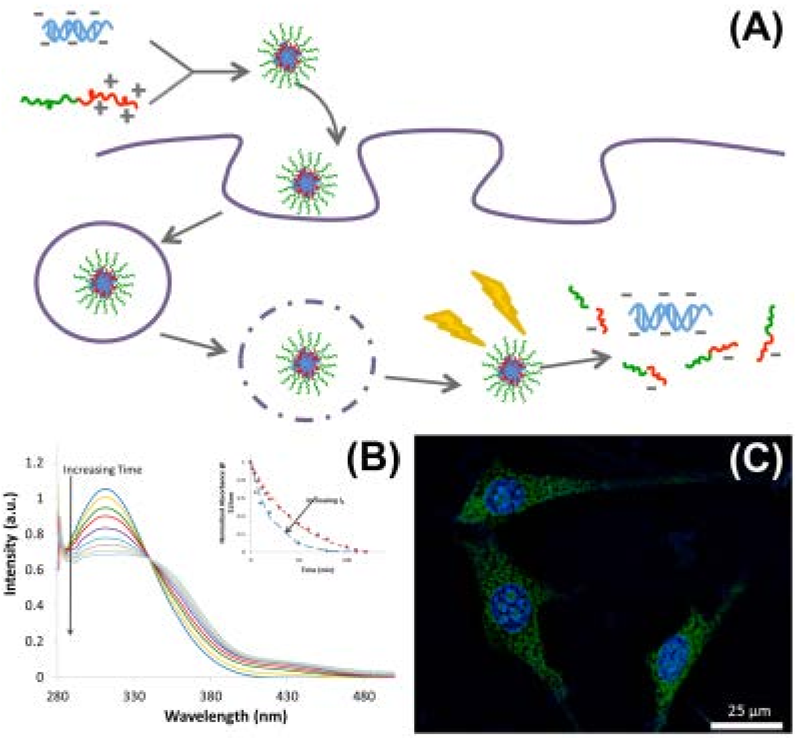
226 - Photo-sensitive polymers for nucleic acid packaging, delivery, and release

Abbygail Palmer, Matthew Green, Raghunath Roy, Thomas H Epps, ***Millicent O Sullivan****, msullivan@udel.edu. Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States*

We have synthesized novel copolymers containing poly(ethylene glycol) (PEG) and photocleavable polycationic units, which compact siRNA and pDNA into nuclease-resistant polyplexes appropriate for nucleic acid delivery applications (Fig. 1A). Photoirradiation of the polymers initiates rapid polymer cleavage along the polycationic backbone (Fig. 1B), and leads to conversion of cationic groups into anionic groups. This light-induced reaction stimulates polyplex disassembly, with implications for user-controlled nucleic acid release within cells. The photocleavable polyplexes are internalized into B16 murine melanoma cells and NIH/3T3 fibroblast cells within minutes (Fig. 1C). Current studies are aimed at utilizing the light-induced disassembly reaction to understand and optimize intracellular release kinetics.



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Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
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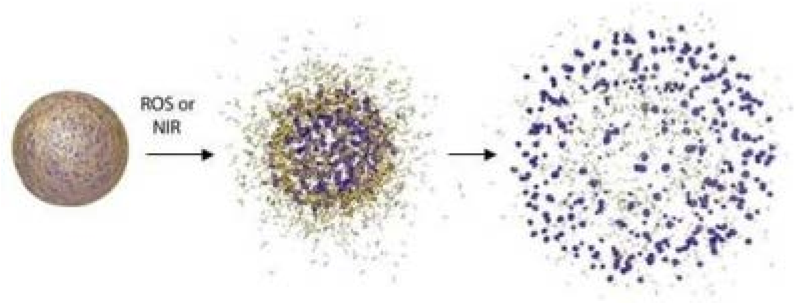
227 - Art of falling apart: Release from nanoparticles on demand

*Caroline de Gracia Lux[1], Mathieu L Viger[1], Shivanjali Joshi-Barr[1], Nadezda Fomina[1], **Adah Almutairi**[1,2], aalmutairi@ucsd.edu. (1) Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, United States, (2) Departments of NanoEngineering and Materials Science, University of California, San Diego, United States*

This presentation is an overview of advances in triggered release to biological and external stimuli. Our recent breakthrough bioresponsive material is the first polymeric nanoparticle to release cargo in response to disease-relevant concentrations of H_2O_2(50 µM) or to activated neutrophils. We have also shown that encapsulation of certain MRI contrast agents in bioresponsive polymers creates an activatable signal.

Our investigations of externally triggered release focus on near infrared (NIR), which provides excellent spatiotemporal resolution and relatively deep tissue penetration. We have amplified the response to NIR through creative architectures, including a self-immolative polymer. To enable responsiveness to continuous wave NIR, which is safer and more economical than pulsed lasers, we have taken advantage of water's absorption at 980 nm to induce a phase change, enabling release from common polymers like PLGA with minimal heating, and are incorporating upconverting nanoparticles into our UV-responsive polymer.

We are also synthesizing polymers with novel backbone designs to allow rapid depolymerization.



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Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)
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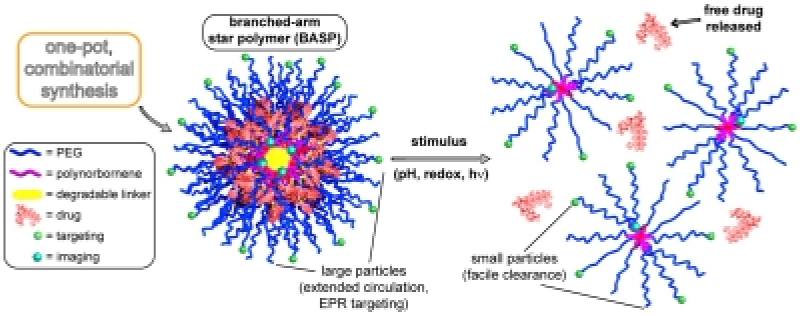
228 - Convergent synthesis of polymer nanostructures for biological applications

Jeremiah A. Johnson, *jaj2109@MIT.EDU, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, United States*

This talk will highlight convergent methods for the synthesis of polymeric nanoparticles. Specifically, new strategies for synthesis of poly(ethylene glycol)-(PEG) based star polymers and branched pseudo-alternating copolymers will be discussed with an emphasis on bottom-up design for applications in biological imaging and drug delivery.



Tuesday, April 9, 2013 11:35 AM

Bottom-Up Design of the Next Generation of Biomaterials (08:30 AM - 11:55 AM)

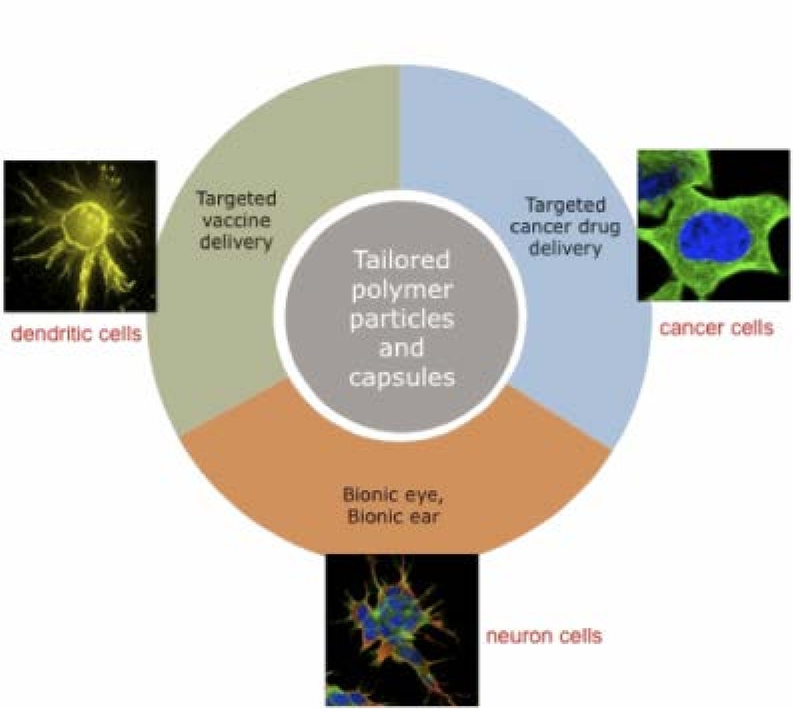
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

229 - Nanoscale engineering of multilayered particles for biomedical applications

Frank Caruso, *fcaruso@unimelb.edu.au, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, VIC 3010, Australia*

he design and assembly of responsive polymers underpins the development of particle carriers for biomedical applications. This presentation will detail various assembly strategies and chemistries to generate multifunctional and responsive polymer capsules, including the well established layer-by-layer (LbL) assembly approach and the recently developed continuous assembly of polymers (CAP) technology. Examples on the application of these capsules for the encapsulation, protection and release of oligonucleotides and peptides to stimulate immune responses will be given. Emphasis will be placed on multilayered hydrogel capsules that possess size and charge exclusion properties that allow for selective permeability of reaction components and facile control over capsule architecture. These capsules afford the continuous synthesis of nucleic acids and the assembly of liposome-subcompartmentalized capsules (capsosomes) that have structures reminiscent of cells.

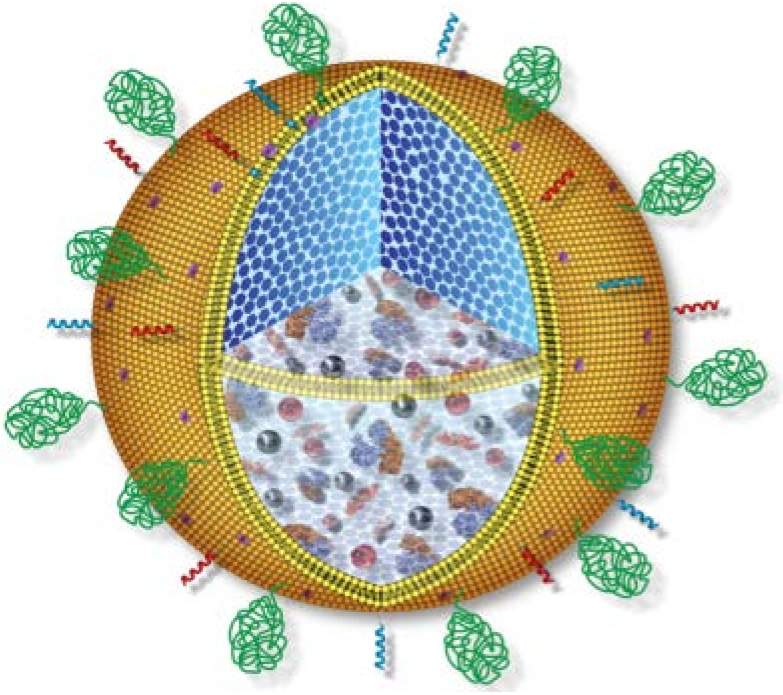


Tuesday, April 9, 2013 01:30 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

230 - Protocells: Mesoporous silica supported lipid bilayers for targeted delivery of multicomponent cargos

C. Jeffrey Brinker[1,2], *cjbrink@sandia.gov, Eric Carnes*[1], *Carlee Ashley*[1], *Jason Townson*[2]. *(1) Sandia National Laboratories, Albuquerque, NM 87106, United States, (2) Chemical and Nuclear Engineering CMEM, University of New Mexico, Albuquerque, NM 87122, United States*

We recently developed a new class of hybrid nanocarriers that synergistically combine features of mesoporous silica nanoparticles and liposomes. Fusion of liposomes to a spherical, high-surface-area, mesoporous silica core followed by modification of the resulting supported lipid bilayer (SLB) with multiple copies of a targeting peptide, an endosomolytic peptide, and PEG results in a nanocarrier construct (the 'protocell') that, compared with liposomes improves on capacity, selectivity, and stability and enables targeted delivery and controlled release of high concentrations of multicomponent cargos (chemotherapeutic drugs, siRNA, etc.) within the cytosol or nucleus of cancer cells .



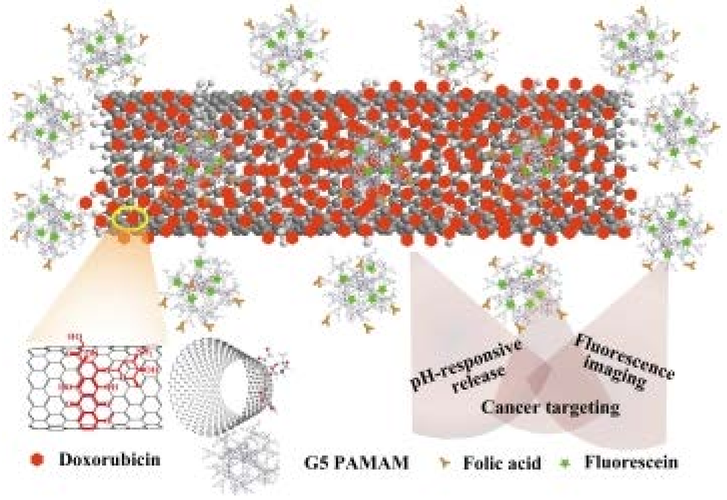
Specifically, owing to its high surface area, the mesoporous silica core possesses a higher capacity for therapeutic and diagnostic agents than similarly sized liposomes. The fluid but stable SLB allows multivalent interactions with the target cell at very low targeting peptide densities, features crucial to maximizing specific binding, minimizing nonspecific binding, reducing dosage, and mitigating immunogenicity.

Tuesday, April 9, 2013 02:00 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

231 - Targeted and pH-responsive delivery of doxorubicin to cancer cells using mutifunctional dendrimer-modified multi-walled carbon nanotubes

Shihui Wen[1], Hui Liu[1], Hongdong Cai[2], Mingwu Shen[1], ***Xiangyang Shi***[1]*, xshi@dhu.edu.cn. (1) College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, Shanghai 201620, China, (2) College of Materials Science and Engineering, Donghua University, Shanghai, Shanghai 201620, China*

We report the use of multifunctional dendrimer-modified multi-walled carbon nanotubes (MWCNTs) for targeted and pH-responsive delivery of doxorubicin (DOX) into cancer cells



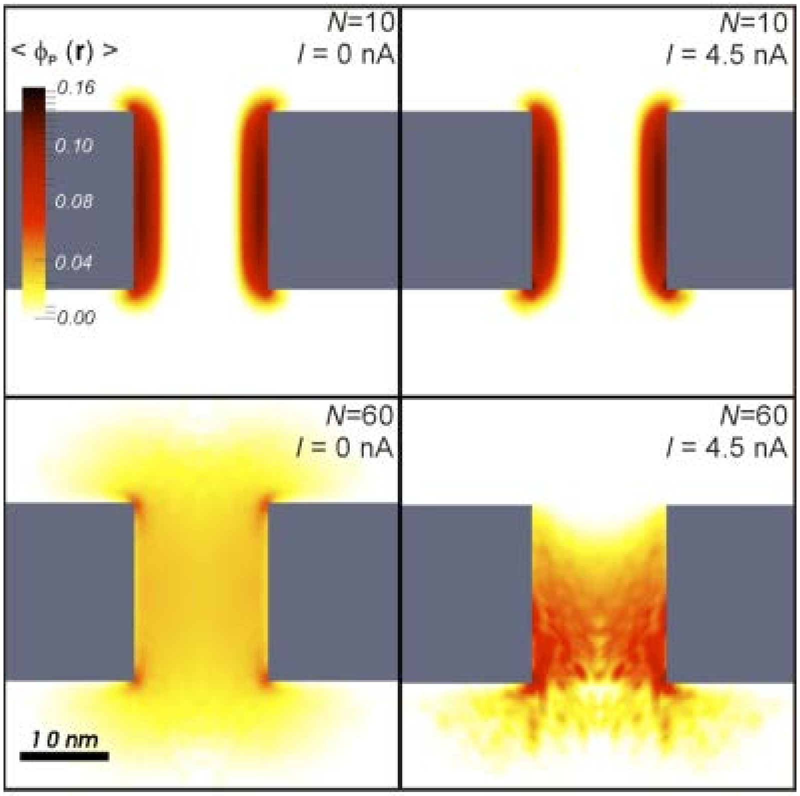
. In this study, amine-terminated generation five poly(amidoamine) (PAMAM) dendrimers modified with fluorescein isothiocyanate (FI) and folic acid (FA) were covalently linked to acid-treated MWCNTs, followed by acetylation of the remaining dendrimer terminal amines to neutralize the positive surface potential. The formed multifunctional MWCNTs (MWCNTs-G5-FI-FA-Ac) were characterized via different techniques. Then, the MWCNTs-G5-FI-FA-Ac was used to load DOX for targeted and pH-responsive delivery to cancer cells overexpressing high-affinity folic acid receptors (FAR). We showed that the MWCNTs-G5-FI-FA-Ac enabled a high drug payload and encapsulation efficiency both up to 98% and the formed DOX/MWCNT-G5-FI-FA-Ac complexes displayed a pH-responsive release property with fast DOX release under acidic environment. Importantly, the DOX/MWCNT-G5-FI-FA-Ac complexes displayed a therapeutic efficacy similar to that of free DOX, and were able to target to cancer cells overexpressing high-affinity FAR and effectively inhibit the growth of the cancer cells. The synthesized multifunctional dendrimer-modified MWCNTs may be used as a targeted and pH-responsive delivery system for targeting therapy of different types of cancer.

Tuesday, April 9, 2013 02:30 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

232 - Molecular organization and transport in polymer modified nanopores

Igal Szleifer, *igalsz@northwestern.edu, Department of Biomedical Engineering and Department of Chemsitry, Northwestern University, Evanston, IL 60208, United States*

Natural and man-made pores and channels of nanoscale dimensions display unique ionic and protein transport behavior. Nanopores modified with supramolecular chemical species (such as polyelectrolyte brushes) have dimensions that are similar to the range of the electrostatic interactions, and also to the molecular size of the tethered macromolecules. The competition between molecular and interaction length scales, as well as the geometry of the surfaces, creates interesting possibilities for the creation of stimuli responsive gates and ion channels and for the fundamental understanding of the interplay between molecular organization and charge transport in nanoconfined environments. In this talk we will discuss recent theoretical developments that enable us to study the structural properties of the modified pores and the coupling that exists between the protonation state of the polyelectrolytes and ionic transport through them.

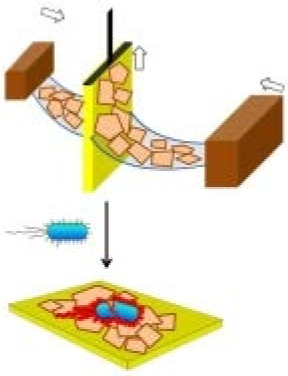


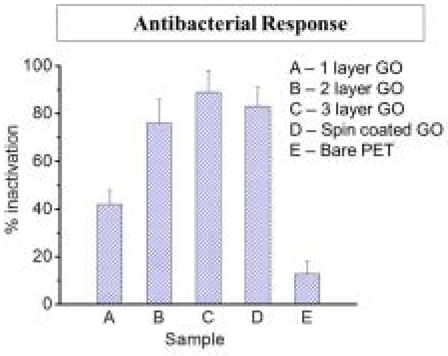
Tuesday, April 9, 2013 03:05 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

233 - Fabrication of multilayered transparent and antibacterial graphene-oxide polymer films

***Joey Mangadlao**[1], jdm185@case.edu, Catherine Santos[2], Mary Jane Felipe[3], Al Christopher De Leon[1], Debora Rodrigues[2], Rigoberto Advincula[1]. (1) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States, (2) Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204, United States, (3) Department of Chemistry, University of Houston, Houston, TX 77204, United States*

Delamination of polymer films over the course of time is inevitable but with multilayering technique, a fresh layer ensures longevity of the material's functions. This project aims to fabricate multilayered graphene or graphene oxide (GO) - polymer films for multifunctional coatings and devices. GO film was deposited through Langmuir-Blodgett (LB) method on poly(ethylene terephthalate) (PET) substrate and its antibacterial activity was evaluated. Results reveal that GO is surface active at air-water interface by displaying a classic Õ-area isotherm. The GO films exhibit antibacterial efficacy that is layer dependent. Compared to spin-cast GO, the films deposited through LB show more stability and retained antibacterial activity even after agitation by ultrasonication. Three layers of GO display roughly 97% transparency. These findings serve as baseline information towards the application of multilayered GO-polymer nanocomposites.



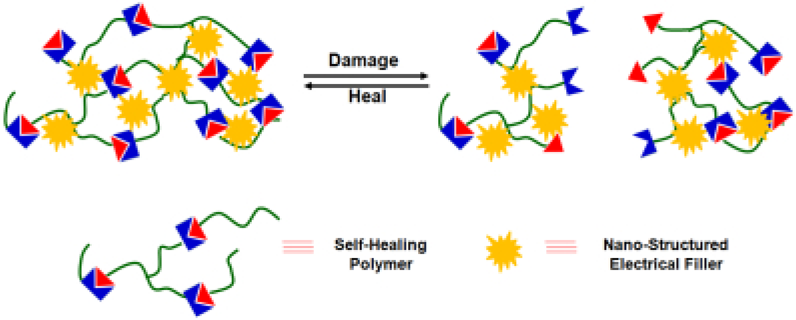


Tuesday, April 9, 2013 03:35 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

234 - Self-healing polymer composites for electronic skin

Chao Wang[1], *wangchao@stanford.edu, Benjamine C-K Tee*[2]*, Ranulfo Allen*[1]*, Zhenan Bao*[1]*. (1) Chemical Engineering, Stanford University, Stanford, California 94305, United States, (2) Electrical Engineering, Stanford University, Stanford, California 94305, United States*

We demonstrated the first example of a repeatable self-healing electronic sensor skin by using a composite of a self-healing supramolecular polymer and nano-structured conductive particles.[1] By rationally varying the composition of the electrically conductive inorganic fillers, we obtain both electrodes and piezo-resistive sensor materials with both electrical and mechanical healing capability at room temperature. The electrical materials were further integrated into a self-healing electronic sensor skin.



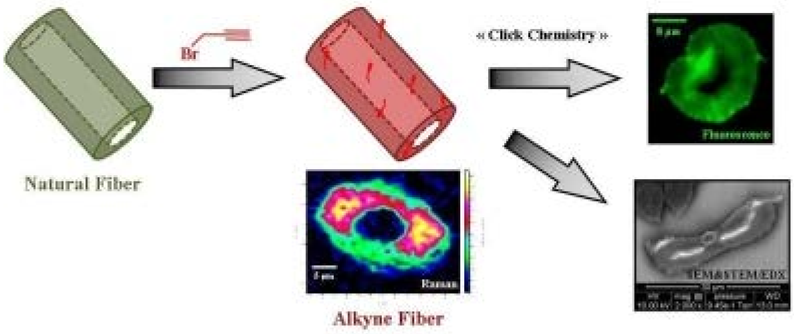
[1] C. Wang*, B. Tee*, Z. Bao et al. *Nat. Nanotechnol.* accepted.

Tuesday, April 9, 2013 03:55 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

235 - Mild and ecofriendly modifications of cellulose fibers toward novel functional biomaterials

Gino Mangiante[1], *gino.mangiante@gmail.com*, *Elisa Zeno*[2], *Michel Petit-Conil*[2], *Marion Gaborieau*[3], *Aurélia Charlot*[1], *Julien Bernard*[1], *Etienne Fleury*[1]. *(1) IMP@INSA Lyon UMR 5223, Villeurbanne, France, (2) Centre Technique du Papier, Grenoble, France, (3) University of Western Sydney, Nanoscale Organisation and Dynamics Group, Penrith, New South Wales 2751, Australia*

Polysaccharides-based materials represent credible and promising alternative regarding the fossil fuel depletion. Herein, we report the heterogeneous alkyne functionalization of bleached Kraft fibers through etherification in mild basic hydroalcoholic or totally aqueous media. These conditions allow for an efficient derivatization without jeopardizing the crystallinity and the inherent properties of the cellulose fibers. Imaging of functionalized-cellulose fibers cross-sections (through Raman and fluorescence confocal microscopies as well as STEM/EDX) emphasized that alkyne moieties are distributed all over the fibers (scheme 1). The resulting cellulose fibers were finally successfully post-functionalized by a panel of molecular probes and macromolecules in aqueous conditions. Cellulose-based biohybrids obtained *via* aqueous “click” coupling were shown substantial enhancement of dry and wet mechanical properties of paper in which they were included.



Scheme 1. Mapping of alkyne functionalization of cellulose fibers

Tuesday, April 9, 2013 04:15 PM
Hybrid Materials (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

236 - Adventures with Tim in polymer science

Edwin (Ned) L. Thomas, *elt@rice.edu, Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77030, United States*

This talk highlites a set of scientific collaborations with Tim dating back to 2000, initially with P. DeRege using high molecular weight block copolymers for photonic crystals, passing to C. Breen's work on polarized photoluminescence using block copolymer templates and S. Thomas pioneering work on iptycenes - which expanded with N. Tsui and A. Paraskos to engender *"molecular barbed wire"* in polyestersfollowed by iptycene containing polycarbonates, firmly establishing the basic principle of minimization of molecular free volume and consequently the novel concept of molecular chain mail via threading of chains. The adventure continues with recent work using functionalized MWCNTs to reinforce epoxy adhesives with S. Sydlik.

Tuesday, April 9, 2013 01:20 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:15 PM - 05:30 PM)
Location: Hilton Riverside
Room: HEC C

237 - Polymeric microspheres as a platform for sensing and detection

David R Walt, *david.walt@tufts.edu, Department of Chemistry, Tufts University, Medford, MA 02155, United States*

The ability to measure many chemical and biochemical components simultaneously has been facilitated by the advent of arrays using advances in micro and nanotechnology. Such arrays offer the potential to create nearly universal sensors that can measure thousands of species simultaneously. Our laboratory has developed functionalized optical imaging fibers as a platform for creating microarrays. These arrays contain thousands of individual sensing polymeric microspheres on each fiber bundle. Many different types of arrays can be prepared using this approach including arrays for single molecule detection. Both the development and commercialization of these arrays will be discussed.

Tuesday, April 9, 2013 02:05 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:15 PM - 05:30 PM)
Location: Hilton Riverside
Room: HEC C

238 - ROMP with stable initiators

robert howard grubbs, *rhg@caltech.edu, Chemistry, California Institute of Technology, Pasadena, CA 91125, United States*

Tim Swager introduced the name ROMP for ring opening metathesis polymerization when he was a a graduate student. Since that time, many new initiators for the ROMP of strained olefins have been developed. Recent advances now allow polymers with precise chain length and composition to be prepared. The synthesis of brush polymers demonstrates the control of polymeric structures that are now possible with modern initiators.

Tuesday, April 9, 2013 02:50 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:15 PM - 05:30 PM)
Location: Hilton Riverside
Room: HEC C

239 - Conjugated polymer-based, broadband explosives trace detection

Aimee Rose[1], *arose@mit.edu, Robert Deansa*[1], *Kristen Mulherin*[1], *William McDaniel*[1], *Timothy M Swager*[2], *Trisha L Andrew*[2], *Jason Cox*[2], *John Ho*[3], *Vladimir Bulovic*[3]. *(1) FLIR Systems, North Billerica, MA 01862, United States, (2) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (3) Department of Computer Science and Electrical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Pioneered in the Swager group, the ability of conjugated polymers to self-amplify sensory signals has led to the development of detection materials that are state-of-the-art in sensitivity. Fluorescence-based detection methods employing these materials are a field and theater proven approach to trace detection of explosives in harsh, demanding environments. However, timely address of emerging threats requires rapid chemical tailoring of detection polymers for new explosives analytes.

In mitigating these threats, we have developed general approaches to developing fluorescence-based detection materials. These materials follow the general paradigm of polymer-based signal amplification coupled with molecular-level specificity to allow detection and identification of explosives. In addition, we are creating new device platforms that enable multichannel explosives detection and classification. These platforms can serve to further miniaturize and portablize this technology, providing a path toward widely distributed, microfabricated trace explosives detectors.

Tuesday, April 9, 2013 03:50 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:15 PM - 05:30 PM)
Location: Hilton Riverside
Room: HEC C

240 - Award Address (ACS Award for Creative Invention sponsored by ACS Corporation Associates). Organic electronics for chemical sensing

Timothy M. Swager, *tswager@mit.edu, Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02129, United States*

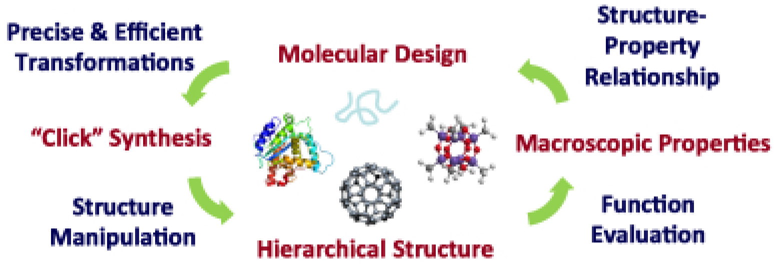
This lecture will detail the creation of ultrasensitive sensors based on electronically active conjugated polymers (CPs) and carbon nanotubes (CNTs). A central concept that a single nano- or molecular-wire spanning between two electrodes would create an exceptional sensor if binding of a molecule of interest to it would block all electronic transport. The use of molecular electronic circuits to give signal gain is not limited to electrical transport and CP-based fluorescent sensors can provide untratrace detection of chemical vapors via amplification resulting from exciton migration. Nanowire networks of CNTs provide for a practical approximation to the single nanowire scheme. New methods for fabrication using solventless deposition methods will be described that allow for economical flexible sensor fabrication. These methods include abrasion deposition and selectivity is generated by covalent and/or non-covalent binding selectors/receptors to the carbon nanotubes. Sensors for a variety of materials and cross-reactive sensor arrays will be described. The use of carbon nanotube based gas sensors for the detection of ethylene and other gases relevant to agricultural and food production/storage/transportation are being specifically targeted and can be used to create systems that increase production, manage inventories, and minimize losses.

Tuesday, April 9, 2013 04:35 PM
ACS Award for Creative Invention: Symposium in Honor of Timothy M. Swager (01:15 PM - 05:30 PM)
Location: Hilton Riverside
Room: HEC C

241 - Self-assembly of giant molecular shape amphiphiles as a new platform for engineering structure

Stephen Z. D. Cheng, *scheng@uakron.edu, Department of Polymer Science, The University of Akron, Akron, OHIO 44325, United States*

The assembly of shape amphiphiles is strongly driven by their interactions and the constraints imposed by the rigid shape fixed fixed volume of the molecular building blocks. To create new functional materials for advanced technologies, control over their hierarchical structure and order is vital for obtaining the desired properties. Our research focuses on this structure-property relationship from design and synthesis of specific shape amphiphiles based on fullerene (C_{60}) and polyhedral oligomeric silsesquioxane (POSS). By diverse periphery functionalization, they serve as versatile building blocks for the construction of giant shape amphiphiles with controlled hierarchical structures in multi-dimensions across different length scales. For example, 1D helical line structure was obtained in a porphyrin-C_{60} dyad with a 129_{44} helix where the C_{60} forms three continuous channels around the column of porphyrin. This is a typical supramolecular “double cable” structure desired in organic photovoltaics. Owing to symmetry breaking both in geometry and chemistry, 2D sheet structure was obtained in two distinct types of nano-Janus particles. The 3D structure with 5~20 nm feature size was generated by a new class of materials called giant surfactants and lipids. It resembles small molecular surfactants in that it possesses a polar, compact head and a flexible hydrophobic tail, yet also resembles block copolymers due to its size and dimension at the nanometer scale. As a result, these materials have surfactant-block copolymer duality.



Tuesday, April 9, 2013 01:30 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

242 - Synthesis of polycyclic aromatics: High performance electronic materials

Timothy MA Swager, *tswager@mit.edu, Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

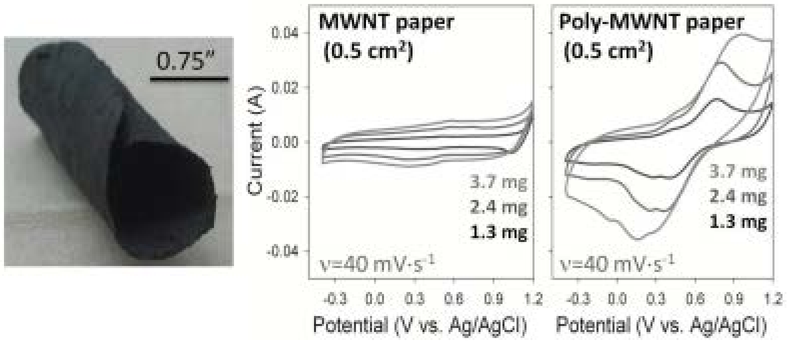
Aromatic rings are fundamental building blocks of most organic electronic materials, including electronic polymers, graphenes, and carbon nanotubes. The rigidity, stability, and delocalization provided by these structures are indispensible elements of any organic electronic material design. This lecture will focus on a number of synthetic methods that can be used to synthesize low molar mass materials and be applied to larger entities, including polymers and nanomaterials. Approaches will include oxidative cyclizations that produce new C-C and C-O linkages. Alkynes will be highlighted as useful elements of unsaturation and methods to convert these into fused aromatic systems will be presented. Electrocyclic reactions are also of interest and both traditional (Diels-Alder) and organometallic processes will be demonstrated in the synthesis of extended polycyclic aromatic structures.

Tuesday, April 9, 2013 02:00 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

243 - Redox electrodes comprised of polymer-modified carbon nanomaterials

Mark E Roberts[1], *mrober9@clemson.edu, Robert K Emmett*[1], *Ramakrishna Podilla*[2], *Apparao M. Rao*[2]. *(1) Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29631, United States, (2) Department of Physics and Astronomy, Clemson University, Clemson, SC 29631, United States*

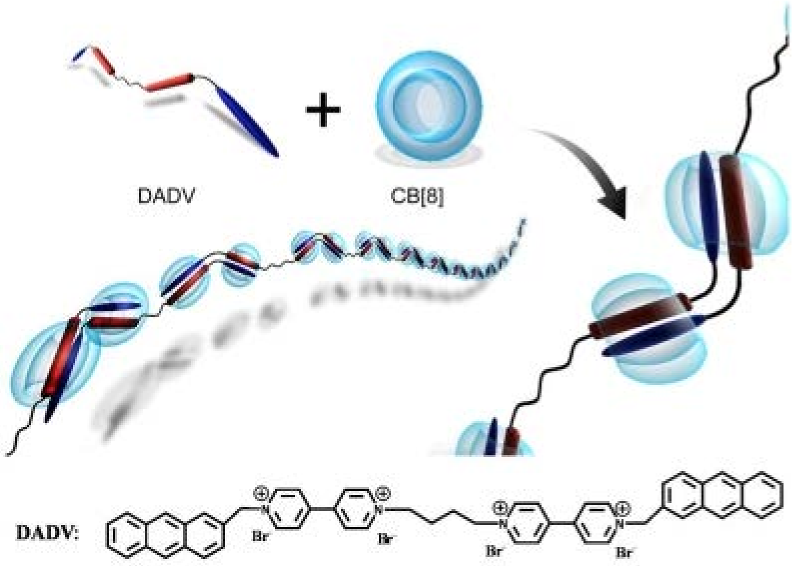
A shift in how we generate and use electricity requires new energy storage materials and systems compatible with hybrid electric transportation and integration of renewable energy sources. Supercapacitors provide a solution to these needs by combining the high power, rapid switching, and exceptional cycle life of a capacitor with the high energy density of a battery. Our research brings together nanotechnology and materials chemistry to address the limitations of electrode materials. Paper electrodes fabricated with various forms of carbon nanomaterials, such as nanotubes, are modified with redox-polymers to increase the electrode's energy density while maintaining rapid discharge rates. In these systems, the carbon nanomaterials provide the high surface area, electrical conductivity, nanoscale and porosity, while the redox polymers provide a mechanism for charge storage through Faradaic charge transfer. The design of redox polymers and their incorporation into nanomaterial electrodes will be discussed with a focus on enabling high power and high energy density electrodes.



Tuesday, April 9, 2013 02:30 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

244 - Supramolecular polymerization driven by host-enhanced noncovalent interactions

***Xi Zhang**, xi@mail.tsinghua.edu.cn, Department of Chemistry, Tsinghua University, Beijing, China 100084, China*



Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions. Although multiple hydrogen bonding has been widely used to drive supramolecular polymerization, we have demonstrated that host-enhanced charge transfer interactions can be used to construct supramolecular polymers as well. For this purpose, we have designed and synthesized a multifunctional monomer, containing anthracene-viologen-viologen-anthracene, which is able to form multiple host-enhanced charge transfer interactions. This kind of molecular design can avoid the formation of cyclic species and dimerization effectively. As a result, supramolecular polymers are formed simultaneously by mixing the multifunctional monomer with cucurbit[8]uril in water. In addition, we have also shown that the similar concept can be extended to enhance pi-pi interaction and developed a method for supramolecular polymerization on the basis of host-enhanced pi-pi interactions. It is anticipated that these new methods of supramolecular polymerization can be used for fabricating functional supramolecular materials.

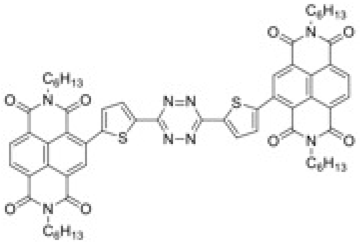
Tuesday, April 9, 2013 03:20 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

245 - Organic semiconductor chemistry

Seth R. Marder, *seth.marder@chemistry.gatech.edu, Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States*

Organic semiconductors have attracted interest for electronic applications due to their potential for use in low-cost, large-area, flexible electronic devices. While many examples of organic semiconductors for p-channel and n-channel organic field-effect transistors (OFETs) have been reported in the recent literature,there is a paucity of high-performance, solution-processable, small-molecule materials for n-channel OFETs. In order to take advantage of the technological potential of organic semiconducting materials, solution-processable, ideally air-stable, electron-transport (ET) materials with low barriers for charge injection, high charge-carrier mobility values (> 1 $cm^2V^{-1}s^{-1}$), large current on/off ratios ($I_{on}/I_{off} > 10^6$), and low threshold voltage (< ±2.5 V) are still desirable.

Here, we report that bis(NDI) derivatives with conjugated bridging groups based on fused heterocycle ring systems (such as that shown below) can be used to create solution-processed films that exhibit OFET electron mobility values of up to 1.5 $cm^2V^{-1}s^{-1}$, which is among the highest yet reported for an n-channel OFET based on a solution-processed small molecule. In addition we will discuss the development of metal complexes that can be used to both n-dope or p-dope organic semiconductors.



Tuesday, April 9, 2013 03:50 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

246 - Integrated polymer design for flexible electronics

Zhenan Bao, *zbao@stanford.edu, Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States*

Polymer semiconductor materials are interesting alternatives to inorganic semiconductors in applications where low cost, flexible or transparent substrates, and large area format is required. Currently they have been incorporated into organic thin-film transistors, integrated display driver circuits, photovoltaics artificial electronic skin, and radio frequency identification tags. One of our fundamental interests is to understand how we can ultimately perform rational design of organic semiconductors. In this talk, I will present our efforts on understanding of molecular design rules for achieving efficient charge carrier transport and controlled growth of organic semiconductors. I will also present applications of these materials and devices for flexible and stretchable electronics applications.

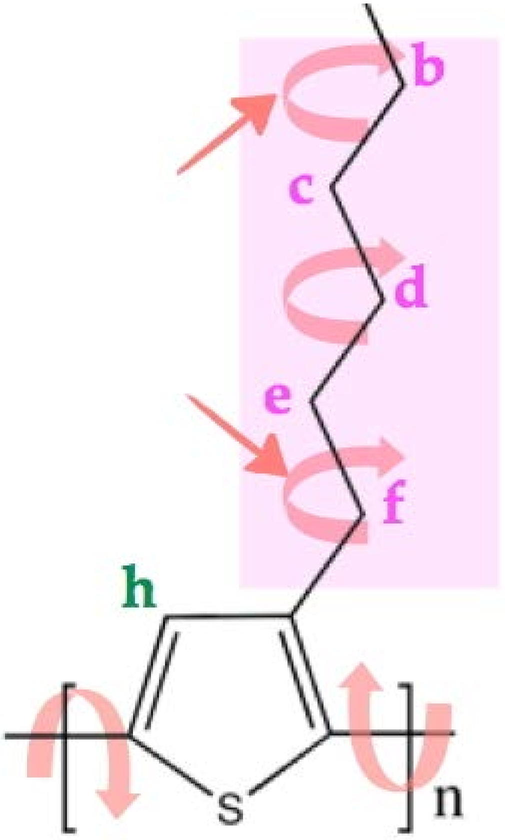
Tuesday, April 9, 2013 04:25 PM
Carl S. Marvel Creative Polymer Chemistry Award (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 12

247 - Dynamics of macromolecules by solid-state NMR: Three different approaches for different systems

Marco Geppi[1,2]*, mg@dcci.unipi.it, Silvia Borsacchi*[1,2]*, Francesca Martini*[1,2]*, Giulia Mollica*[1]*, Silvia Spera*[3]*, Umayal P Sudhakaran*[1]*. (1) Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, PI 56126, Italy, (2) Unità di Pisa, INSTM, Italy, (3) Istituto Donegani, ENI, Novara, Italy*

Deeply understanding the dynamic behavior of a macromolecular system at a molecular level may be very important not only to increase its basic knowledge, but also to find meaningful relationships with its macroscopic properties. Solid-state Nuclear Magnetic Resonance Spectroscopy offers many tools, most of which based on nuclear relaxation times, that can be exploited to derive detailed dynamic information.

Here, three different cases will be shown, where dynamic information has been derived for different macromolecular systems: biomacromolecules, synthetic polymers and organic-inorganic nanocomposites. Based on the different chemical nature, phase properties, and degree of complexity of the systems, these studies were conducted using quite different experimental and theoretical approaches. It will be shown how, even for complex macromolecular sytems, the availability of large and variegated sets of experimental data allows very detailed information on specific molecular motions to be obtained and to be related to morphological properties (interfaces, phase separation, etc.).

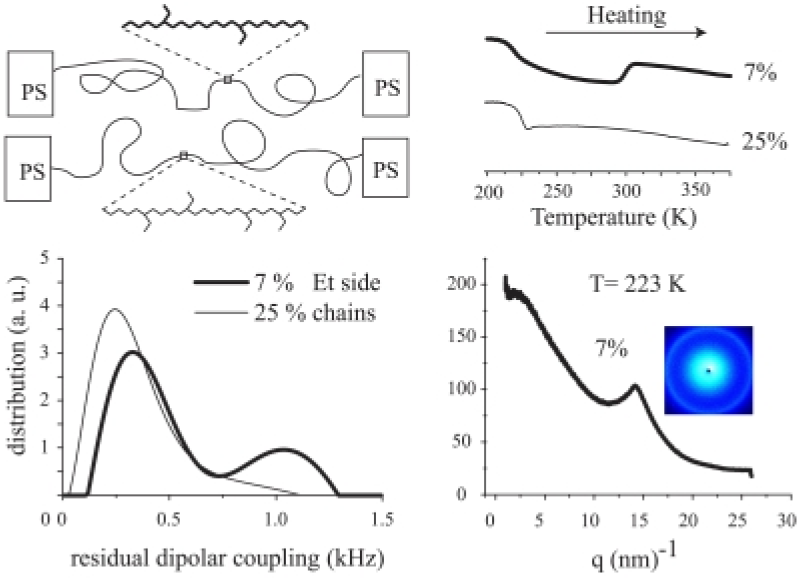


Tuesday, April 9, 2013 01:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

248 - Dynamics and crystallization of poly(ethylene butene) nanoconfined in SEBS

Michele Mauri[1], *michele.mauri@yahoo.it*, *Lucio Mauri*[1], *George Floudas*[2,3], *Roberto Simonutti*[1]. *(1) Department of Materials Science, Università di Milano-Bicocca, Milano, MI 20125, Italy, (2) Department of Physics, University of Ioannina, Ioannina, Greece, (3) Max Planck Institute for Polymer Research, Mainz, Germany*

In poly(styrene-b-ethylene butene) copolymers, the EB phase is nanoconfined by glassy PS regions. WAXS and DSC on samples with 7% ethyl side chains indicate crystallization, not detected in similar EB polymers. Multiple Quantum TD-NMR indicates dynamic inhomogeneity with highly dipolar coupled regions over the EB melting temperature, suggesting a rotator phase. MAS NMR detects extended PE stems at low temperature. Instead, SEBS with 25% side chains exhibit a homogeneous EB phase with isotropic chain dynamics and absence of any crystallization.



Tuesday, April 9, 2013 01:55 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)

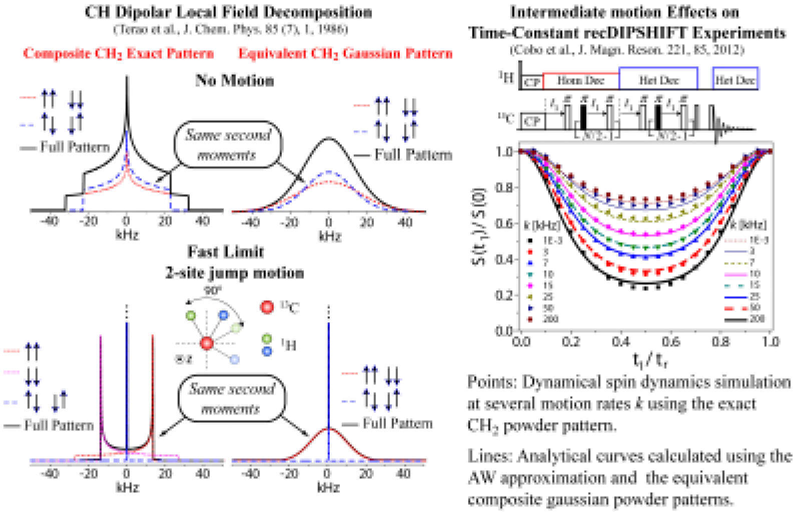
Location: Hilton Riverside

Room: Ste. C, Sec 15

249 - Separated-local field NMR methods as tools for characterizing intermediate-regime motions in polymers

*Marcio F Cobo[1], Anja Achilles[2], Gregório C Faria[1], Detlef Reichert[2], Kay Saalwächter[2], **Eduardo R deAzevedo**[1], azevedo@ifsc.usp.br. (1) Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, São Paulo 13560970, Brazil, (2) Institut fur Physik, Martin-Luther-Universitat Halle-Wittenberg, Halle, Germany*

Developments on ^{1}H-^{13}C DIPSHIFT recoupled variants are discussed as tools for characterizing intermediate-regime motions. Experimental results, spin dynamics simulations and Anderson-Weiss (AW) analytical treatments show the possibility of extracting motional rates (*k*) in an almost model free fashion. Based on the CH_n dipolar pattern decomposition, a multi-gaussian approach that improves the AW treatment to CH_2 and CH_3 groups is proposed, see figure. The techniques were applied to study molecular motions in semiconducting polymers and find correlations with their optoelectronic properties.



Points: Dynamical spin dynamics simulation at several motion rates *k* using the exact CH_2 powder pattern.

Lines: Analytical curves calculated using the AW approximation and the equivalent composite gaussian powder patterns.

Tuesday, April 9, 2013 02:20 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)

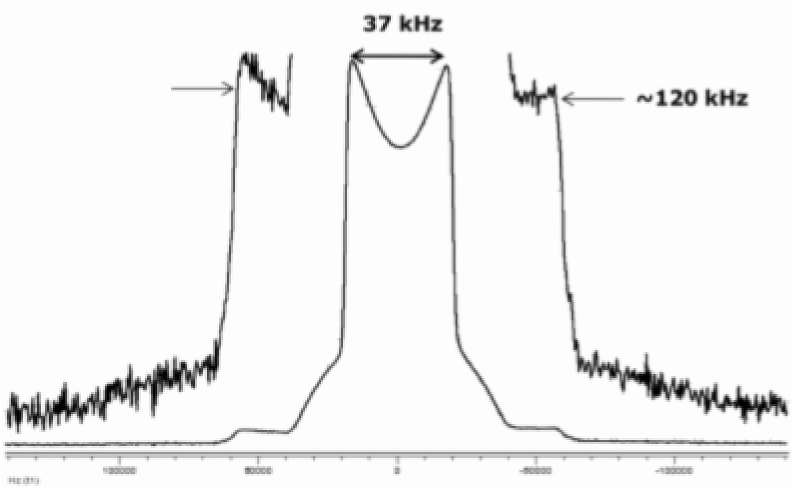
Location: Hilton Riverside

Room: Ste. C, Sec 15

250 - Dynamics of bulk and adsorbed poly(isopropyl acrylate-d₇)

Frank D. Blum[1], *fblum@okstate.edu, Piyawan Krisanangkura*[2]. *(1) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States, (2) Department of Chemistry, Missouri S&T, Rolla, MO 65409, United States*

The segmental dynamics of bulk and adsorbed poly(isopropyl acrylate)-d_7(PIPA-d_7) was studied as a function of temperature using quadrupole echo ^{2}H solid-state NMR. The spectra of both bulk and surface PIPA-d_7 showed superimposed powder patterns due to two methyl groups and a methine group on the polymer side chain. The experimental spectra were fitted using superimpositions of calculated spectra, which were simulated from the MXQET program, with different jump rates. In the ^{2}H NMR spectra for the adsorbed sample, the residual powder pattern at the higher temperatures indicated that some of the polymer segments were strongly bound to the silica surface, which was consistent with an increase in the glass transition temperature (T_g) of the PIPA-d_7-silica composite. The change in the thermal behavior of the adsorbed PIPA-d_7 was also probed with modulated differential scanning calorimetry (MDSC) experiments.



Tuesday, April 9, 2013 02:45 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)

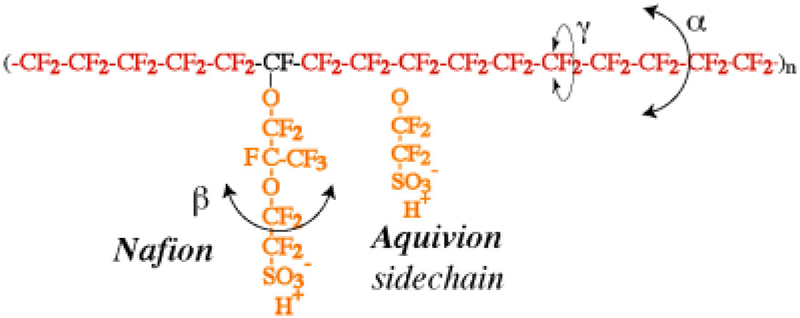
Location: Hilton Riverside

Room: Ste. C, Sec 15

251 - NMR-based assignment of a- and b-relaxations in Nafion to backbone and side-group motions

Klaus Schmidt-Rohr[1,2], *srohr@iastate.edu, Jean Cui*[1,2]. *(1) Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States, (2) Division of Materials Sciences & Engineering, Ames Laboratory US DOE, Ames, Iowa 50011, United States*

The molecular motions associated with the dynamic-mechanical relaxations in Nafion, a perfluorinated ionomer and benchmark proton exchange membrane material for H_2/O_2 fuel cells, have been investigated by ^{19}F and ^{19}F-^{13}C NMR. They are compared with those in Aquivion, which has shorter side groups and superior properties at elevated temperatures. Large-amplitude >100 kHz motions around the backbone axis can be related to the low-T g-relaxation. The b-relaxation is studied by MAS NMR, while the a-relaxation backbone dynamics are investigated by static $^{19}F(^{13}C)^{13}C$ exchange pseudo-2D NMR near 125°C; Nafion exchanged with Na^+, whose a-relaxation is 100°C higher, serves as a reference.



Tuesday, April 9, 2013 03:25 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)

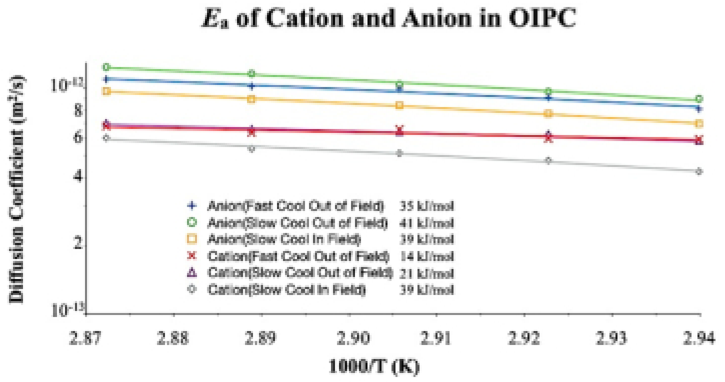
Location: Hilton Riverside

Room: Ste. C, Sec 15

252 - Transport dynamics in a bis-imidazolium-based organic ionic plastic crystal

Bryce E. Kidd[1], *bryce5@vt.edu, Mark D. Lingwood*[2], *Minjae Lee*[1], *Harry W. Gibson*[1], *Louis A. Madsen*[1]. *(1) Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Department of Chemistry, Saint Mary's College of California, Moraga, California 94556, United States*

A new contender in the race for highly conductive organic materials, organic ionic plastic crystals (OIPCs), display conductivity values up to s $=10^{-3}$ S cm^{-1}. OIPCs commonly show multiple solid-solid phase transitions, accompanied by a low DS_f value. Ion conduction of OIPCs, within some or all of the solid phases, is attributed to crystalline vacancies (Schottky defects) and/or nanometer to micron-scale defects (e.g., grain boundaries). We seek to answer two main questions: 1) What are the mechanisms of ion conduction for OIPC cations and anions? 2) Is it possible to induce alignment in the polycrystalline structure of OIPCs? We employ pulsed-field-gradient (PFG) NMR to quantify separate cation and anion diffusion and activation energy (E_a) in these materials. We are beginning OIPC studies with 1,2-bis[*N*-(*N'*-hexylimidazolium-d_2(4,5))]C_2H_4 $2PF_6^-$. We have measured the cation (^1H) and anion (^{19}F) diffusion in the second-to-lowest temperature solid phase, upon fast and slow cooling outside of the magnetic field (B_0 = 9.4 T) and upon slow cooling in B_0. Our studies suggest a change in transport mechanism (local molecular environment) for the cations upon varying thermal treatment (see figure), evidenced by a change in translational activation energy. Variable temperature ^2H solid-state NMR also provides further evidence of a change in microstructure of the material upon heating and cooling in B_0. These results are the first of their kind observed for OIPCs.



Diffusion Arrhenius plots with E_a values for cations and anions in phase S_3. Varying thermal treatment (e.g., fast and slow cooling out of B_0 and slow cooling in B_0) gives a drastically different E_a for the cation, signifying a change in ion transport mechanism.

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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
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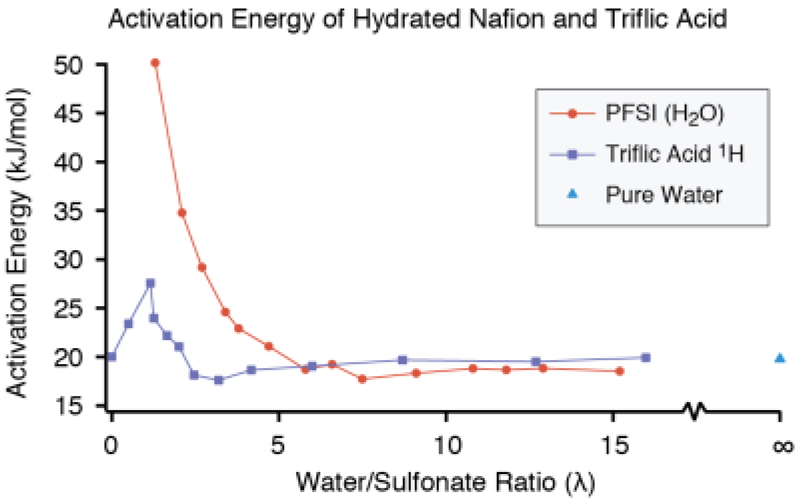
253 - Unraveling the local energetics of molecular transport in a polymeric ion conductor

Mark D Lingwood[1,2], *mdl4@stmarys-ca.edu, Zhiyang Zhang*[1], *Bryce E Kidd*[1], *Kacey B McCreary*[1], *Jianbo Hou*[1], *Louis A Madsen*[1]. *(1) Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061, United States, (2) Department of Chemistry, Saint Mary's College of California, Moraga, CA 94556, United States*

A hierarchy of material structures and molecular interactions influence bulk transport in ionomer membranes used in applications such as reverse-osmosis, fuel cells, mechanical actuators, and batteries. Mobile species within these membranes (e.g., ions, water, alcohols) move according to local chemical interactions as well as morphological features (e.g., ion channels). The fundamental processes of ion transport occur on the scale of several molecules (< 1 nm), which is a lengthscale that is experimentally difficult to access. Here, we show that the Arrhenius activation energy of diffusion (E_a) provides insight into the fundamental nature of ion transport on the < 1 nm scale. E_a is obtained through temperature-dependent pulsed-field-gradient (PFG) NMR, allowing for chemically specific measurements on intact, hydrated membranes. We have explored the activation energy of diffusion in the perfluorosulfonate ionomer (PFSI) Nafion® as a function of hydration level (see figure), allowing us to draw conclusions about the local interactions that govern ion transport. We also find quantitative parallels between experimental activation energies for the ionomer and hydrated triflic acid (CF_3SO_3H), thus emphasizing the importance of the polymer ion moiety on transport. We will further discuss the physical significance of E_a and the pre-exponential factor D_0 in liquid and soft solid systems.

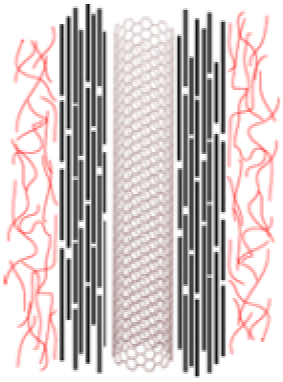


Tuesday, April 9, 2013 04:15 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

254 - Developments in PAN/CNT based carbon fibers

Satish Kumar, *satish.kumar@mse.gatech.edu, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0295, United States*

Carbon nanotubes (CNTs) act as a nucleating agent for polymer crystallization and as a template for polymer orientation. When well dispersed and exfoliated, a very small weight percentage (less than 1 wt%) of CNTs can affect the performance of relatively large amount of polymer. For example, highly ordered polyacrylonitrile (PAN) in the vicinity of CNTs can graphitize at a relatively low temperature of 1100 °C, while PAN normally is not known to graphitize until above 2000 °C. As a result, the presence of 1 wt% CNT in PAN can result in up to 50% increase in tensile strength and modulus of the resulting carbon fiber. Fiber tensile strength also increases with decreasing fiber diameter. Small diameter (about 1 micrometer or less) carbon fibers can be processed by electro-spinning or by islands-in-a-sea fiber spinning approach. The latter approach has been used in our work. Addition of CNTs also affects polymer rheology. Results of PAN/CNT solution preparation, precursor fiber spinning, carbon fiber processing, along with fiber structure and properties will be presented.



Tuesday, April 9, 2013 01:35 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

255 - Investigation into the relationships between the synthetic method, molecular weight distribution, and solution behavior of acrylonitrile/methylacrylate (AN/MA) copolymers

Sue J Mecham, *sjmecham@vt.edu, Priya Pisipati, Susan A. Beck, Ronald M. Joseph, James E. McGrath. Macromolecules and Interfaces Institute Department of Chemistry, Virgina Tech, Blacksburg, VA 24061, United States*

Polyacrylonitrile-co-methyl acrylate copolymers have been synthesized via both heterogenous and homogeneous methods. Evidence of aggregation of copolymer chains in NMP solution has been shown via SEC with static light scattering. This is of particular interest with respect to the production of precursor fibers for carbon fiber. It has been shown that the use of very high molecular weight polyacrylonitrile leads to higher strength carbon fiber, likely due to the extent of drawing available with the highly entangled chains. Copolymers have been synthesized via suspension, emulsion, and solution RAFT methods utilizing a variety of copolymer compositions, initiators, and temperatures to explore the reaction conditions related to molecular weight and structure control. This has produced a variety of materials with molecular weights ranging from 30,000 g/mole to 2,000,000 g/mole. Addition of LiBr to the NMP has been shown to break up the aggregation of most copolymers but some examples retain the presence of very high molecular weight chains even with the added salt. Aggregation has been identified in both emulsion copolymers and RAFT copolymers regardless of copolymer composition.

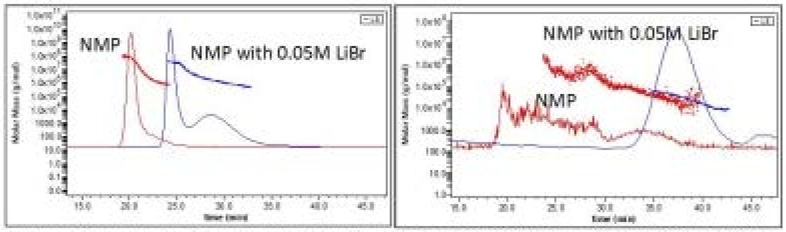


Figure 1. Polyacrylonitrile-co-methyl acrylate copolymer SEC in NMP and in NMP with 0.05M LiBr shows presence of aggregated fractions in the copolymers and the effect of adding salt to the mobile phase.

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Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)

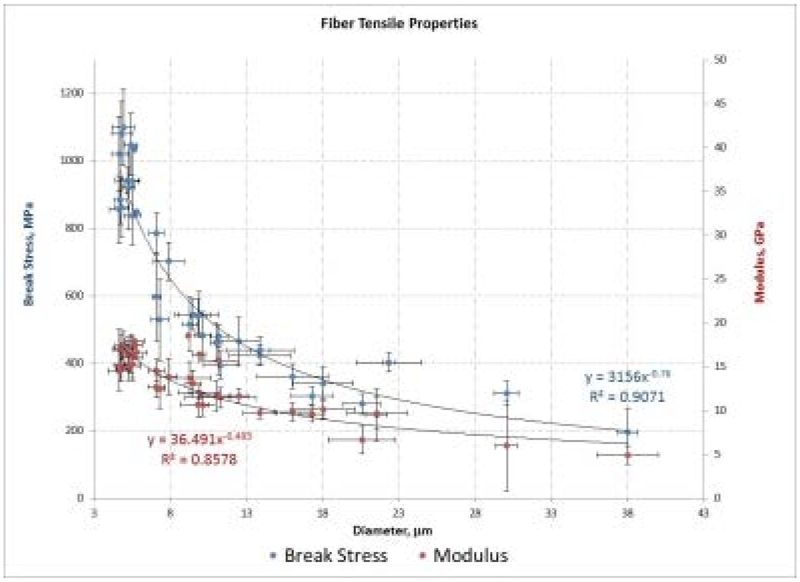
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

256 - Hybrid dry-jet gel spinning for production of high strength, small diameter polyacrylonitrile precursor fiber

Matthew Weisenberger[1], *matt.weisenberger@uky.edu, Ashley Morris*[1], *Terry Rantell*[1], *Stephanie Billiter*[1], *Mohamed Abdallah*[2]. *(1) Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, United States, (2) MGA – Advanced Composites & Engineering, Inc., Salt Lake City, UT 84108, United States*

The use of a hybrid method of dry-jet solution spinning and gel spinning led to the production of polyacrylonitrile-based precursor fiber with exceptional strengths, utilizing a high molecular weight (HMW) copolymer (weight average molecular weight equal to 1.5 million). HMW polymers allow for high drawability during spinning, and reduced solids content in the dope, both of which lead to smaller diameter fibers, and increased tensile strength and modulus properties. A strong relationship between filament diameter and tensile properties was observed.



Tuesday, April 9, 2013 02:25 PM

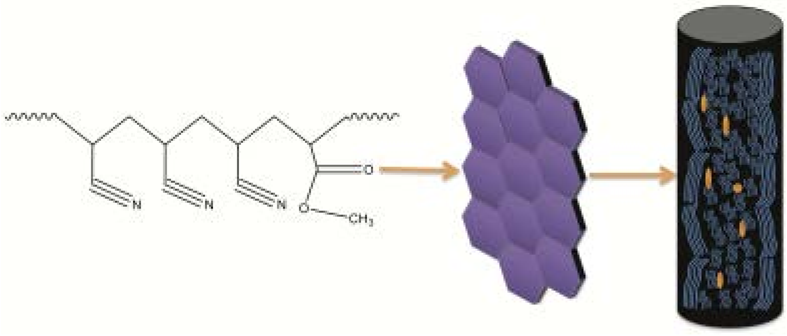
Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)

Location: Hilton Riverside

Room: Ste. B, Sec 7/10

257 - Structure and properties of carbon fibers

Soydan Ozcan, *ozcans@ornl.gov, Amit K Naskar. Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*



Although carbon fibers are produced using similar process steps, formation of thermoplastic fibers, stabilization, and carbonization, their final structures that govern the end properties may be significantly different. Process parameters have slight effect on microstructure; however, the final structure strongly depends on the starting polymer precursor. Polyacrylonitrile (PAN) and Pitch are the most predominant polymer precursors used in the production of carbon fibers. PAN-based carbon fibers consist of nanocrystalline graphitic domains typically 1.5 - 5 nm in size surrounded by amorphous carbon; instead pitch-based carbon fibers are 10 to 50 nm crystallites where the graphitic (002) planes (d = ~0.334 nm) are mostly aligned parallel to the fiber axis. These fibers typically show a difference in nanostructure between the skin and core of the fiber. It has been seen that the skin-core structure plays significant role on mechanical properties. Design of more homogenous carbon fiber microstructure by controlling the starting polymer and process parameters resulted in different set of tensile strength and elastic modulus properties which has not been observed in skin-core structure PAN carbon fibers. The microstructural defect distribution (0.1nm to 200nm) measured by small angle X-Ray scattering also showed direct relationships with tensile strength of carbon fibers. Therefore, research into understanding the formation of carbon structures from various polymer precursors offers opportunity for designing microstructures leading to improved properties and reduced cost carbon fiber.

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Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)
Location: Hilton Riverside
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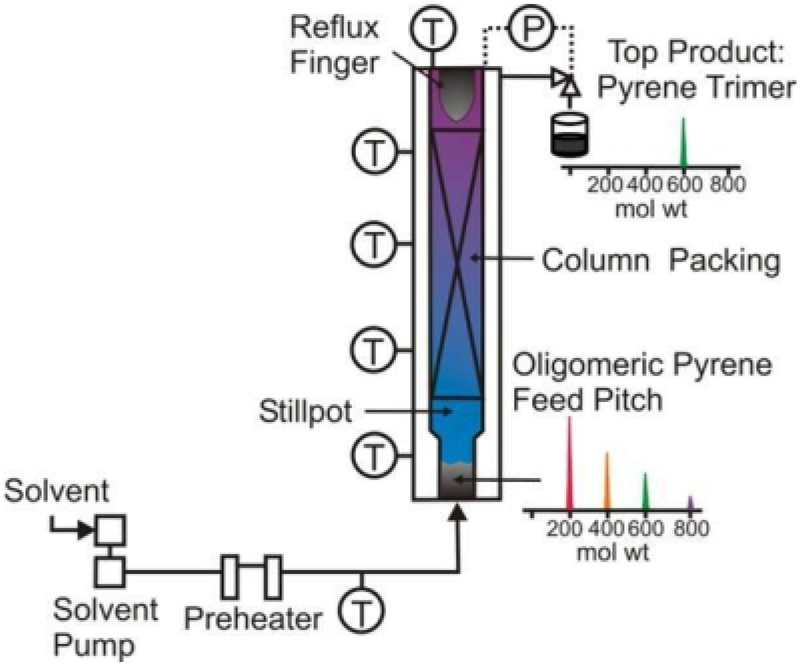
258 - Fractionation and characterization of oligomeric pyrene pitches via supercritical extraction

David F. Esguerra[1], Sourabh U. Kulkarni[1], ***Mark C. Thies[1]****, mcths@clemson.edu, Wesley P. Hoffman[2]. (1) Department of Chemical and Biomolecular Engineering, and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634-0909, United States, (2) AFRL-RZSM, Air Force Research Laboratory, Edwards, CA 93523, United States*

The key molecular species present in model pyrene pitches both thermally and catalytically polymerized from pyrene have been unambiguously identified. Packed-column, dense-gas extraction, using supercritical toluene as the solvent and NMP as the co-solvent, was used to fractionate the pitches into pure monomer, dimer, and trimer cuts. An unexpected benefit of the use of NMP is that it was found to suppress the condensation reaction between toluene and the pyrene oligomers - apparently by forming a Lewis acid-base complex with the AlCl3 catalyst - that can occur in the extraction column at temperatures above 350 °C. The resultant fractions were then analyzed for molecular-structure information via matrix-assisted, laser desorption/ionization (MALDI) mass spectrometry and by HPLC with UV-vis detection.

Results indicate that there are significant differences between the products of catalytic vs. thermal polymerization of pyrene. For example, catalytic polymerization is highly selective with respect to isomerization, with only one of the two possible isomers of pyrene dimer, that is, 1.14,7.8-dibenzoperopyrene, being present. In addition, alkylation of the pyrene monomer, dimers, trimers, and tetramers occur during the catalytica polymerization process. On the other hand, no such alkylation occurs during thermal polymerization, and oligomers are formed by connecting the monomer units by 5-membered rings (vs. 6-membered rings that dominate catalytically).



Tuesday, April 9, 2013 03:30 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

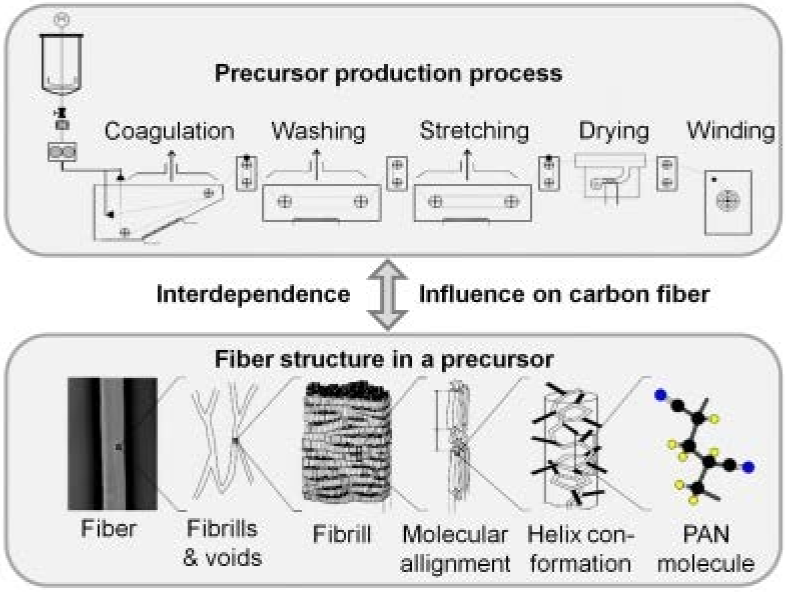
259 - Relationship between process technology, structure development, and fiber properties in modern carbon fiber production

***C Wilms**, christian.wilms@ita.rwth-aachen.de, G. Seide, T. Gries. Institut fuer Textiltechnik of RWTH Aachen University, Aachen, Germany*

The carbon fiber production based on polyacrylonitrile (PAN) is divided into two process steps: solution spinning of the precursor fiber and thermal conversion to the final carbon fiber. It is in the first step where most of the properties of the final carbon fiber are determined. A high quality precursor is the key and a prerequisite for a high performance carbon fiber.

The mechanical properties are mainly determined by the polymer that is used and by the structure of the fibers. As the polymer is taken here as fixed, the fiber formation process in solution spinning has to be evaluated. Different variables are important to understand what is happening in the nozzle and in the first centimeters behind the nozzle. The macromolecules have to be aligned, the solvent has to be removed from the forming fiber and the filament has to be stretched. The diffusion of solvent out of the fiber and coagulant into the fiber has to be carefully controlled in order to avoid a pronounced sheath/core structure. The stretching of the fiber determines the strength and stiffness of the precursor and final carbon fiber. The position in the process and the amount is here the key for a high performance fiber.

The evaluation of the structure formation process in precursor production is followed by an analysis, what different properties of the precursor mean for the final carbon fiber.



Tuesday, April 9, 2013 04:00 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

260 - Applications of carbon fiber composite materials

***Mohamed G Abdallah**, agm1144@yahoo.com, MGA-Advanced Composites & Engineering, Inc, Salt Lake City, Utah 84108-3243, United States*

An overview of the applications of carbon fiber composite materials in various industries is discussed. Various materials forms of carbon fiber products in the market chain supply depending on its precursor origin will be shared followed by the structural applications of carbon fiber in the area of alternatives energies such as batteries, wind energy, automotive, and offshore oil production and exploration. Traditional uses of carbon fiber composites in aerospace, commercial aircraft, and military industries will also be presented. New application of carbon fiber in civil engineering such as infrastructure rehabilitation, seismic protection and transportation and composites in sport and medical products would be reviewed. The presentation would conclude by providing an overview of the technologies and methods of manufacturing carbon fiber composites structures.

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Polymer Precursor-Derived Carbon (01:30 PM - 04:45 PM)
Location: Hilton Riverside
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261 - Design of drug-loaded devices for the prevention of lung tumor recurrence: From hydrophobic films to superhydrophobic meshes

Mark W. Grinstaff, *mgrin@bu.edu, Departments of Biomedical Engineering and Chemistry, Boston University, Boston, MA 02215, United States*

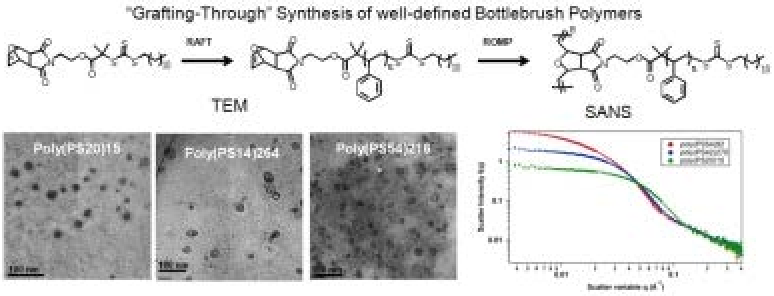
The most effective treatment for stage I patients with localized non-small cell lung cancer (NSCLC) is surgical resection. However, if disease recurs, the long-term survival is dismal with a 2-year survival of only ~20%. The risk of local recurrence in early stage lung cancer is greater in patients receiving smaller sublobar resection compared to larger lobectomy. At the surgical resection margin, residual microscopic tumor cells remain and are present in ~40% of patients following a “curative” wedge resection, demonstrating a need to treat those remaining cancer cells (*Journal of Controlled Release*, **2012** , *159*, 14-26). We have designed, synthesized, and evaluated two types of drug loaded polymeric materials, for the prevention of lung tumor recurrence, which can be implanted at the time of resection surgery. Specifically, I will discuss hydrophobic films (*Annals of Surgical Oncology*, **2010** , *17*, 1203-1213; *Biomacromolecules*, **2012** , *13*, 406-411) and superhydrophobic meshes (*Journal of the American Chemical Society*, **2012** , *134*, 2016-2019; *Journal of Controlled Release*, **2012** , *162*, 92-101) as low-dose drug delivery devices, and their performance in a series of *in vitro* and *ex vivo* experiments.

Tuesday, April 9, 2013 01:30 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

262 - Synthesis and conformational analysis of bottlebrush polymers by small angle neutron scattering

Stacy L Prukop[1], *slp4@rice.edu, Xianyu Li*[1], *Boualem Hammouda*[2], *Rafael Verduzco*[1]. *(1) Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77025, United States, (2) Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States*

Bottlebrush polymers are highly branched macromolecules with potential applications as anti-fouling coatings, rheological modifiers, and drug delivery systems. Polystyrene side-chains (DP_{sc} = 14-54) and polynorbornene backbones (DP_{BB} = 10-264) of bottlebrushes (M_w = 36-3140 kg mol^{-1}) were synthesized by “grafting-through”. We observed a conformational transition in solution from spherical to elongated polymers from small angle neutron scattering (SANS). Bottlebrush polymer radii and contour length increase with DP_{SC} and DP_{BB}, respectively. Transmission electron micrographs are in good agreement with SANS results.

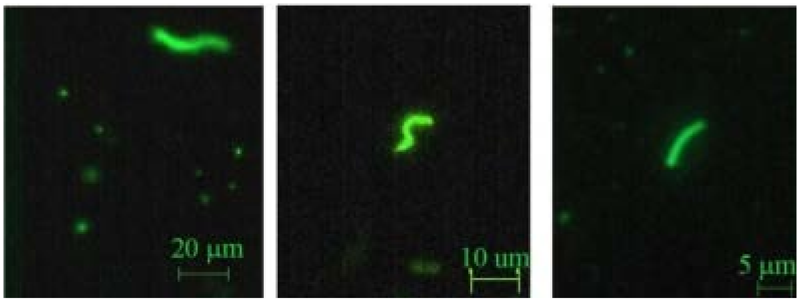


Tuesday, April 9, 2013 02:00 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

263 - Preparation of stable worm-like aggregates using amphiphilic biodegradable graft copolymers

Toufik Naolou, ***Joerg Kressler***, *joerg.kressler@chemie.uni-halle.de, Regina Schöps. Department of Chemistry, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany*

Solution properties of poly(glycerol adipate)-*g*-poly(e-caprolactone-*b*-ethylene oxide) are investigated. The polymers form spherical micelles of 20 nm diameter when micelles are prepared by dialysis. Stable worm-like aggregates are obtained instead when using a cosolvent/evaporation method. Fluorescence images evidence that the worms are rigid with a contour length between 3 and 20 µm.



TEM images of negative stained samples reveal that the worms are composed of vesicle aggregates. Vigorous stirring during preparation is responsible for the formation of worm-like aggregates.

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Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
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264 - Morphological influence on the bactericidal efficacy of polyurethanes with tethered quaternary ammonium salts: The consequence of electrospinning

Peter N Coneski, *peter.coneski.ctr@nrl.navy.mil*, *Preston A Fulmer*, *James H Wynne. Department of Chemistry, United States Naval Research Laboratory, Washington, DC 20375, United States*

Electrospinning is a versatile technique utilized to fabricate nanometer to micrometer-sized fibers from synthetic and natural polymers, composites, ceramics, and metals. The high surface area to volume ratios of resulting fibers have made electrospun materials ideal for applications which benefit from enhanced surface activity such as filtration, catalysis, and medicine. Herein, we report on the synthesis of a family of surface active biocidal polyurethanes containing tethered quaternary ammonium salt (QAS) moieties and the resulting fabrication of electrospun nanofiber mats. The influence of electrospinning on the biocidal activity of these polymers is examined and compared to solvent-cast films and correlations between surface area to volume ratio and antibacterial efficacy are investigated. Furthermore, nano- and microscale morphological differences are investigated as a means to improve the antimicrobial effectiveness of the synthesized polymers.

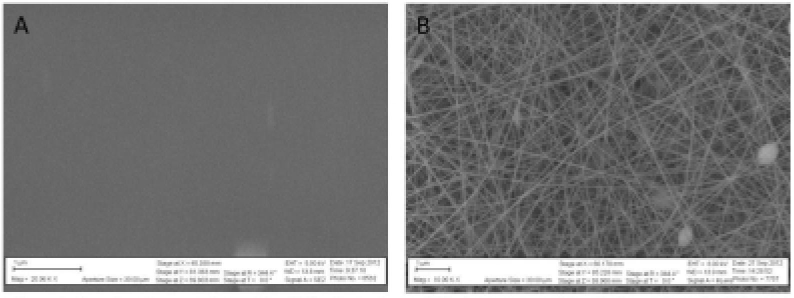

Figure 1. Scanning electron micrographs of (A) solvent-cast and (B) electrospun surfaces fabricated from biocidal polyurethanes. Scale bars represent 1 μm.

Tuesday, April 9, 2013 02:40 PM

Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)

Location: Hilton Riverside

Room: Ste. C, Sec 13/16

265 - Poly(ester amide)s bearing pendant functional groups: Versatile materials for tissue engineering and drug delivery

*Darryl K. Knight[2], Gregory J. Zilinskas[3], Kibret Mequanint[2], **Elizabeth R Gillies**[1,2], egillie@uwo.ca. (1) Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada, (2) Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario N6A 5B9, Canada, (3) Graduate Program in Biomedical Engineering, The University of Western Ontario, London, Ontario N6A 5B9, Canada*

Poly(ester amide)s (PEAs) are promising backbones for the development of new biomaterials. They are composed of non-toxic components, are readily synthesized, and can be tuned through both the selection of monomers, as well as through post-polymerization functionalization to impart the desired properties and functions for a diverse range of applications. This presentation will describe our team's development of PEAs bearing pendant functional groups and their application in vascular tissue engineering and drug delivery.

Tuesday, April 9, 2013 03:15 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

266 - Densely functionalized polyesters and polyurethanes as novel biomaterials

Sachin Gokhale, Ying Xu, Ricky Kaiser, John Swanson, ***Abraham Joy****, abraham@uakron.edu. Department of Polymer Science, The University of Akron, Akron, OH 44325, United States*

Biological processes, for example angiogenesis and wound healing, require the concerted action of multiple growth factors to bring about the desired effect. This orchestrated action of several molecules is a common feature of biological processes. The current generation of biomaterials is ill equipped to provide such multifunctional signaling in a biological environment. The design of appropriately functionalized biomaterials is currently being actively addressed by several labs. Our laboratory has recently developed a library of polyesters and polyurethanes with multiple pendant groups. Each monomer is synthesized with a pendant group and polymerized at room temperature by carbodiimide mediated coupling. Although the polymers have the same type of backbone, their physical, mechanical and biological properties are influenced by the pendant backbone. During this presentation, we will discuss our results and demonstrate potential applications for these novel biomaterials.

[figure 1: Idealized synthetic polymer having the required components for angiogenesis]

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Location: Hilton Riverside
Room: Ste. C, Sec 13/16

267 - Terpene containing polyphosphazenes as potential tissue engineering scaffolds

***Jessica L. Nichol**, jln237@psu.edu, Nicole L. Morozowich, Thomas E. Decker, Harry R. Allcock. Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United States*

Increases in the number of ligament and tendon injuries, in combination with limited options for their repair and replacement, have created a demand for synthetic polymer based systems. Polyphosphazenes are a unique class of polymers with alternating nitrogen and phosphorus backbone atoms, with two organic groups attached to each phosphorus atom. Different side groups control the final polymer properties and allow for a high degree of optimization. Previously studied amino acid containing polyphosphazenes, developed for scaffolding applications, were shown to be biocompatible and biodegradable. However, few showed elastomeric characteristics. In this investigation polyphosphazenes bearing amino acids and terpenes were developed and studied. Terpenes have anti-inflammatory, antioxidant, and antibacterial properties that can enhance the biological activity of an artificial scaffold. They were also chosen as potential crosslinking agents to impart elastomeric behavior to the final material. The current goal is to generate bioactive, biodegradable, and elastomeric ligament and tendon tissue scaffolds.

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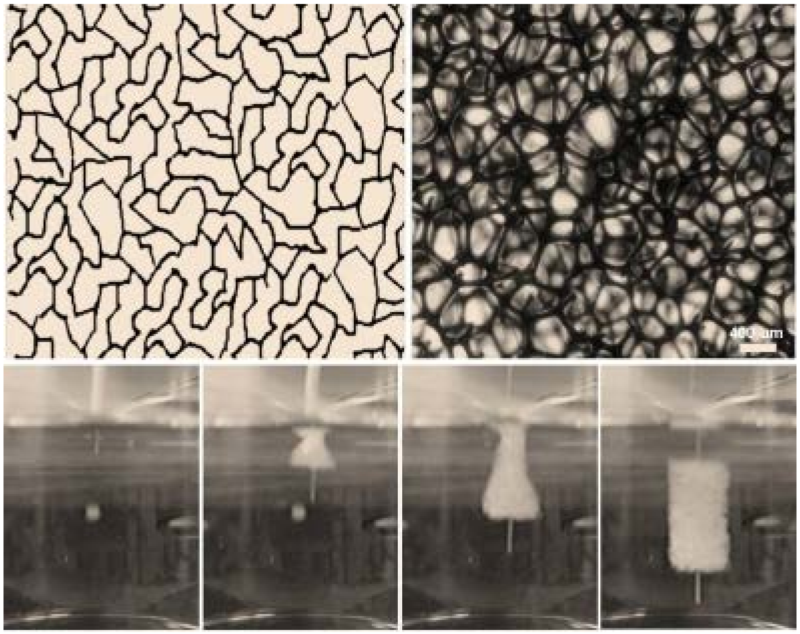
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

268 - Ultra low density amorphous shape memory polymer foams

__Pooja Singhal__[1,2], pooja52k2@tamu.edu, Ward Small[2], Jennifer N. Rodriguez[1], Steve Letts[2], Duncan J. Maitland[1], Thomas S. Wilson[2]. (1) Biomedical Engineering, Texas A&M University, Livermore, CA, College Station, TX, United States, (2) Chemical Sciences Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550, United States

Thermally actuated shape memory polymers (SMPs) are a class of smart materials that have gained significant interest in recent years. Multiple reviews and applications of these SMPs are available in the literature. In porous form, as SMP foams, these materials have additional biomedical applications, such as tissue regeneration scaffolds and embolic devices for treatment of aneurysms. According to one strategy, a smart SMP foam device in its secondary shape, can be delivered to a target location in the body, such as an aneurysm, via a minimally-invasive catheterization process. Once at the desired location, it can be actuated to its primary spherical shape, thus embolizing the aneursym. Here we report the synthesis of novel porous SMPs based on a highly chemically crosslinked network structure. Key physical properties of these materials such as high volume expansion on actuation, and simultaneous presence of ultra low density and a high modulus demonstrate strong potential of their utility in embolic biomedical applications.



Tuesday, April 9, 2013 04:25 PM
Bottom-Up Design of the Next Generation of Biomaterials (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

269 - "Patchy" nanoparticles via kinetically arrested co-assembly of block copolymers

Margarita Herrera-Alonso, *herrera@jhu.edu, Jose Luis Santos. Department of Materials Science and Engineering, The Johns Hopkins University, Baltimmore, MD 21218, United States*

Understanding biological processes governed by multivalent ligand-receptor interactions is relevant for modulating cellular behavior, but also for the rational design of materials used in drug delivery, such as block copolymer micelles. Current studies focus on elucidating the synergistic effect of ligand multivalency and clustering to enhance cell-specific targeting. Aside from the molecular characteristics of the building blocks, processing methods also influence the properties of self-assembled constructs. We will discuss our findings on the co-assembly of block copolymer amphiphiles with distinct macromolecular architecture to form “patchy” nanoparticles. Specifically, we have studied the co-assembly of linear and linear-dendritic polymer amphiphiles, the latter of which provides a pre-assembled “patch” with well-controlled chemical functionality and dimensions. These constructs were formed under kinetically arrested conditions through a large and rapid change in solvent quality. We discuss the use of these constructs to probe nanoparticle-cell interactions.

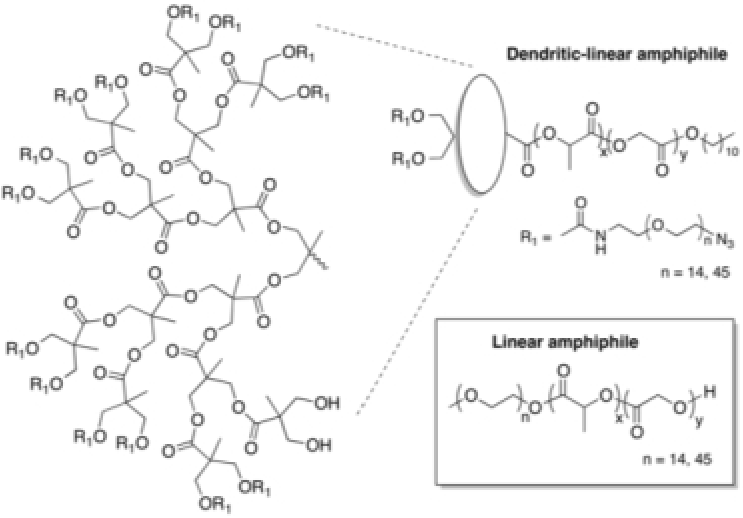


Figure 1. Structures of linear and linear-dendritic amphiphiles based on PEG and PLGA as hydrophilic and hydrophobic components, respectively. Shown is a G4 dendron. The azido end-groups of PEG will serve as reactive handles for labeling and/or targeting applications.

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270 - Protein-based synthesis of carbon nanotube-titana hybrid to enhance the efficiency of dye-sensitized solar cells

Ippei Inoue[1], *ippei_inoue@ajinomoto.com, Kiyoshi Watanabe*[2], *Hirofumi Yamauchi*[2], *Yasuaki Ishikawa*[2], *Hisashi Yasueda*[1], *Yukiharu Uraoka*[2,3], *Ichiro Yamashita*[2]. *(1) Institute for Innovation, Ajinomoto Co. Inc., Kawasaki, Kanagawa 210-8681, Japan, (2) Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan, (3) CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan*

The transport of photo-generated electrons across TiO_2 electrode is one of bottlenecks limiting energy conversion efficiency of dye-sensitized solar cells (DSSCs). Single-walled carbon nanotubes (SWNTs) have been attracted massive attention in improving photoelectron mobility in photoelectrode of DSSC, because of their high conductivity (1). To improve photoelectron transport efficiency, we synthesized a SWNT-TiO_2 nanocomposite using genetically modified cage-shaped protein without functionalization of SWNTs (2). The protein supramolecule could selectively deposit titanium onto SWNT surface by their SWNT-binding and Ti-mineralization activities. After sintering the SWNT-titanium hybrid, we obtained TiO_2-coated SWNTs consisted of a central SWNT and surrounding mesoporous TiO_2 layer with nano-pores derived from the protein (Figure a). The DSSC with SWNT-TiO_2 nanocomposite showed a power conversion efficiency of 6.5% (Figure b). A small amount of the nanocomposite in photoelectrode increased for 180% *Jsc* and decreased for 30% a series resistance, respectively. Those results suggested that additional the SWNT-TiO_2 nanocomposite acted as a superior electron transfer path-way and improved electron mobility in the photoelectrode.

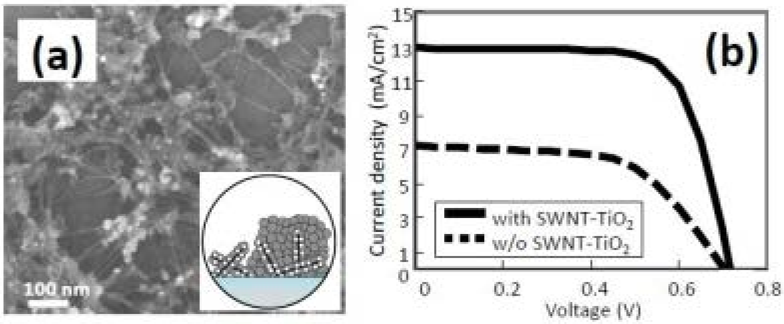


Figure. (a) SEM image of SWNT- TiO_2 nanocomposite. (b) *J-V* curve of DSSC with the nanocomposite.

(1) Dang, X.; Yi, H.; Ham, M.-H.; Qi, J.; Yun, D. S.; Ladewski, R.; Strano, M. S.; Hammond, P. T.; Belcher, A. M. *Nat. Nanotechnol*. **2011** , *6*, 377.

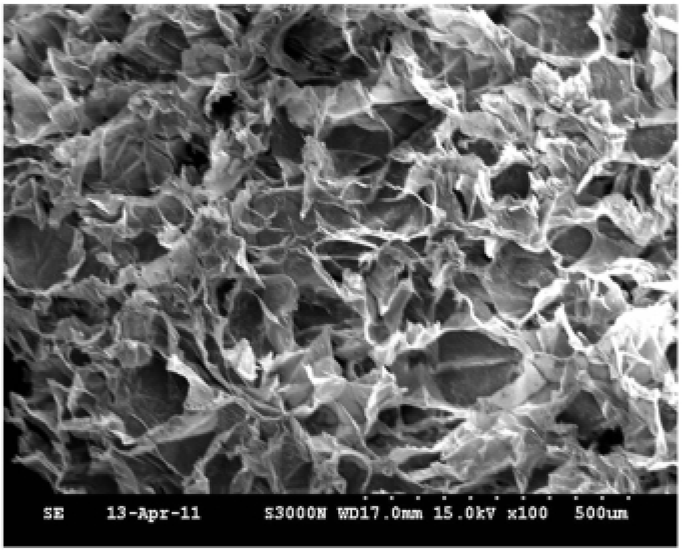
(2) Inoue, I.; Zheng, B.; Watanabe, K.; Ishikawa, Y.; Shiba, K.; Yasueda, H.; Uraoka Y.; Yamashita, I. *Chem. Commun.*, **2011** , *47*, 12649.

Tuesday, April 9, 2013 05:30 PM
Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

271 - Cryogels composed of gelatin/chitosan/hyaluronic acid, and platelet-rich plasma as skin wound repair biomaterial

*Wen-Chi Hsieh, **Jyh-Ping Chen**, jpchen@mail.cgu.edu.tw. Department of Chemcal and Materials Engineering, Chang Gung University, Kwei-San, Taoyuan 333, Taiwan Republic of China*

Cryogels are gel matrices synthesized at subzero temperatures using monomeric or polymeric precursors. These gels can be obtained through the formation of both physically and covalently crosslinked homogeneous or heterogeneous polymer networks. Cryogels have some important characteristics which include interconnected macroporous structure, mechanical stability and elasticity. Platelet rich plasma (PRP) is considered to be advanced wound therapy for chronic and acute wounds. The effects of PRP have been demonstrated in several studies in both nonhealing and healing wounds. The fact that platelets secrete growth factors and active metabolites means that their applied use can have a positive influence in clinical situations requiring rapid healing and tissue regeneration. In this study, gelatin, chitosan, hyaluronic acid, and platelet-rich plasma were crosslnked at -20 degree C to prepare macroporous cryogel. The cryogel was characterized for its physico-chemical properties and was found to be a suitable three-dimensional scaffold for proliferation and differentiation of porcine adipose-derived stem cells (ADSCs). In vivo experiments using nude mice full-thickness wound model confirm the usefulness of PRP and ADSCs in promoting wound healing.



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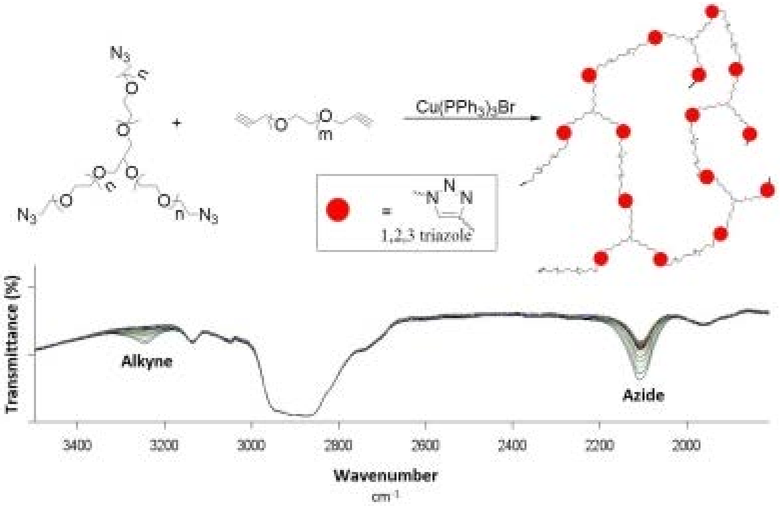
272 - Formation of poly(ethylene glycol) model networks using “click” chemistry

Muhammad Haris Samiullah[1], Ruda Powel[2], ***Jörg Kressler[1]****, joerg.kressler@chemie.uni-halle.de. (1) Department of Chemistry, Martin Luther University Halle-Wittenberg,, Halle (Saale), Germany, (2) Department of Chemistry, Wrocław University of Technology, Poland*

In order to investigate the bulk reaction and gelation kinetics of polymer networks, well-defined Poly(ethylene glycol) networks were synthesized by joining three-arm and linear PEG chains using Cu-Catalyzed Azide Alkyne Huisgen Cycloaddition (click) reaction. Bromotris(triphenylphosphine)copper(I) was used as catalyst for the “Click” reaction.



Real-Time FTIR spectroscopic measurements, at different temperatures, were performed in order to follow the reaction kinetics while in-situ rheology experiments were conducted to determine the gel point of the PEG networks.

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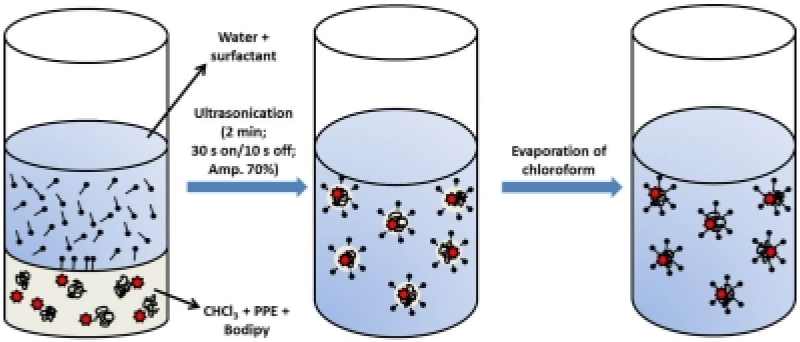
273 - Poly(phosphate) nanoparticles for drug delivery systems

Evandro M. Alexandrino, *alexandrino@mpip-mainz.mpg.de, Filippo Marsico, Sandra Ritz, Volker Mailänder, Katharina Landfester, Frederik Wurm. Max Planck Institute for Polymer Research, Mainz, Rheinland-Pfalz 55128, Germany*

The overlapping between polymer science and medicine is an emergent topic. Particles loaded with Bodipy or with an anti-cancer drug (Paclitaxel) were obtained with diameters around 80 - 300nm and low polydispersity, using SDS and Vitamin E-TPGS mixtures. Adhesion of particles to calcium phosphate showed dependence on polymer structure. Cell uptake studies revealed better uptake of particles with just SDS. Cytotoxicity to HeLa cells increased with the content of Vitamin E-TPGS and no cytotoxicity was evidenced with just SDS after 48h.



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Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
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274 - Tobacco mosaic virus as a template for smart polymer nanoparticles

Jaqueline D Wallat[1], *jdw114@case.edu*, *Amy M Wen*[2], *Nicole F Steinmetz*[2,3,4], *Jonathan K Pokorski*[1]. *(1) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States, (2) Department of Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States, (3) Department of Material Science, Case Western Reserve University, Cleveland, Ohio 44106, United States, (4) Department of Radiology, Case Western Reserve University, Cleveland, Ohio 44106, United States*

Viruses are an emerging class of biological nanomaterial scaffolds, which assemble into homogeneous particles with structures known to atomic resolution. Tobacco mosaic virus (TMV), a rod shaped virus particle (300nm x 18nm) is amenable to both interior and exterior surface modifications, imparting novel functions into the particle. We report the TMV-templated synthesis of polymer composite nanoparticles. Both surfaces of the virus have been modified to incorporate tertiary bromides, followed by polymerization via atom transfer radical polymerization (ATRP). We demonstrate the utility of these nanoparticles as fluorine MRI agents, an imaging technique which provides non-radioactive “hot-spot" imaging of particles. An 8-PEG methyl methacrylate monomer with a trifluoromethyloxy-end group, was synthesized by trifluoromethylation of the alcohol terminated PEG monomer and was incorporated into protein:polymer hybrid materials via ATRP. The resulting particles showed a strong single resonance peak in ^{19}F NMR, which should correspond to excellent contrast in ^{19}F MRI.

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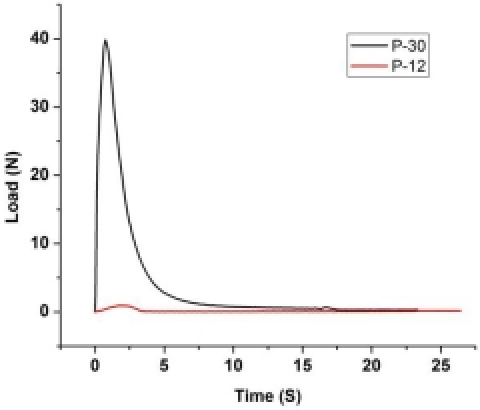
275 - Pendant functionalized biodegradable polymers bearing multiple catechol units

Ying Xu[1], *yx19@zips.uakron.edu, Dharamdeep Jain*[2]*, Ila Badge*[2]*, Ali Dhinojwala*[2]*, Abraham Joy*[1]*. (1) Department of Polymer Science, The University of Akron, Akron, OH 44325, United States, (2) Department of Polymer Science, The University of Akron, Akron, OH 44325, United States*

Marine organisms such as mussels demonstrate high adhesivity in aqueous conditions under high shear and salt conditions. 3,4-dihydroxy-L-phenylalanine (DOPA), has been shown to play a critical role in the adhesive property of mussels. Currently there is extensive interest in synthesizing DOPA containing polymers due to their potential applications such as wet tissue sealants. Our lab has designed biodegradable polymers having multiple catechol units functionalized onto the polymer backbone. These polymers demonstrate substantial increase in adhesive strength upon functionalization. The synthesis, characterization and properties of these polymers will be presented



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Location: Morial Convention Center
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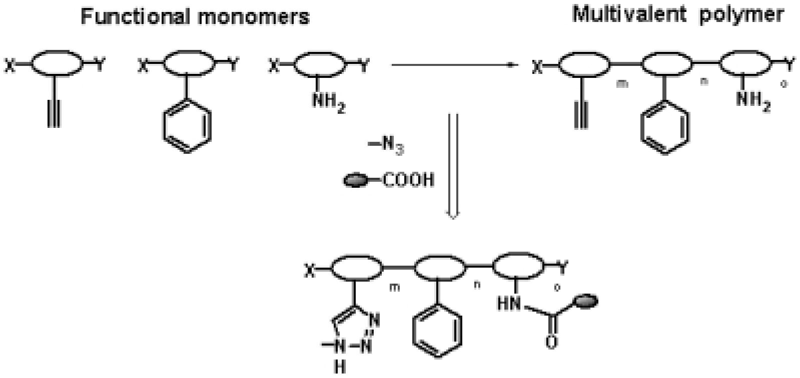
276 - Design and synthesis of multivalent "peptide-like" polyesters

__Sachin S Gokhale__, gokhale@uakron.edu, Ying Xu, Abraham Joy. Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States

Current class of biomaterials including polylactic acid have good mechanical and biodegradable properties. But they are devoid of capabilities when it comes to signaling cues for integration with the cellular environment. On the other hand natural materials like proteins provide both structural and functional roles due to their multivalent and self-organizing character. One of the main interests of our group is to develop novel synthetic materials having the ability to present functional cues in a biological environment like proteins. Here we present our current work in the synthesis of functionalized monomers and their polymers. The method of use is carbodiimide coupled room temperature polymerization. We have used this method to prepare a library of polyesters whose properties are dictated by pendant groups. We believe that these materials have a great potential in the fields of wound healing, angiogenesis and stem cell differentiation, which will be illustrated in the presentation



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277 - Protein:Polymer conjugates for programmed delivery of epidermal growth factor

Si-Eun Kim, *sxk782@case.edu, Jack Edelbrock, Kerry Martenis, Jonathan K Pokorski. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States*

Recently protein-polymer conjugates have seen rapid growth in the pharmaceutical industry due to their improved biological properties. An emerging method for preparing these materials is the use of “graft from” approaches where proteins serve as macro-initiators for controlled radical polymerizations, such as atom transfer radical polymerization(ATRP). These methods have proven effective in aqueous environments and have applications for diverse biomedical fields. In this study, sidechain functionalized biocompatible polymers were grown from the surface of the protein epidermal growth factor (EGF). From this hybrid material, hydrogels were formed using the copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) between an azide functionalized polymer and a trivalent alkyne cross-linker. EGF was also genetically engineered to include a matrix metalloproteinase(MMP) cleavage site to control the protein's release. The results indicated that the CuAAC reaction is an efficient method for hydrogel synthesis and that the release of fabricated protein could be programmed in vitro.

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278 - Stimulated release of a protein from a peptide hydrogel

Melanie A. Hutnick*, mah227@case.edu, Stacy M. Yeh, Jonathan K. Pokorski. Department of Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

Tissue engineering is concerned with the fabrication of materials that can act as substitutes for damaged biological tissues and promote their repair. One key aspect of this process is the presentation of growth factors to damaged tissues in a way that promotes cellular regeneration or differentiation of progenitor cells. We describe affinity-based methods for incorporating growth factors into peptide hydrogels to effect programmable release of proteins from material scaffolds. Using recombinant DNA technology, bone morphogenetic protein-2 (BMP-2) has been cloned and expressed with several different affinity tags for complexation with a synthetic peptide hydrogel, MAX8. The negative charge of the affinity tag electrostatically interacts with the lysine residues of the highly cationic hydrogel for slow and sustained protein release under physiological conditions. We describe the fabrication of MAX8 hydrogels, BMP-2 production, and release profiles from the newly fabricated materials.

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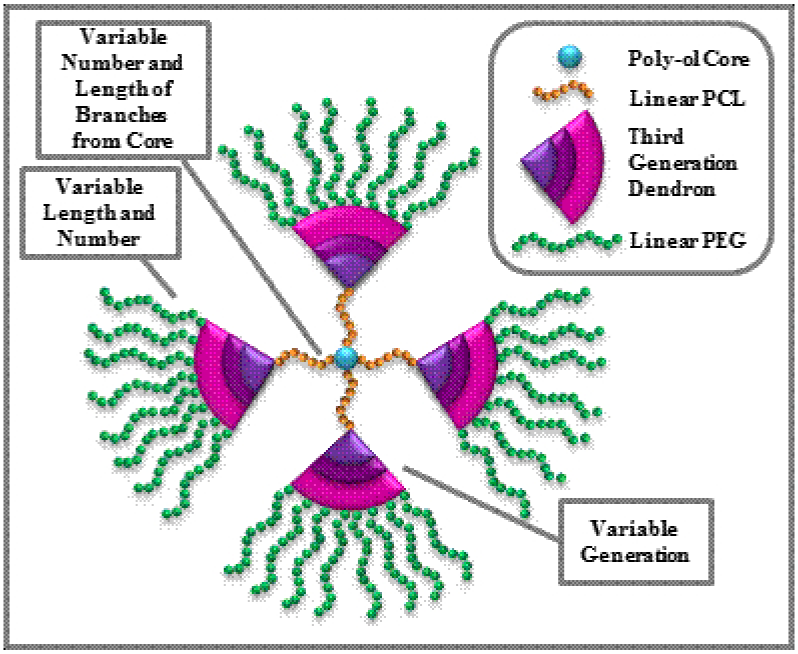
279 - Star-dendritic-linear polymers as a modular platform to probe unimolecular micelles

Brittany Myers, *bmyers1@tulane.edu, Scott Grayson. Department of Chemistry, Tulane University, United States*

Conventional micelles receive attention because of their ability to encapsulate guest molecules. While small molecule amphiphiles are known to yield micelles with limited stability, amphiphilic linear block copolymers can be used to improve and tune the size and stability of the resultant aggregates. However, even linear polymers are susceptible to disaggregation at low concentrations.Thus, branched, covalently-bound amphiphilic units are attractive. These resulting “unimolecular micelles” are robust when conventional micelles would disaggregate and exhibit no critical micelle concentration.

Dendrimers are highly branched macromolecules, ideal for preparing unimolecular micelles because their end-groups increase exponentially with each generation and are easily functionalized with groups of contrasting polarity. However, potential problems arise if guest molecules are particularly large or require substantial loading efficiencies. One way to construct modular unimolecular micelles with larger void spaces is to incorporate linear polymers between dendritic branching units. For example, unimolecular micelles can be prepared from a star core, such as linear polycaprolactone (PCL) grown from a poly-ol initiator, with dendrons, and an exterior linear chain such as polyethylene glycol (PEG). This design allows for larger void space while still exhibiting unimolecular micelle behavior.

These molecules are attractive both fundamentally and practically, however the structural parameters which define aggregation behavior and encapsulation are not well-understood. This study is designed to probe these parameters in order to synthesize molecules for use as drug delivery vehicles, sequestering agents, and surfactants.



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Room: Hall E

280 - Intermolecular forces in DNA condensation with cationic dendrimers

Min An, *man223@uky.edu, Jason DeRouchey. Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States*

In order to compact DNA, linear cations are believed to bind in DNA grooves and to interact with the phosphate backbone of apposing helices. The DeRouchey group has previously shown a length dependent attraction resulting in higher packaging densities with increasing charge for linear cations. Hyperbranched polycations, such as polycationic dendrimers, presumably would not be able to bind to DNA and correlate their charges with the phosphates of adjoining DNA in the same manner as linear cations. We use osmotic stress coupled with x-ray scattering to study fundamental molecular scale interactions and supramolecular self-assembly of low generation poly(amido amine) (PAMAM) dendrimer-DNA complexes. Dendrimer-DNA assembly displays fundamentally different physical behavior; higher dendrimer generation number give lower DNA packaging densities. The salt and pH dependence of packaging in dendrimer-DNA complexes was also measured. These studies begin to elucidate the role of cation topography in DNA condensation.

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281 - Probe and nanoparticles diffusion in polymer gels

Xiaolu Zhang[1], *xiaolu.zhang@uky.edu, Nathanael A Stocke*[2]*, James Z Hilt*[2]*, Jason DeRouchey*[1]*. (1) Department of Chemistry, University of Kentucky, Lexington, KY 40506, United States, (2) Department of Chemical Engineering, University of Kentucky, Lexington, KY 40506, United States*

Controlled transport of nanoparticles (NPs) through biological gels, such as mucus or extracellular matrix (ECM), is critical to NP and drug delivery in cells. Using fluorescence correlation spectroscopy (FCS), we have studied transport and dynamics of probe molecules and charged dendrimers in polymeric gels. In the first study, transport of probe molecules was studied as a function of crosslinking density, crosslinker molecular weight, and water content during synthesis. In the second study, diffusion of cationic polyamidoamine (PAMAM) dendrimers in polymeric solutions was measured. Diffusion of PAMAM in the presence of charged polymer solutions greatly influenced the diffusion coefficients of PAMAM compared to the same uncharged polymer solution. The ability to control specific interactions to develop better mucus penetration nanoparticles and novel synthetic *in vitro* mucus model would be highly beneficial due to the significant work required to deliver drugs to tissues covered in this biological barrier to transport.

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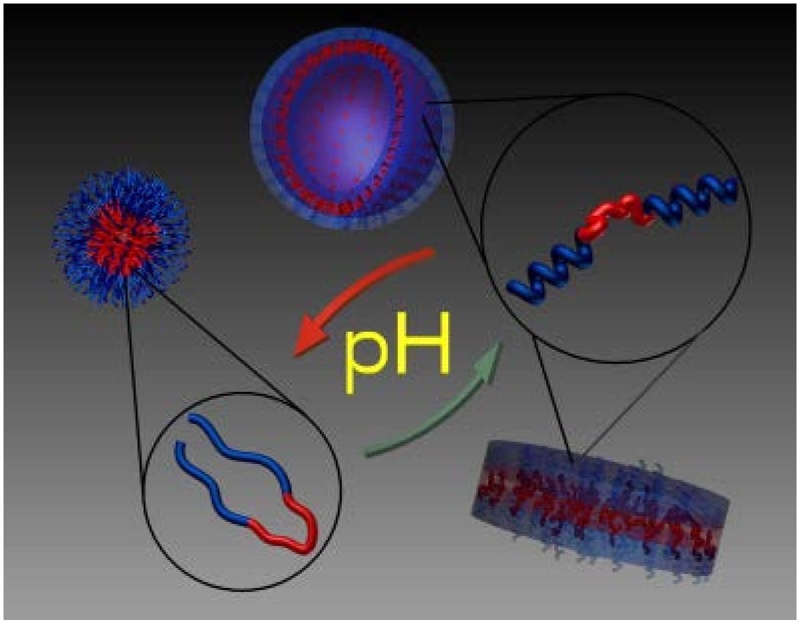
282 - Morphological tunability of pH-responsive, self-assembled polypeptide block copolymers through molecular design and polymer composition

Ashley J Johnson, *ashley.montgomery@eagles.usm.edu, Jacob G Ray, Andrew C Holley, Charles P Easterling, Jack T Ly, Daniel A Savin. School of Polymers, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

This study involves the bottom-up design and tunability of responsive, amphiphilic peptide block copolymers which display unique pH-induced morphology transitions due in part to changes in the secondary structure of the peptide. Variations in the molecular architecture lead to diverse morphologies that have potential as drug delivery vehicles. Model systems for this study are based on hydrophilic blocks of poly(L-lysine) or poly(glutamic acid), with high peptide weight fractions. In order to tune the pH-response of these assemblies for drug delivery, the peptide alanine was incorporated into the hydrophilic block at various mole fractions, thus altering the local environment of the peptide chain. Light scattering and TEM were used to determine aggregate size and morphology as a function of pH, and circular dichroism (CD) spectroscopy was used to secondary structure within the peptide blocks. Drug release profiles were created to show the triggered release of doxorubicin with change in pH. This study demonstrates how controlling the molecular design and pH responsiveness of these assemblies is a potential handle to control drug release.



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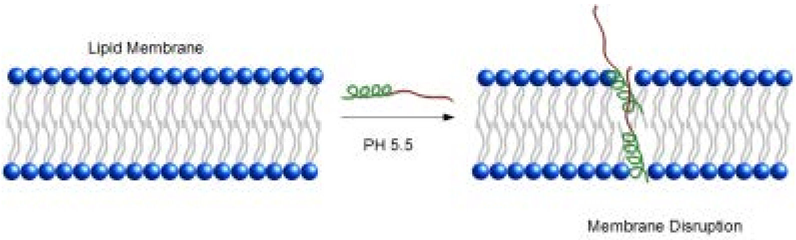
283 - HPMA-b-NCA copolymers with pH-responsive helical segments for membrane disruption

Andrew C Holley[1], *andrew.holley@eagles.usm.edu*, *Jacob Ray*[1], *Wen M Wan*[1], *Brooks Able*[1], *Keith H Parsons*[1], *Daniel Savin*[1], *Charles L McCormick*[1,2]. *(1) Department of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States, (2) Department of Chemistry and Biochemistry, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States*

A series of pH-responsive block copolymers was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization of N-(2-hydroxypropyl)methacrylamide (HPMA) and subsequently chain extended via N-carboxyanhydride polymerization (NCA) of Glu(oBzl)-OH. After deprotection of Glu(oBzl)-OH, block copolymer helicity with respect to pH was determined utilizing circular dichroism. At endosomal pH, the glutamic acid blocks self-assemble into a-helices providing a charged, hydrophobic handle to promote membrane disruption, while HPMA confers water solubility and biocompatibility. Red blood cell hemolysis was utilized to determine copolymer concentration necessary for disruption of the membrane. Moderate concentrations ranging from 100 - 200 mg/mL prompted sufficient release of hemoglobin (60-70%) at pH 5.5. Fluorescein loaded POPC liposomes were utilized to investigate a-helical content on membrane disruption. It was found that higher a-helical content increased fluorescein release.



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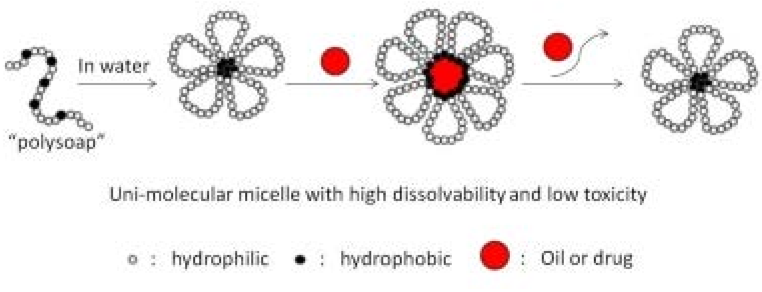
Room: Hall E

284 - Uni-molecular micelles or “Polysoaps” as biomaterials for remediation and drug delivery applications

Wen-Ming Wan, *wenming.wan@usm.edu*, ***Phillip D Pickett***, *phillip.pickett@eagles.usm.edu*, *Charles L McCormick. Department of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, MS 39401, United States*

Conventional surfactants exhibit disadvantages upon sequestration of material in dilute concentrations and are typically environmentally harmful due to their toxicity. Developing uni-molecular micelles with lower toxicity that can sequester material without concentration dependence is the goal of this work. Amphiphilic polymeric surfactants (“polysoaps”) with varying composition of hydrophobic/hydrophilic acrylamide monomer units (such as AMPS and docecyl acrylamide) have been synthesized via reverse addition fragmentation chain transfer (RAFT) polymerization, producing structurally defined polymers with controlled molecular weights and narrow molecular weight distributions. In an aqueous environment these amphiphilic copolymers will consist of a hydrophobic domain for hydrocarbon sequestration surrounded by a hydrophilic exterior for stabilization in water. The conceptual aspect of this approach, as well as the synthesis, characterization and behavioral properties of the uni-molecular vs. multi-molecular micelles will be discussed.



Uni-molecular micelle with high dissolvability and low toxicity

Tuesday, April 9, 2013 05:30 PM
Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

285 - Program for excellence in nanotechnology: Development of novel polymer nanostructures and translation to the clinic

Eric D Pressly, *pressly@mrl.ucsb.edu, Nate A Lynd, Craig J Hawker, Daniel Klinger. Materials Research Lab, University of California, Santa Barbara, CALIFORNIA 93106, United States*

The Program for Excellence in Nanotechnology is a multi-institute collaboration for the development and translation of nanostructures for lung and cardiovascular diseases. Herein, we describe our efforts for the translation of a late stage polymer nanostructure developed for early diagnosis of cardiovascular disease. Additionally, we discuss early stage development of shape changing and degradable nanostructures.

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Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
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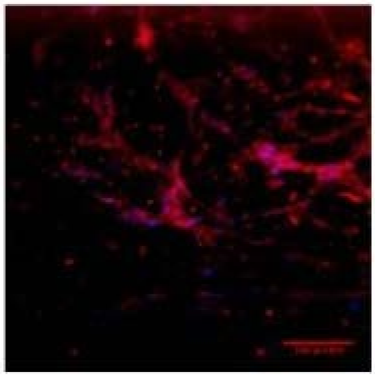
286 - Controlling vascularization within the hyaluronic acid based hydrogel

Amit K Jha[1], *amitjha@berkeley.edu, Jianqin K Ye*[2,4], *Yerem Yeghiazarians*[2,4], *Kevin E Healy*[1,3]. *(1) Department of Bioengineering, University of California, Berkeley, California 94720, United States, (2) Division of Cardiology, University of California, San Francisco, California 94143, United States, (3) Department of Material Science and Engineering, University of California, Berkeley, California 94720, United States, (4) Department of Medicine, University of California, San Francisco, California 94143, United States*

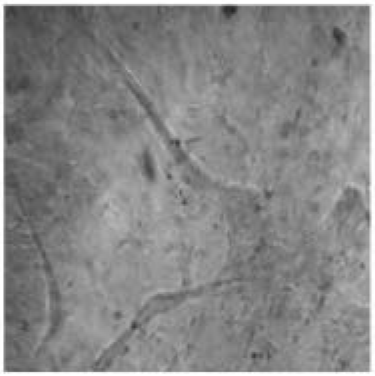
Ischemic heart diseases are one of the leading causes of heart failure resulting the blockage of coronary arteries that cause damages to the heart muscle. Generation of functional vascular network is required for rapid treatment of ischemic heart diseases. In this work, we have studied vascularization in 3D hydrogel system utilizing endogenous cardiac progenitor Sca-1$^+$CD45$^-$cells (CPC) owing their ability to differentiate into diverse multipotent cardiovascular cell lineages. Hyaluronic acid (HyA) based hydrogel system was synthesized that contains peptide sequences for cell attachment, heparin for spatial and temporal release of growth factors, and enzymatically degradable matrix metalloproteinase (MMP) sensitive peptide. Viscoelastic properties of the hydrogel can be tuned by varying the crosslinking density and weight percentage of HyA in the network. Matrix stiffness of the hydrogel can be tuned from 10Pa to 850Pa. Immobilized heparin in the HyA network supported the sustained release of transforming growth factor b1 (TGF b1) at the rate of 1.5% cumulative release per day.

Sca-1$^+$CD45$^-$CPCs were viable, proliferating and forming vascular tube networks inside the hydrogel. Size and density of tubes can be controlled by changing the peptide density and stiffness of the matrix. HyA hydrogel system is the promising candidate for tissue regeneration and drug delivery applications.

CD31 staining at day12



Bright Field Image at day 12



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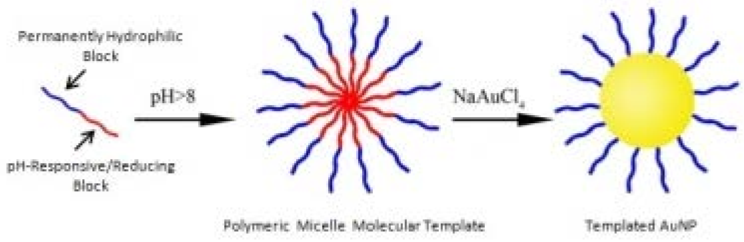
Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

287 - Gold nanoparticles via polymer micelle molecular templates for pulmonary imaging

Keith H Parsons[1], *parsonskh@gmail.com*, *Keisha Walters*[3], *Keith Walters*[4], *Robert Hester*[5], *Charles L McCormick*[1,2]. *(1) Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406, United States, (2) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406, United States, (3) Department of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762, United States, (4) Department of Mechanical Engineering, Mississippi State University, Mississippi State, MS 39762, United States, (5) Department of Physiology, University of Mississippi Medical Center, Jackson, MS 39216, United States*

Polymeric molecular templates offer a new route to synthesis of uniform gold nanoparticles (AuNPs) with on-demand size control. Stimuli-responsive block copolymers have been synthesized with pH-responsive blocks that serve the dual purpose of inducing self-assembly and gold salt reduction. These polymer micelles, in the presence of $NaAuCl_4$, act as molecular templates for AuNP synthesis by controlling the size and shape of the nanoparticle through the length of the gold-reducing block. Polymers with varying block lengths have been synthesized to establish a relation between block length and AuNP size. Once “on-demand” AuNP size control has been established, AuNPs of varying sizes will be targeted for inhalation and imaging studies of nanoparticle flow and deposition in isolated rat lungs. Successful completion will not only provide a novel route to AuNP synthesis, but will also establish a better understanding of inhaled nanoparticle toxicity and effects on pulmonary diseases.



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Bottom-Up Design of the Next Generation of Biomaterials (05:30 PM - 07:30 PM)
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288 - Peptide-directed assembly of scaffolds for applications in tissue engineering

***Xiaochu Ding**, xding@mtu.edu, Jagadeesh Janjanam, Martin Thompson, Ashutosh Tiwari, Patricia Heiden*. Department of Chemistry, Michigan Technological University, Houghton, MI 49931-1295, United States*

The ability to load different proteins into 3D scaffolds is crucial for cell activities such as migration, proliferation and differentiation for tissue engineering. In this work, a novel peptide-functionalized amphiphilic block copolymer was designed to self-assemble into polymeric nanoparticles and then into fibers, leading to 3D fiber scaffolds

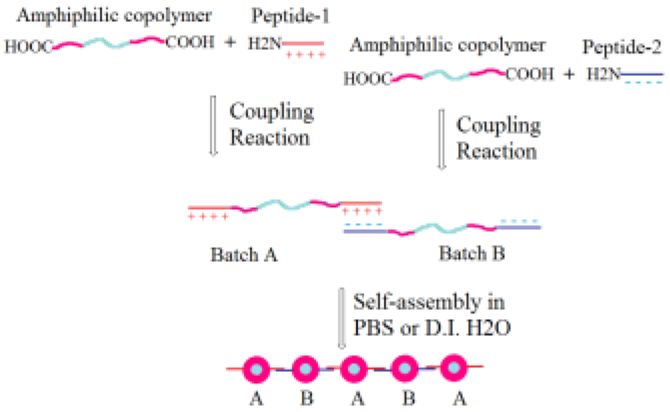

Figure1.The general procedure to synthesize peptide-functionalized amphiphilic copolymers with subsequent formation of nanoparticles into fibers as directed by a b-sheet assembly of peptides.

. Two peptide sequences (peptide-1 and peptide-2) were synthesized that assemble into b-sheets in aqueous solution with a pH value between 4.4 ~ 10. Amphiphilic triblock copolymers (PVP-co-PMMA-co-PVP, PHEMA-co-PMMA-co-PHEMA) with carboxylic acid terminals (HOOC-A-B-A-COOH) were synthesized by RAFT polymerization using S,S¢-bis(a,a¢-dimethylacetic acid) trithiocarbonate (BDAT) as the chain-transfer agent. The amphiphilic copolymer was then reacted with the peptides between carboxylic acid terminals and peptide amine group to form peptide-copolymer conjugates. Optical microscopy photographs confirmed the formation of the nanoparticle assembly into fibers and scaffolds with and without protein (here insulin was used). The different nanoparticle compositions used here controlled the release of insulin from the assembled nanoparticles for three weeks. Cytotoxicity tests using SW-620 cell lines were performed by MTS and showed that the synthesized peptides, copolymers and peptide-functionalized copolymers were biocompatible with SW-620 cell. The self-assembled nanoparticle fibers and 3D scaffolds combine the advantages of flexible hydrogel scaffolds and versatile controlled release systems.

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Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
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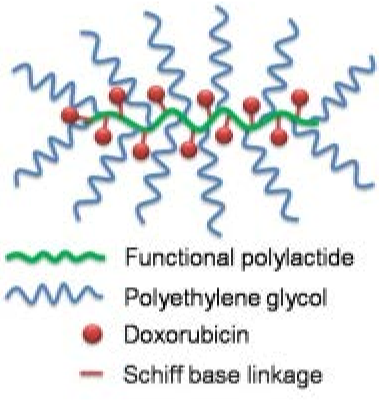
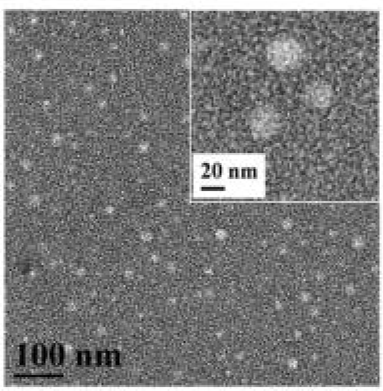
289 - Biodegradable brush polymer-drug conjugates for pH-responsive release of doxorubicin

Yun Yu[1], *yyu9@buffalo.edu, Chih-Kuang Chen*[1], *Wing-Cheung Law*[2], *Paras N Prasad*[2], *Chong Cheng*[1]. *(1) Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States, (2) Institute for Lasers, Photonics and Biophotonics, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States*

Since biodegradability and environmental responsivity are highly desired for drug delivery systems, a brush polymer-drug conjugate (BPDC) consisting of polylactide-based biodegradable scaffold and pH-responsive Schiff base drug conjugation was investigated. The biodegradable scaffold was synthesized via copper-catalyzed alkyne-azide click reaction. Results revealed the BPDC had well-defined nanostructure and high acid-sensitivity of doxorubicin release. Also, cytotoxicity and cell internalization studies of BPDC in MCF-7 breast cancer cells suggested its great potential for application as a novel anticancer nanomedicine.





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Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
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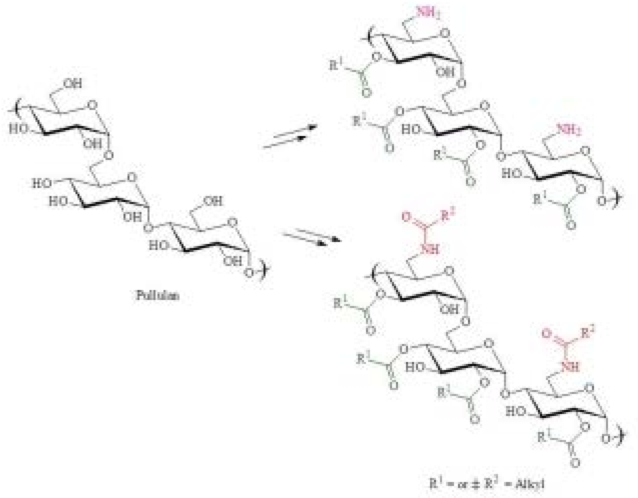
290 - Regioselectively modified pullulan derivatives containing amine and amide groups: Potential for biomedical applications

Junia Pereira[1], *juniamp@gmail.com, Kevin J. Edgar*[2]*. (1) Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States, (2) Department of Sustainable Biomaterials, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States*

A range of pullulan derivatives, containing amine and amide groups were synthesized by applying the dynamic Staudinger reduction. These chemical groups are known to play an important role in the biological activity of important polysaccharides, such as chitosan and chitin. Pullulan is blood compatible and non-immunogenic; therefore, chemically modified pullulan, with appealing characteristics, such as amino and amidopullulan esters are promising candidates for biomedical applications.



Tuesday, April 9, 2013 05:30 PM

Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)

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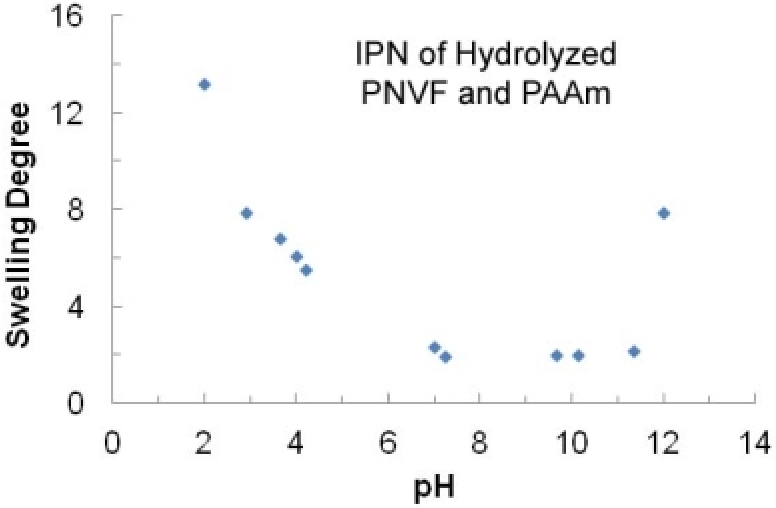
Room: Hall E

291 - Interpenetrating network hydrogels based on poly(N-vinylformamide) and polyacrylamide with controlled charge complexation

Tiffany C. Suekama[1], *tsuekama@ku.edu, Cory Berkland*[1,2], *Stevin H. Gehrke*[1]. *(1) Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, Kansas 66045, United States, (2) Department of Pharmaceutical Chemistry, The University of Kansas, Lawrence, Kansas 66045, United States*

We controlled the charge through combinations of different polymers: polyacrylamide (PAAm), poly(acrylic acid) (PAA), poly(N-vinylformamide) (PNVF) and polyvinylamine (PVAm). First, the synthesis and characterization of a novel polymer, PNVF, was created from N-vinyl formamide (NVF). NVF is an isomer of acrylamide (AAm), is a liquid monomer at room temperature, which is easier to process than the solid form of AAm; and is less toxic than AAm. PNVF can be easily hydrolyzed to form the cationic gel PVAm. PVAm cannot be formed through direct methods but is beneficial because it has a high charge density and can be readily functionalized. PNVF hydrogels were synthesized by cross-linking aqueous NVF solutions into using a novel cross-linker, 2-(N-vinylformamido)ethylether (NVEE) and the thermally-activated initiator VAZO-44. Although for the same formulation of PNVF as PAAm the PNVF is slightly more hydrophilic, a PNVF formulation can be modified to match the same swelling of a given PAAm gel, thus have the same mechanical strength. Interpenetrating networks have been made of combinations of PNVF, PVAm, PAAm and PAA. Following hydrolysis of the IPN, complexation is controlled at different length scales. With the correctly balanced formulations these gels a collapse due to charge complexation. These materials are being explored as drug delivery platforms.



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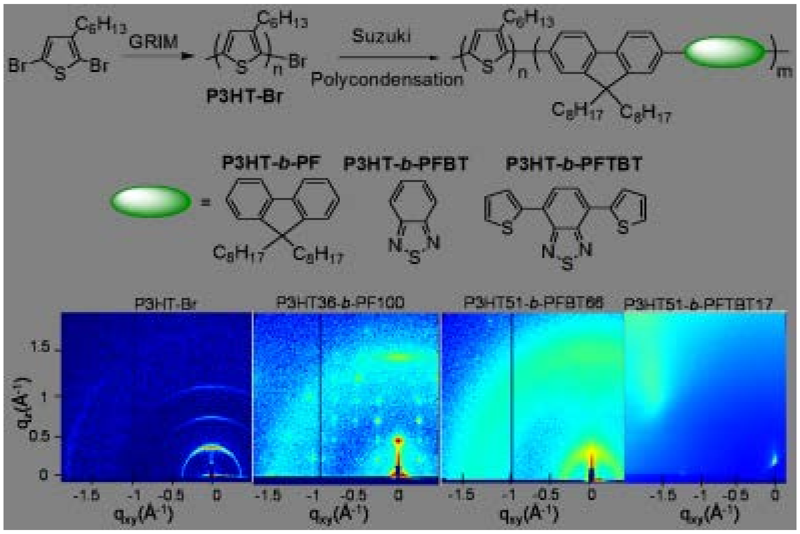
Room: Hall E

292 - Synthesis and crystallinity of all-conjugated poly(3-hexylthiophene) block copolymers

Yen-Hao Lin, *yl30@rice.edu, Rafael Verduzco. Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States*

An all-conjugated block copolymer connecting an electron donor and an electron acceptor polymer blocks introduces a solution to prevent micron-scale phase separation which is detrimental to charge transportation in all-polymer photovoltaics (OPVs). However, the synthesis of donor-acceptor all-conjugated block copolymers is limited by the presence of homopolymer impurities and a low molecular weight of the final product. This study presents an improved synthetic method toward high molecular weight (M_w > 50 kg/mol) P3HT-based all-conjugated block copolymers involving a combination of GRIM with LiCl additive and Suzuki polymerization. A series of P3HT block copolymers with three different conjugated polymer blocks is demonstrated. Analysis of the resulting block copolymers by grazing-incidence X-ray scattering indicates that P3HT crystallinity is reduced or completely suppressed in all-conjugated block copolymers. This contrasts with previous studies of P3HT-based all-conjugated block copolymers and indicates that competitive crystallization occurs in the all-conjugated block copolymers studied.



Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
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Tuesday, April 9, 2013 05:30 PM
Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
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Room: Hall E

293 - Non-covalent incorporation of specific binding sites onto organic transistors via block-copolymer templating

Mallory L. Hammock, *mhammock@stanford.edu, Oren S. Knopfmacher, Zhenan Bao. Stanford University, Stanford, California 94305, United States*

Organic transistors provide unique platforms for chemical and biological detection; however, there exists a need to incorporate specific recognition sites into the transistor architecture. In order to achieve this goal, we have spin coated a poly(styrene-*block*-2-vinylpyridine) film loaded with a gold salt onto the surface of our water-stable transistors. Using this platform, we have demonstrated the selective detection of chemical species (Hg^{2+})and biological species (thrombin) *in situ,* and investigated the affect of receptor spacing on the device's sensitivity.

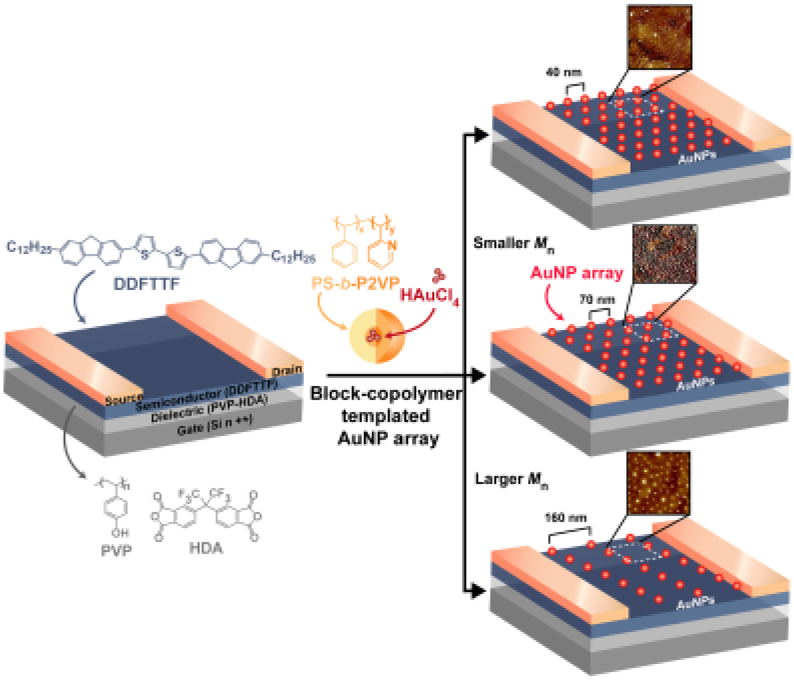

Figure 1. Incorporation of AuNPs onto a water-stable transistor using block-copolymer templating. This technique allows for easy manipulation of the interparticle spacing by varying the M_n of the PS-*b*-P2VP, allowing for easy investigation of the effect of receptor density on sensitivity.

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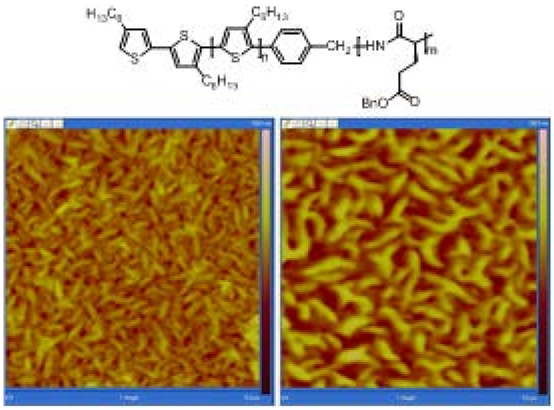
Room: Hall E

294 - Self-assembly and optoelectronic properties of a rod-rod semiconducting liquid crystalline block copolymer containing poly(3-hexylthiophene)

***Mahesh P Bhatt**, mpb080020@utdallas.edu, Mihaela C Stefan. Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States*

The self assembly of the rod-rod block copolymer poly(3-hexylthiophene)-*b*-poly(g-benzyl-L-glutamate) (P3HT-*b*-PBLG) thin film on organic field effect transistors (OFETs) has been studied. Chloroform and 1,2,4-trichlorobenzene (TCB) were used as solvents for the diblock copolymer. The P3HT-*b*-PBLG diblock copolymer solution either in chloroform or TCB was deposited on OFETs by drop-casting. The OFET devices were annealed under vacuum at three different temperatures (80 °C, 120 °C, and 150 °C) after the polymer deposition. We attempted to correlate the field-effect mobilities with the surface morphology of the P3HT-*b*-PBLG films deposited on OFETs. The surface morphologies of thin films were investigated by TMAFM in the channel region of the OFET devices. X-ray diffraction studies were also carried out on thin films cast from both the solvents to investigate the crystallinity of polymer thin film. The films formed from both chloroform and TCB displayed field effect mobilities in the order of 10^{-4} cm^2/Vs. However, the TMAFM images of the films displayed a substantial change in morphology upon annealing. The non-annealed film showed densely packed ribbon-like domains. An incremental change in the length of the nanoribbons was observed upon annealing the films at 80 °C and 120 °C. The independence of the field-effect mobility with respect to the film morphology indicates that the P3HT block self-assembles near the SiO_2dielectric surface where charge transportation occurs whereas PBLG block assembles at the top of the thin film.



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Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
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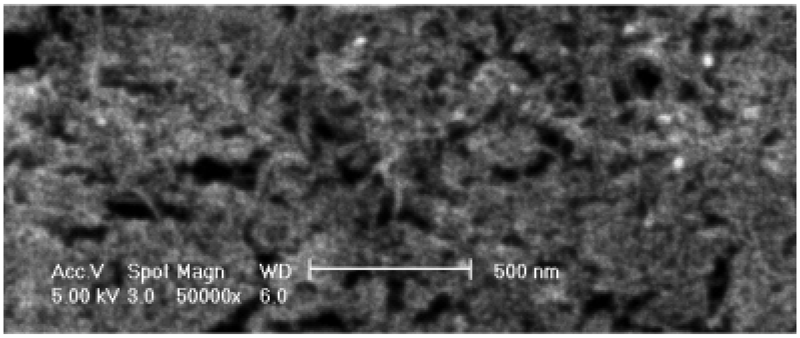
Room: Hall E

295 - Supercapacitors stabilized with stimuli-responsive osmotic spheres

***Corman Park**, parkcorman@gmail.com, John Texter. School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI 48197, United States*

Stimuli responsiveness in polymer design is providing basis for diversely new and advanced materials. Osmotic spheres exhibiting high affinity for nanocarbon (graphene) interfaces have been synthesized as nanolatex copolymers of a reactive ionic liquid surfactant and methyl methacrylate. These nanolatexes appear ideal stabilizers for waterborne dispersions and immunize dispersions against Debye-Hückel charge screening induced colloidal destabilization. We demonstrate these nanolatexes to provide the most concentrated waterborne dispersions of multi-wall carbon nanotubes (MWCNT) to date, and we also illustrate coating processes amenable to large scale manufacturing where these nanolatexes also function as binders. We develop some of these coatings as advanced supercapacitors, and we illustrate our results for waterborne coatings to be competitive with the state of the art for electrical double layer capacitors with and without vanadium oxide doping and achieving 500 mF/cm^{2}and 200-1,000 F/g. We also illustrate the use of such coatings for developing synergistic responses with electrically conducting polymers.



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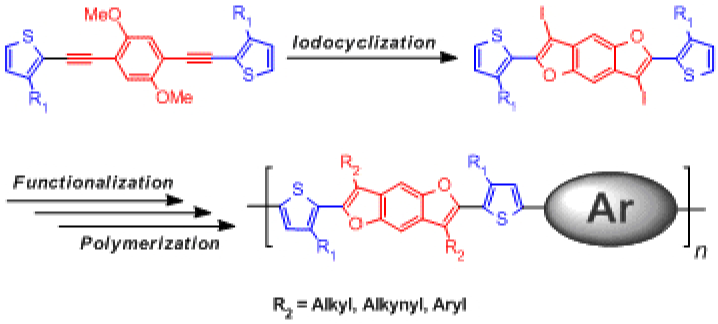
296 - Benzodifurans and more: Modifiable building blocks for the synthesis of conjugated polymers and their application in organic photovoltaic cells

Brandon M. Kobilka, *bkobilka@iastate.edu, Monique D Ewan, Benjamin J. Hale, Malika Jeffries-El. Department of Chemistry, Iowa State University, Ames, Iowa 50010, United States*

As of late, benzo[1,2-*b*:4,5-*b*']dithiophene has become a popular building block for use in high-efficiency bulk-heterojunction photovoltaic cells (BHJ-PVCs). Recently, we reported the synthesis and characterization of analogous, oxygen-containing benzo[1,2-*b*:4,5-*b*']difurans (BDFs)and their incorporation into conjugated polymers. The BDF core and functional handles are simultaneously achieved through an iodine-promoted double cyclization. Here, we report a related series of chalcogen-containing monomers with functional alkyl and aryl side groups. These building blocks are synthesized in good yields and used in conjugated polymers for BHJ-PVCs.



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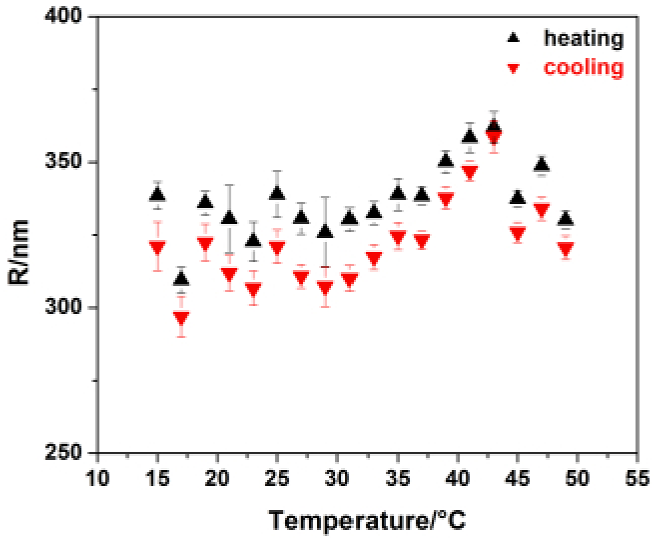
297 - Responsive colloids following the inverse a-helix-to-coil transition of silica tethered poly(N^{e}-carbobenzyloxy-L-lysine) in m-cresol with a blend of techniques: NMR, DLS, SLS and SAXS

Cornelia Rosu[1], *crosu1@tigers.lsu.edu, Rafael Cueto*[1]*, Dale Treleaven*[1]*, Mohammad Abu-Laban*[1]*, John Pople*[2]*, Paul S Russo*[1]*.*
(1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States, (2) Stanford Linear Accelerator Center, Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309, United States

Poly(N^{e}-carbobenzyloxy-L-lysine), PCBL, undergoes an inverse helix-to-coil transition in m-cresol as a function of temperature. When tethered on a silica sphere, the colloidal size, either on heating or cooling mode, measured by DLS and SLS decreases to a minimum corresponding to the transition temperature and then jumps gradually to a maximum and then tends to decrease again. In addition, the profile of T×T1/h_o and SAXS data suggest the presence of broken or interrupted helices.



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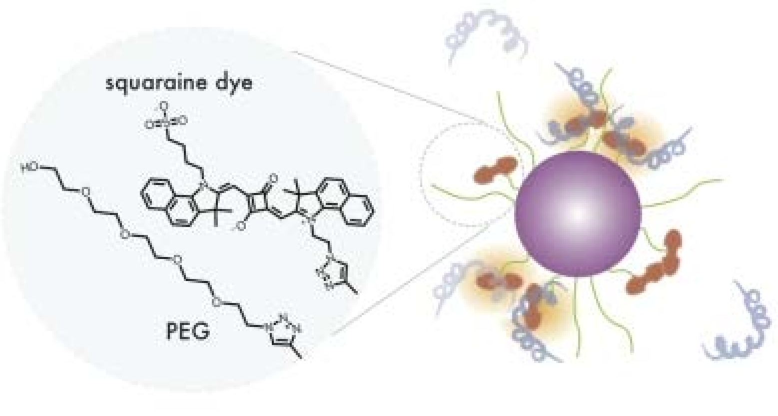
298 - Switchable fluorescence of near-infrared nanoparticles via protein interaction

Ragini Jetty[1], *rjetty@clemson.edu, Yuriy P Bandera*[1], *Michael A Daniele*[1], *Stephen H Foulger*[1,2], *Hsin-I Hung*[3], *Venkat Ramshesh*[3], *Megan Duperreault*[3], *Anna-Liisa Nieminen*[3], *John J Lemasters*[3,4]. *(1) School of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, United States, (2) Department of Bioengineering, Clemson University, Clemson, South Carolina 29634, United States, (3) Department of Pharmaceutical & Biomedical Sciences, Medical University of South Carolina, Charleston, South Carolina 29425, United States, (4) Department of Biochemistry & Molecular Biology, Medical University of South Carolina, Charleston, South Carolina 29425, United States*

Imaging with near-infrared fluorescing colloidal particles is emerging as an attractive tool for therapeutics and diagnostics in nanoparticle-based medicine. We report here on a general approach for the activation/deactivation of emission of near-infrared emitting nanoparticles. Sub-100 nm poly(propargyl acrylate) (PA) particles were synthesized and surface modified through copper-catalyzed azide/alkyne cycloaddition to attach azide-terminated squaraine derivative (azSQ), a near-infrared emitter, and poly(ethylene glycol) (azPEG) chains. The emission of functionalized particles is deactivated when dispersed in aqueous solutions due to the aggregation of the hydrophobic azSQ. The fluorescence of azSQ on the particles can be switched on when the fluorophores complex with serum albumin to form host/ guest assemblies, while the disruption of the azSQ/ albumin assemblies is utilized to turn off the emission of the functionalized particles. To achieve the deactivation, the fluorescing particles were incubated with trypsin which digests the albumin. The fragments of peptide chains cannot form complexes with the azSQ and causes the fluorophore to dimerize once again and subsequently the emission of particles is switched off. The activation/ deactivation of functionalized particles was also demonstrated *in vitro* in A549 and UMSCC22A cells using confocal studies. The confocal studies suggested that the particles were taken up by cells through endocytosis and accumulated into lysosomes.



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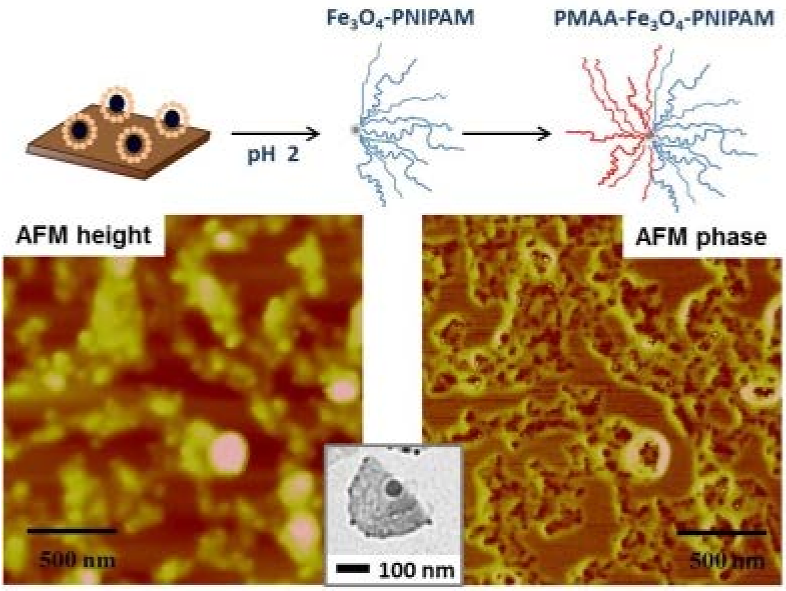
299 - Stimuli-responsive biphasic-polymer Janus magnetic nanoparticles prepared via electrostatic interactions and surface-confined ATRP

Erick S. Vasquez[1], *esv13@msstate.edu, I-Wei Chu*[1,2], *Keisha B. Walters*[1]. *(1) Department of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762, United States, (2) Institute for Imaging and Analytical Technologies, Mississippi State, MS 39762, United States*

Synthesis of three-dimensionally asymmetric amphiphilic Janus magnetic nanoparticles (MNPs) was achieved by a multi-step process: (1) electrostatic particle retention on mica, (2) surface-confined ATRP of PNIPAM on the exposed NP surface, (3) release of MNP from mica, and (4) surface-confined ATRP of PMAA on the second side of the MNPs (back-fill). AFM and TEM were used to demonstrate the morphology of the Janus MNPs after each of the reaction steps. ATR-FTIR, XPS, and EDS were used to determine chemical modifications.



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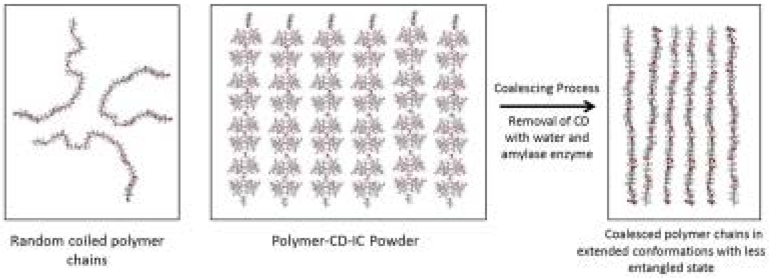
300 - Combined experimental and simulation approach to tailor the microstructures of polymer materials through inclusion complex formation and subsequent release

Alper Gurarslan[1,2], *agurars@ncsu.edu, Melissa A Pasquinelli*[1], *Alan E. Tonelli*[1]. *(1) Departmen of Fiber and Polymer Science, North Carolina State University, Raleigh, North Carolina 27695, United States, (2) Department of Material Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States*

Numerous polymers can form non-covalently bonded inclusion complexes (ICs) with host molecules such as cyclodextrin and urea. Combined experimental and simulation studies can improve our understanding of the fundamentals of IC formation. Recent results suggest that the hydrophobicity of polymers plays a key role in IC formation. Hydrophobic polymers are able to “push out” and replace less hydrophobic polymers that are initially inside the host molecule ICs, a phenomenon called “Competitive IC Formation”. Another scope of our research is the behavior of polymers that are coalesced from nano-confinement in their ICs made with cyclodextrin or urea host molecules. The microstructures of such coalesced polymers are distinct from their as-received counterparts and yield superior physical properties. These coalesced polymers can be used as self-nucleating agents and in self-reinforced composites (SRC), which consist of chemically identical matrix and reinforcement components. We have observed that the tailored microstructures of coalesced polymers provide good reinforcement to the as-received matrices.



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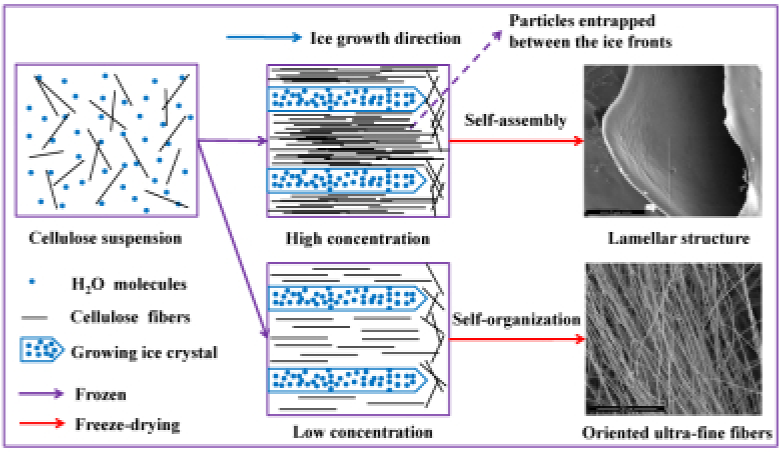
Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

301 - Self-assembling behavior of cellulose nanoparticles during freeze drying: Effect of suspension concentration

Jingquan Han[1], *hjingq1@tigers.lsu.edu, Qinglin Wu*[2]*. (1) Department of Renewable Natural Resources, Louisiana State University, Baton Rouge, Louisiana 70803, United States, (2) Department of Renewable Natural Resources, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

Cellulose nanocrystals (CNCs) with average length and width of 149 ± 40 and 9 ± 2 nm were isolated from bleached wood fibers by acid-hydrolysis. During lyophilization, CNCs in aqueous suspension self-organized into a lamellar structured foam composed of aligned thin membrane layers with width between 0.5 and 3 mm at the concentration of 1.0%. At 0.05 %, they self-assembled into oriented ultra-fine fibers with diameters of 0.57 ± 0.17 mm, instead of sheet-like structure by sublimating ice molecules.



Tuesday, April 9, 2013 05:30 PM

Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)

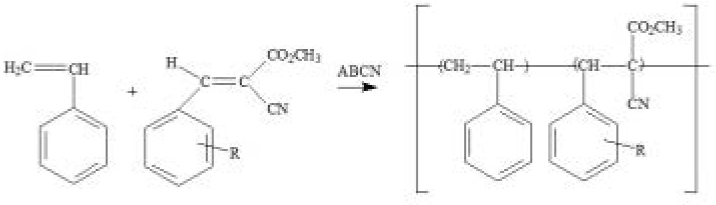
Location: Morial Convention Center

Room: Hall E

302 - Novel functional copolymers of styrene and ring-substituted methyl cyanopropenoates

Sonia E Chavez, *sonia_elena@sbcglobal.net, Gregory B Kharas. Department of Chemistry, DePaul University, Chicago, IL 600614, United States*

New functional copolymers of styrene and multifunctional trisubstituted ethylenes were prepared as potential building blocks for novel materials. Styrene and some ring-substituted methyl 2-cyano-3-phenyl-2-propenoate copolymers were prepared in solution with radical initiation.



The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C NMR. The copolymers were characterized by GPC, DSC, and TGA.

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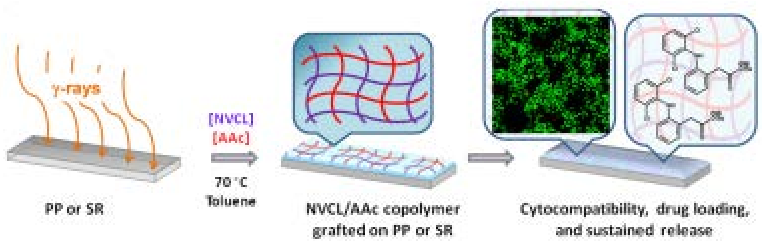
303 - Radiation-grafting of thermo- and pH-sensitive poly(N-vinylcaprolactam-co-acrylic acid) on silicone rubber and polypropylene films

*Caroline C Ferraz[1], Ademar B Lugao[1], **Emilio Bucio**[2], ebucio@nucleares.unam.mx. (1) Chemist, IPEN, Sao Paulo, Sao Paulo 05422-970, Brazil, (2) Chemist, ICN-UNAM, Mexico City, DF 04530, Mexico*

This work focuses on the effect of gamma-ray radiation conditions on the stimuli-responsiveness of polypropylene (PP) films and silicone (SR) rubber substrates grafted with N-vinylcaprolactam (NVCL) and acrylic acid (AAc). PP films and SR rubber were weighed and placed into glass ampoules and exposed to Co-60 gamma-source (Gammabeam 651 PT, MDS Nordion) in the presence of air at room temperature, at dose rate around 12 kGy/h and dose between 5 and 70 kGy. Solutions of NVCL and AAc (1/1, v/v), 50 % monomer concentration (v/v) in toluene were added to samples, the ampoules were degassed by repeated freeze-thaw cycles (5 times per 20 min) and sealed. The ampoules were heated at 60 and 70 °C at reaction time per 12 h. To extract the residual monomer and homopolymer formed during the grafting, the samples were soaked in ethanol for 24 h and then in distilled water, followed by drying under vacuum to constant weight. Samples where characterized by FTIR-ATR, DSC, swelling, LCST, and pH critical point.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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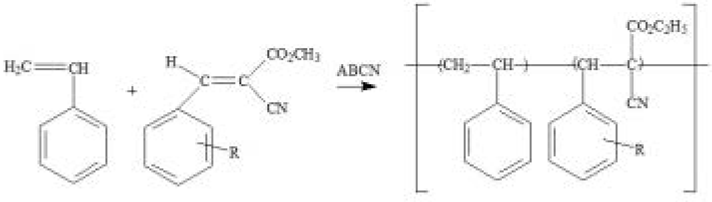
Room: Hall E

304 - Novel functional copolymers of styrene and para-ring substituted ethyl cyanopropenoates

ERIC S MOLINA, *emolina32@gmail.com, Gregory B Kharas. Chemistry, DePaul University, Chicago, IL 60614, United States*

Electrophilic trisubstituted ethylenes, ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2C_2H_5$ (where R is 4-CH_3CO_2, 4-CH_3CONH, 4-CN, 4-$(CH_3)_2N$, 4-$(C_2H_5)_2N$) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and ethyl cyanoacetate, and characterized by CHN analysis, IR, ^1H and ^{13}C-NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^1H and ^{13}C-NMR. Relatively high T_g of the copolymers in comparison with that of polystyrene indicates a decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 250-500°C range with residue, which then decomposed in the 500-800°C range.



Tuesday, April 9, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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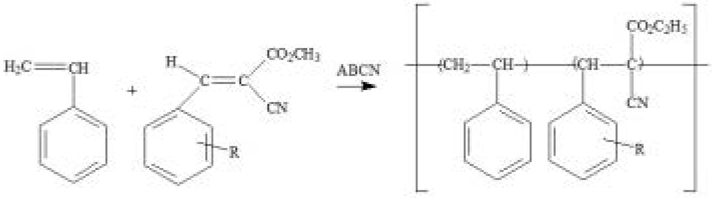
Room: Hall E

305 - Novel functional copolymers of styrene and oxy ring-substituted ethyl cyanopropenoates

ALEXANDER A. DELGADO, *aadelgado25@yahoo.com, Gregory B Kharas. Chemistry, DePaul University, Chicago, IL 60614, United States*

Electrophilic trisubstituted ethylenes, ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2C_2H_5$ (where Ris 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy, 3-phenoxy) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and ethyl cyanoacetate, and characterized by CHN analysis, IR, ^{1}H and ^{13}C-NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^{1}H and ^{13}C-NMR. Relatively high $T_g$of the copolymers in comparison with that of polystyrene indicates a decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 250-500°C range with residue (3-8% wt.), which then decomposed in the 500-800°C range.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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306 - Synthesis and characterization of PMMA containing graphene nanosheets by in situ bulk polymerization using microwave irradiation

Mohammad A Aldosari[1], *aldosari@kacst.edu.sa, Ali Othman*[2], ***Edreese H Alsharaeh***[2], *ealsharaeh@alfaisal.edu. (1) KACST, Riyadh, Riyadh 11442, Saudi Arabia, (2) Department of Natural Sciences, Alfaisal.university, Riyadh, Riyadh 115533, Saudi Arabia*

This work presents a facile method for *in situ* preparation of PMMA containing graphene sheets. In one of the approach, a mixture of graphene oxide (GO), a free radical initiator, s and methyl methacrylate (MMA) monomers were polymerized using bulk polymerization method and then the product was reduced using conventional microwave after adding a reducing agent rGO-(PMMA). In a second approach, a mixture of graphene (GR), a free radical initiator, and methyl methacrylate monomer were polymerized using bulk polymerization method to obtain 2%GR-(PMMA). In this work we will present a comparative study between the composites that were prepared by using *in situ* bulk polymerization method and to the composites that were obtained from the microwave irradiation(MWI) method. . The results indicate that the composite obtained from MWI has a better morphology and increased dispersion with enhanced thermal stability.

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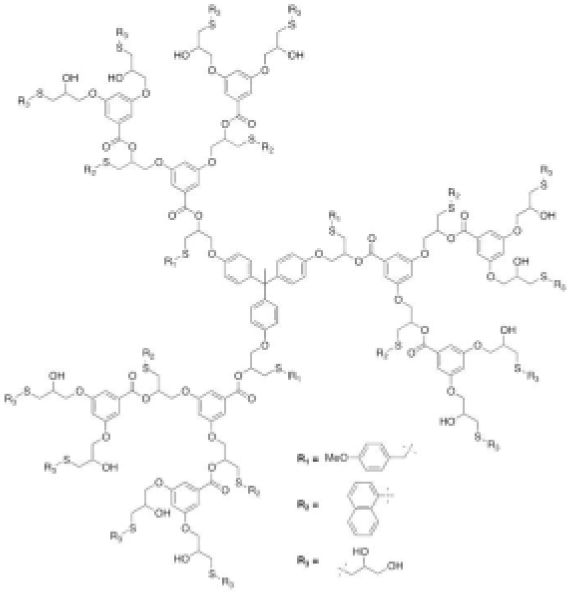
307 - Generation-specific functionalization in dendrimers: Synthetic access through thiol-epoxy “click” chemistry

Ikhlas Gadwal, *ikhlas.gadwal@mat.ethz.ch, Anzar Khan. Department of Materials, ETH-Zürich, Laboratory of Polymer Chemistry, Zürich, Switzerland*

A modular synthetic strategy will be presented for the preparation of polyfunctional dendrimers. In this strategy, thiol-epoxy 'click' chemistry and the esterification reaction are employed for a facile construction of the dendritic scaffold. The cascade nature of these processes sets the synthetic pathway free from the typical protection/deprotection requirements of the dendrimer synthesis. Most importantly, the sequence of reactions permits for the introduction of a desired functional group at each dendritic layer.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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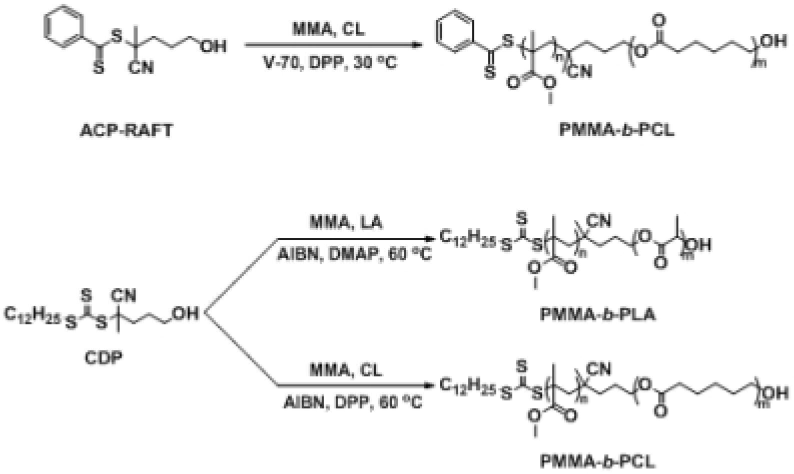
308 - One-step synthesis of block copolymers using a hydroxyl-functionalized RAFT agent as a dual initiator

Young Chang Yu, Hyun Uk Kang, Sang Jin Shin, Seung Hyun Kim, ***Ji Ho Youk****, youk@inha.ac.kr. Nano system, Inha university, Incheon, Republic of Korea*

4-Cyano-1-hydroxypent-4-yl dithiobenzoate (ACP-RAFT) and 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanol (CDP), hydroxyl-functionalized RAFT agents, were synthesized and tested as dual initiators for the one-step synthesis of a range of block copolymers. Diphenyl phosphate (DPP) was used as a catalyst for the ring-opening polymerization (ROP) of *d*-valerolactone (VL), *e*-caprolactone (CL), and trimethylene carbonate (TMC), and 4-dimethyamino pyridine (DMAP) was used as a catalyst for the ROP of L-lactide (LA).



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

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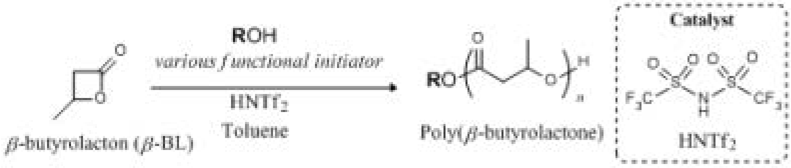
Room: Hall E

309 - Synthesis of end-functionalized poly(b-butyrolactone) using super Brønsted acid

Seiya Kikuchi[1], *kikuchi@poly-bm.eng.hokudai.ac.jp, Kosuke Makiguchi*[1], *Harumi Kaga*[2], *Toshifumi satoh*[3], *Toyoji Kakuchi*[3]. *(1) Department of Biological Chemistry and Engneering course, Graduate School of Chemical Sciences and Engineering, Hokaido University, Sapporo, Hokkaido 060-8628, Japan, (2) Department of Bio-material Engineering Research Group, National Institute of Advanced Industrial Science and Technology, Sapporo, Hokkaido 062-8517, Japan, (3) Division of Biotechnology and Molecular Chemistry, Faculty of Engneering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*

We report the ring-opening polymerization (ROP) of b-butyrolactone using a super Brønsted acid as an organocatalyst and 3-phenyl-1-propanol (PPA) as the initiator. The polymerization homogeneously proceeded with well-controlled molecular weights and narrow polydispersity indices. The ^{1}H NMR, SEC, and MALDI-TOF MS measurements of the obtained poly(b-butyrolactone) also indicated the presence of the PPA moiety at the a-chain end. In addition, we expanded this polymeric system to the synthesis of end-functionalized PBL using various functional alcohols as the initiator.



Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
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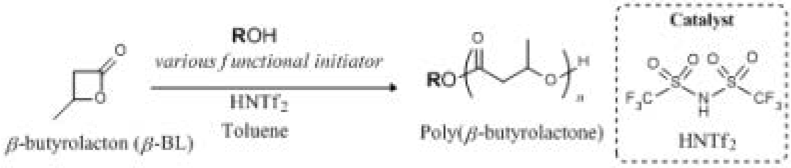
Tuesday, April 9, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

309 - Synthesis of end-functionalized poly(b-butyrolactone) using super Brønsted acid

Seiya Kikuchi[1], *kikuchi@poly-bm.eng.hokudai.ac.jp, Kosuke Makiguchi*[1], *Harumi Kaga*[2], *Toshifumi satoh*[3], *Toyoji Kakuchi*[3]. *(1) Department of Biological Chemistry and Engneering course, Graduate School of Chemical Sciences and Engineering, Hokaido University, Sapporo, Hokkaido 060-8628, Japan, (2) Department of Bio-material Engineering Research Group, National Institute of Advanced Industrial Science and Technology, Sapporo, Hokkaido 062-8517, Japan, (3) Division of Biotechnology and Molecular Chemistry, Faculty of Engneering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*

We report the ring-opening polymerization (ROP) of b-butyrolactone using a super Brønsted acid as an organocatalyst and 3-phenyl-1-propanol (PPA) as the initiator. The polymerization homogeneously proceeded with well-controlled molecular weights and narrow polydispersity indices. The ^{1}H NMR, SEC, and MALDI-TOF MS measurements of the obtained poly(b-butyrolactone) also indicated the presence of the PPA moiety at the a-chain end. In addition, we expanded this polymeric system to the synthesis of end-functionalized PBL using various functional alcohols as the initiator.



Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
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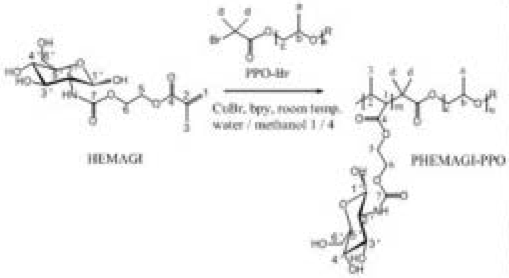
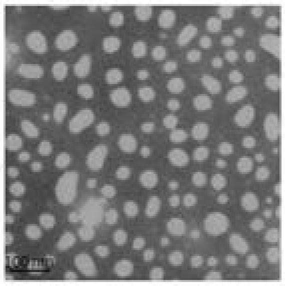
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

311 - Polymeric micelles carrying sugar moieties and their interaction with lectin

Bo Yuan, *bzy0002@tigermail.auburn.edu, Gisela Buschle-Diller. Department of Polymer & Fiber Engineering, Auburn University, Auburn, AL 36849, United States*

Glycopolymers may play an important role in a wide range of biomolecular events such as cellular recognition, adhesion, cell growth regulation, cancer cell metastasis, and inflammation. Depending on the ratio of hydrophilic to hydrophobic segments, glycopolymers are capable of forming micelles useful for recognition of biological molecules. In this work, a thermo-responsive amphiphilic glycopolymer: poly(2-{[(D-glucosamin-2N-yl)carbonyl]oxy} ethylmethacrylate)-b-poly(propylene oxide) (PHEMAGI-PPO) was synthesized via atom transfer radical polymerization (ATRP). The chemical structure of glycomonomer (HEMAGI), macroinitiator (PPO-Br), and glycopolymer was confirmed by ^{1}H-NMR or ^{13}C-NMR spectra. From ^{1}H-NMR, the degree of functionalization of PPO-Br was determined to be more than 99%. The critical micelle concentration (CMC) of the glycopolymer was measured by dye micellization method and the diameter of the formed micelles was determined by transmission electron microscopy (TEM). The lectin recognition property was measured using Con A as a model lectin. The Figure shows synthesis and micelle formation seen with TEM.





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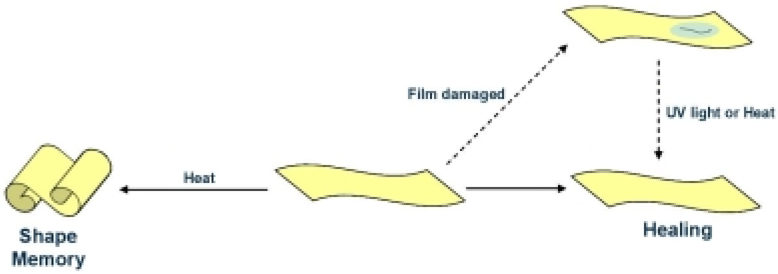
312 - Multi-functional stimuli-responsive polymers

Brian T Michal, *brian.michal@case.edu, Stuart J Rowan. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States*

Materials exhibiting both shape memory and self healing properties have been synthesized. These materials are semicrystalline, covalently crosslinked network polymers containing disulfide bonds. The combination of crystallinity and covalent crosslinks gives the material a means to hold a temporary shape and recover to a remembered shape, allowing it to display shape memory properties. The disulfide bonds in the material make the entire network dynamic as they can be exchanged when exposed to UV light or heat. By activating this disulfide exchange, the network can be allowed to flow and heal small defects and change its shape. Shape memory experiments showed high degrees of both fixing and recovery and healing experiments showed that the film was able to recover from a scratch whose depth is approximately half the thickness of the film.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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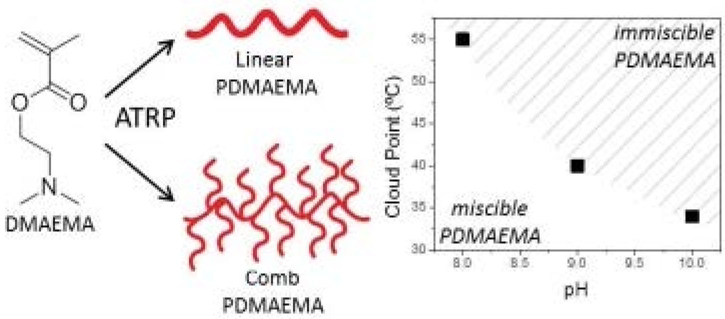
313 - Synthesis and reversible self-assembly of linear and comb architectures of poly(2-(dimethylamino)ethyl methacrylate)

Austin R. Bol, *bolar42@gmail.com*, ***Dylan G. Karis***, *karisdg@uwec.edu, Michael S. Farrell, Patrick J. Baker, Elizabeth M. Glogowski. Department of Materials Science, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54701, United States*

“Smart” polymers, or polymers that respond to stimuli such as pH, temperature, or ionic strength, can be synthesized and self-assembled for a wide range of potential applications, including delivery or advanced materials applications. The “smart” homopolymer poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) has been synthesized by Atom Transfer Radical Polymerization (ATRP). This “smart” polymer exhibits reversible hydrophobicity as a function of pH, temperature, and polymer architecture. A synthetic approach has been developed to control the polymer architecture, *i.e.* linear vs. comb PDMAEMA chains, to investigate the impact of polymer architecture on thermoresponsive behavior. The linear and comb polymers were characterized by 1H-NMR, size exclusion chromatography, and MALDI-TOF MS. Cloud points of both linear and comb PDMAEMA chains were measured as a function of pH using UV-Visible spectroscopy. Molecular weight, molecular weight distribution, functional group density, and polymer architecture were varied to determine the impact on PDMAEMA thermoresponsive behavior.



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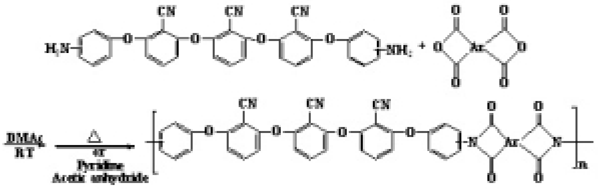
314 - Synthesis and characterization of polyimides containing multi-benzonitrile groups for dielectric applications

David H Wang[1,2], ***Brian A Kurish***[1,2], *brian.kurish@wpafb.af.mil, Lianyun Yang*[3], *Lei Zhu*[3], *Loon-Seng Tan*[1]. *(1) Materials & Manufacturing Directorate, AFRL/RXAS, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7750, United States, (2) UES Inc., Dayton, OH 45432, United States, (3) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

Polyimides (PIs) represent one of the most important classes of specialty polymers. They have found many applications in high performance films and fibers, coatings, microelectronics, optoelectronics, adhesives, aerospace structures, nonlinear optical devices, light-wave guiding materials, and liquid crystal displays. Polyimides containing benzonitrile units have been studied for the piezoelectric and other dielectric applications due to the high polarity of nitrile groups. In our previous research, one unsymmetric and two symmetric diamines as well as the respective polyimides containing benzonitriles were synthesized. Introduction of the unsymmetrical structures improved the processibility of poly(amic acids) (PAAs) and increased the PI dielectric constants while the dielectric loss was low. As a continuing effort to probe the structural factors to balance the need for high dielectric constant, low dielectric loss, and thermal stability in high temperature capacitors, polyimides containing three benzonitrile groups were synthesized. Thus, diamines containing three benzonitriles were synthesized via a 3-step route. They were polymerized with four commercial dianhydrides in DMAc to afford poly(amic acid) solutions, which were thermally cured up to 300 °C to form tough, creasable films. Most of polyimides are soluble in common solvents. Their glass transition temperatures range from 216 to 305 °C. The polyimides are stable up to 400 °C. The dielectric constants of these polyimides increased from 2.9 (CP2) to 4.3 (6FDA-based polyimide) at 10 Hz.



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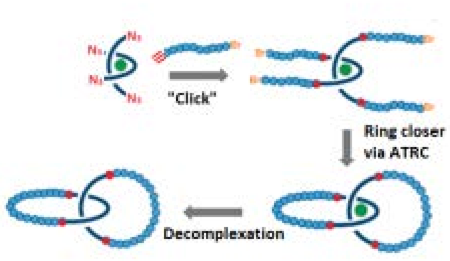
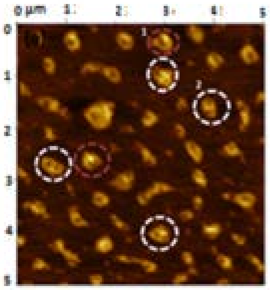
315 - Synthesis of polymer catenanes via combination of “grafting to” approach by click method and atom transfer radical coupling

Ajaykumar Bunha[1], *avbunha@uh.edu, Joey Mangadlao*[2], *Edward Foster*[1], *Katrina Pangilinan*[2], *Rigoberto Advincula*[1,2]. *(1) Department of Chemistry, University of Houston, Houston, TX 77204, United States, (2) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

A novel route for the synthesis of polymer catenanes was demonstrated by (1) grafting an alkyne functionalized polymer to an azide functionalized phenanthroline copper(I) complex via CuAAC “click” reaction, and (2) ring closing via intra-molecular atom transfer radical coupling of the resulting four arm-type polymers with halide as an end group functionality. The metal free polymer catenanes was obtained by removal of copper from the template and characterized by reduced hydrodynamic volume in GPC and direct visualization by AFM.





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316 - Cu(0)-mediated living radical polymerizations

Christopher Waldron*, c.s.waldron@warwick.ac.uk, David M Haddleton, Paul Wilson, Athina Anastasaki. Department of Chemistry, The University Of Warwick, Coventry, England CV4 7AL, United Kingdom*

Herein, recent developments in Cu(0)-mediated radical polymerization from the Haddleton group will be presented.

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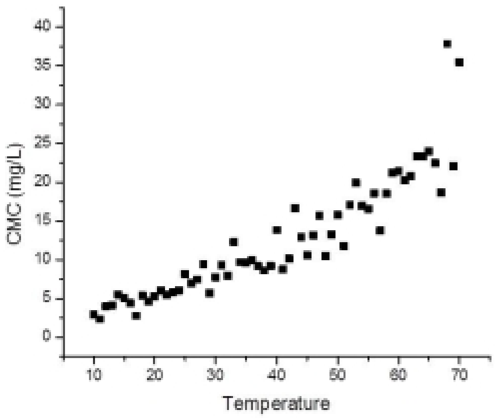
317 - On the thermal behavior, drug loading capacity, and thermally triggered release from polymer micelles made from poly(ethylene glycol-b-caprolactone-b-ethylene glycol) triblock polymers

***Jacqueline A Nikles**[1], nikles@uab.edu, Amanda L Glover[2], Sarah M Nikles[1], David E Nikles[2]. (1) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240, United States, (2) Department of Chemistry, The Univesity of Alabama, Tuscaloosa, Alabama 35487-0336, United States*

Two triblock polymers were prepared by condensing two equivalents of the diblock copolymer, CH_3O-$(CH_2CH_2O)_{43}$-$(COCH_2CH_2CH_2CH_2CH_2O)_9$-H, with one equivalent of either hexamethylene diisocyanate or isophorone diisocyanate. Another triblock polymer was prepared by condensing two equivalents of poly(ethylene glycol) monomethylether, M_n~2,000, two equivalents of isophorone diisocyante and one equivalent of polycaprolactone diol M_n~14,000. The CMC increased with increasing temperature, see figure below, and was in the range of 5 to 10 mg polymer per liter at 25 °C. Microcal DSC showed a melting endotherm indicating the polycaprolactone core was semi-crystalline. Dibucaine was loaded into the polymer micelles and the isothermal release rate was determined at 37 °C and at 57 °C.



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

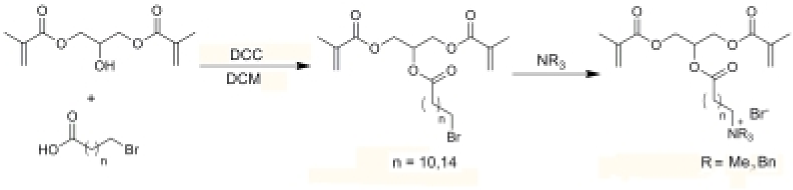
Location: Morial Convention Center

Room: Hall E

318 - Synthesis and characterization of new antibacterial dental monomers

***Stephen Costin**, scosti@lsuhsc.edu, Yapin Wang, Sumei Liao, Zezhang T. Wen, Thomas Lallier, Xioming Xu. Comprehensive Dentistry and Bimaterials, Louisiana State University Health Sciences Center, New Orleans, Louisiana 70119, United States*

The objective of this study is to synthesize new antibacterial dental monomers based on quaternary ammonium salts and test them for cytotoxicity and antibacterial activity against cariogenic bacteria and other bacteria. New antibacterial dental monomers have been synthesized and characterized by NMR, IR and MS. They have been tested for cytotoxicity with human gingival fibroblast cells and all were found to be biocompatible at concentrations of 10^{-5} M and below. Their efficacy in inhibition of planktonic growth of four bacteria (*Streptococcus mutans, Lactobacillus casei, Staphylococcus aureus and Pseudomonas aeruginosa)* was examined using Bioscreen^{TM}. The results indicate that monomers containing a long (i.e. hexadecyl) alkyl chain are superior to their shorter chain counterparts. The monomers containing alkyl dimethylbenzyl ammonium salts were better than the similar structures containing 1,4-diazabicyclo[2.2.2]octane (DABCO) in some cases. The long-chain antibacterial dimethacrylate monomers showed activities slightly less than or comparable to chlorhexidine in all cases.



Synthesis of new antibacterial quaternary ammonium dimethacrylates

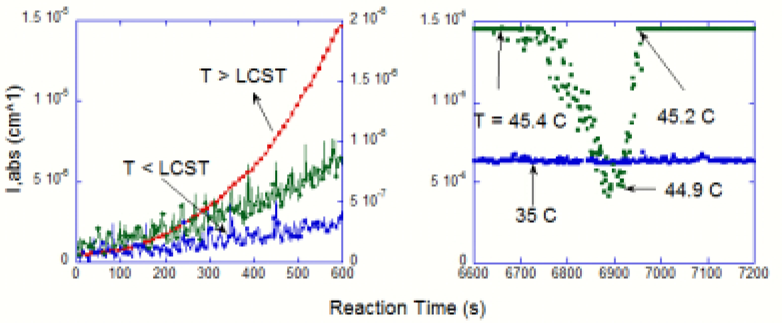
Tuesday, April 9, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

319 - LCST of NIPAM-Am copolymers: During synthesis characterization and salt effects

Colin A McFaul, *cmcfaul@tulane.edu, Michael F Drenski,* ***Wayne F Reed****, wreed@tulane.edu. Department of Physics and Engineering Physics, Tulane Univesity, New Orleans, LA 70118, United States*

Second Generation ACOMP (SGA) is used to measure, during synthesis, the LCST of copolymers of N-isopropyl acrylamide (NIPAM) and Acrylamide (Am). The polymers are synthesized in aqueous solution below the LCST via a redox-coupled initiation. The instrument consists of a series of temperature controlled light scattering flow cells attached to a custom-built ACOMP system (automatic continuous online monitoring of polymerization reactions). In this work, the ACOMP detector stream provides copolymer composition, molecular weight, viscosity, etc. SGA provides light scattering detection of LCST, allowing correlation of LCST behavior with polymer characteristics as they evolve during the reaction. Light scattering is highly sensitive to aggregation: the absolute Raleigh scattering ratio (I,abs, left-hand side of the figure) indicates LCST almost immediately in the reaction.

Several authors have demonstrated that the copolymer system of N-isopropyl acrylamide and Acrylamide is very low drift, and have measured the variation of LCST with composition within this system.The temperature probes of SGA operate on a time scale much faster than the reactions used in this work. As a result, SGA can measure LCST very precisely via a sweep of the temperature controller during the reaction (right-hand side), while the polymer properties remain essentially unchanged. Offline reactions measure the effect of salt on the resulting copolymers.



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

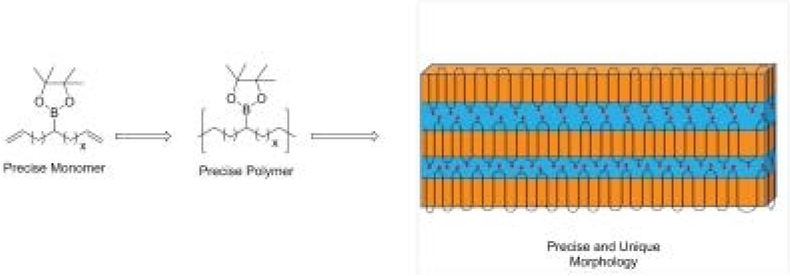
Location: Morial Convention Center

Room: Hall E

320 - Precision boronic ester polymers

Chester Simocko, *simocc@ufl.edu, Thomas Young, Ken Wagener. George and Josephine Butler Polymer Research Laboratory, University of Florida, Gainesville, Florida 32611, United States*

By using Acyclic Diene Metathesis (ADMET) polymerization, precision boronic ester polymers have been made. Both aryl and alkyl precision monomers have been synthesized using a copper (1) catalyzed borylation reaction. Polymerization of the precise monomers in BMIM-PF_6 yielded polymers with $M_w$of over 100kDa. These polymers were then exhaustively hydrogenated to form a polymer with boronic ester pendant groups and a polyethylene backbone. The thermal properties of both the unsaturated and saturated polymers have been studied.



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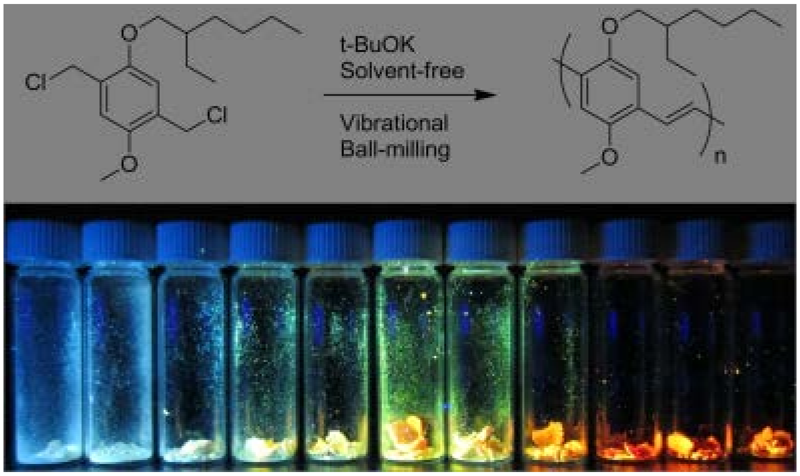
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

321 - Ball-Milling, a method for solid state polymerization

***Jens B Ravnsbaek**, jensb@mit.edu, Timothy M Swager. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Ma 02139, United States*

Conjugated organic polymers are a promising class of materials with a wide range of applications. Conjugated polymers, such as poly(phenylenevinylene)s, are typically synthesized by solution-based chemistry.

Here we report the synthesis of conjugated organic polymers by a mechanochemical method, namely ball milling. Poly(phenylenevinylene)s were prepared by solid state polymerization. The polymers were characterized by NMR, GPC, IR and UV-Vis. Moreover, the scope and generality of the solid state ball mill polymerization were examined by utilizing monomers incompatible with solution-based polymerization.

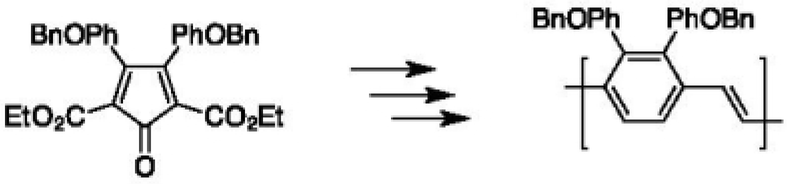


Tuesday, April 9, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

322 - Benzyloxy substituted poly(phenylene vinylene)s

Ryan Oostendorp, *roostey@gmail.com, William Feld. Chemistry, Wright State University, Dayton, OH 45435, United States*

Poly(p-phenylenevinylene)s (PPV) have been used in electronic devices such as LED displays and semi-conducting systems. Cyclopentadienones (CPD) have been employed as PPV precursors as carriers of various electron-donating and electron-withdrawing substituents. Alkoxy substituted PPV precursor cyclopentadienones are rare because of the low solubility of the CPD benzil component. Thus, 4,4'-dimethoxybenzil was demethylated and alkylated with benzyl chloride to provide a bisbenzyloxy CPD precursor. Conversion to the corresponding PPV will be presented.



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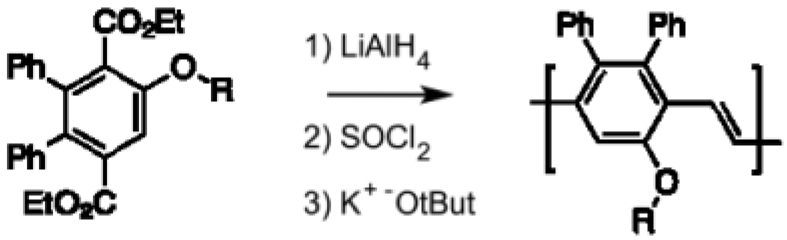
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

323 - Main chain alkoxy/hydroxy substituted PPV

Jeremy M. Lear, *lear.2@wright.edu, William A. Feld. Department of Chemistry, Wright State University, Dayton, OH 45435, United States*

Phenylene vinylenes (PPV) have been employed as LEDs and as components in solar cells. The addition of a phenolic function to the PPV main chain should influence not only the electronic properties of the PPV but the processing parameters as well. The reaction of 2,5-dicarboethoxy-3,4-diphenylcyclopentadienone and ethynylboronic acid MIDA ester produced an aromatic boronate which when oxidized provided a scaffold for main chain ether substitution. The corresponding polymer was analyzed by GPC, TGA, DSC and for photoconductivity.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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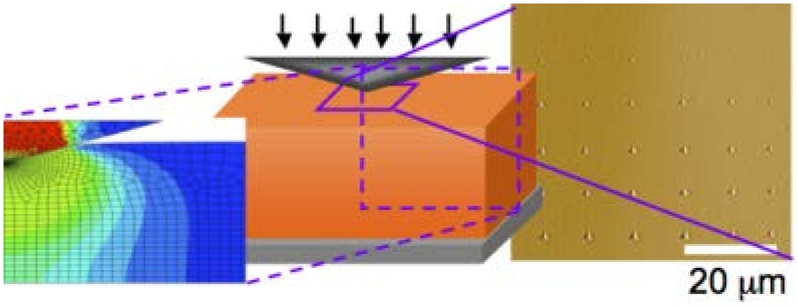
Room: Hall E

324 - New nanoindentation methodology for measuring local elastic modulus of nanostructured polymer systems

Supinda Watcharotone[1,2], *supinda@u.northwestern.edu, Xu Cheng*[1], *Yang Li*[3], *L. Cate Brinson*[1,3]. *(1) Mechanical Engineering, Northwestern University, Evanston, Illinois (IL) 60208, United States, (2) National Nanotechnology Center, National Science and Technology Development Agency, Pathum Thani, Pathum Thani 12120, Thailand, (3) Materials Science and Engineering, Northwestern University, Evanston, Illinois (IL) 60208, United States*

Nanostructured polymers play an important role in functional composite materials and thin films in various applications from electronics to medicine. A method to directly measure local mechanical properties of nanostructured polymer systems will be presented. A nanoindentation technique was implemented to investigate confined polymer systems and deconvolute the effects of substrates and chemical interactions at interfaces. Poly(methyl methacrylate), polystyrene and poly(2-vinyl pyridine) films coated on silica and alumina substrates were measured by nanoindentation. Results show that non-covalent chemical interactions are critical to the local changes of modulus. The chemical interactions at interfaces were determined indirectly by the work of spreading and surface energies based on the acid-base approach. This work sheds light on the roles of confinement and chemistry on mechanical properties.



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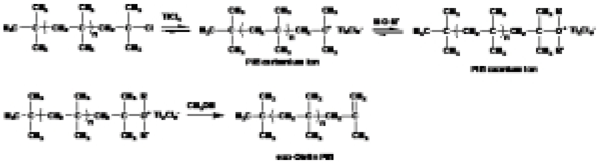
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

325 - Quantitative synthesis of *exo*-olefin-terminated polyisobutylene by ether quenching of living polyisobutylene

Subramanyam Ummadisetty, *s.ummadisetty@gmail.com*, *Robson F Storey*. *School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States*

Abstract: Addition of a dialkyl ether, e.g., diisopropyl ether (DIPE) or di-*sec*-butyl ether (DSBE), to a TiCl$_4$-co-initiated, living carbocationic polymerization of isobutylene (IB) results in capping of the chain ends with PIB diisopropyl oxonium cations, as evidenced by cessation of polymerization. Structure of PIB diisopropyl oxonium cations was determined using low temperature 500 MHz ^{1}H NMR, by introducing diisopropyl ether to a mixture of TiCl$_4$ and 2-chloro-2,4,4-trimethylpentane (TMPCl), a model for the PIB chain end, at -70°C in CS$_2$/CD$_2$Cl$_2$ (50/50, v/v). One-pot, two-step quantitative synthesis of mono- and *telechelic* (difunctional) *exo*-olefin-terminated polyisobutylene (PIB) was achieved by quenching living PIB with DIPE, followed by termination with methanol at -60°C. TMPCl and 1,3-*bis*(1-chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC) were used as mono- and difunctional initiators respectively for IB polymerization. ^{1}H NMR spectroscopy was used characterize the end-group composition of PIBs. Percent formation of *exo*-olefin was directly related to the steric bulk of the ether, i.e., *sec*-butyl (100%) » isopropyl (100%) > *n*-alkyl (68.5-81.5%). For [DIPE]/[CE] = 3, quantitative mono- and *telechelic* (difunctional) *exo*-olefin-terminated PIB was observed at [CE] = 0.1 M, for reaction volumes about 1 dL.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
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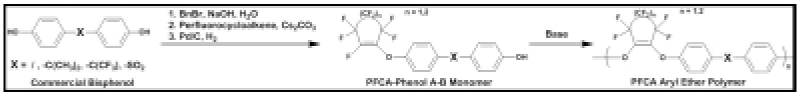
326 - AB-type monomers for the synthesis of perfluorocycloalkene (PFCA) aryl ether polymers

Raymond Campos, *raymond.campos.32@gmail.com, Dennis W Smith. Department of Chemistry and The Alan G. MacDiarmid Nano Tech Institute, The University of Texas at Dallas, Richardson, Texas 75080, United States*

AB-type monomers for the synthesis of perfluorocycloalkenyl (PFCA) aryl ether polymers were successfully prepared via a 3-step process using commercially available reagents. AB monomers and intermediates were characterized by multi-nuclear NMR spectroscopy, GC-MS, FTIR-ATR, combustion elemental analysis, and single crystal X-ray diffractometry. Resultant polymers were characterized by multi-nuclear NMR spectroscopy, GPC, TGA, DSC, and MALDI-TOF MS. Significant gains in molecular weight, molecular weight reproducibility and polymerization rate were observed with the newly synthesized monomers in comparison to analogous AA/BB systems. Melt-phase and block copolymerizations are also enabled with title monomers, expanding the utility of recently developed perfluorocycloalkene containing aryl ether polymers. Full characterization of title compounds as well as initial polymerization rate and molecular weight data will be presented and discussed.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

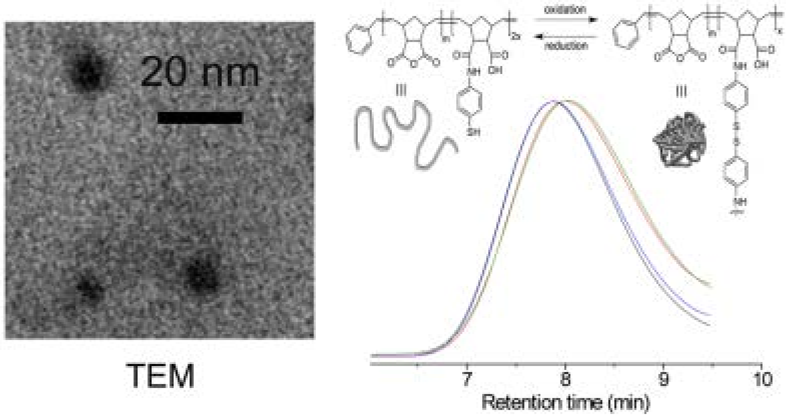
Location: Morial Convention Center

Room: Hall E

327 - Single-chain polymer nanoparticles via reversible disulfide bridges

Bryan T. Tuten, *btr43@wildcats.unh.edu, Danming Chao, Christopher K Lyon, Erik B Berda. Department of Chemistry and Materials Science Program, University of New Hampshire, Durham, NH 03824, United States*

We report the synthesis of a linear polymer that reversibly undergoes intramolecular cross-linking to fold from an expanded coil into a globule utilizing disulfide bridges. We showcase this route to synthesizing robust, reversible single-chain polymeric nanoparticles that respond to reductive and oxidative stimuli. Characterization via size exclusion chromatography with in-line multi-angle laser light scattering and viscometry confirms changes in absolute molecular weight and conformation.



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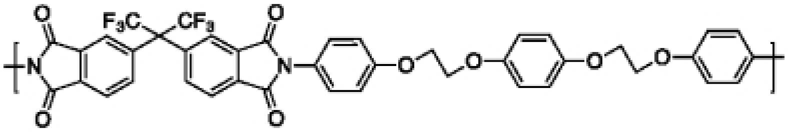
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

328 - Novel oxyalkylene polyimides

Kristy Wickman, *wickman.3@wright.edu, William A Feld. Wright State University, Dayton, Ohio 45435, United States*

Flexible oxyalkylene ether linkages within the polyimide backbone have been shown to decrease T_g but do not have a deleterious effect on thermal stability. We have investigated the incorporation of the 1,4-bis(phenoxyethoxy)phenyl unit into polyimides employing a variety of dianhydrides. The diamine can be synthesized by reaction of p-fluoronitrobenzene with 1,4-bis(hydroxyethoxybenzene to give the dinitro compound followed by reduction to the diamine by catalytic or chemical hydrogenation. The high melting point of the diamine correlates well with physical properties.



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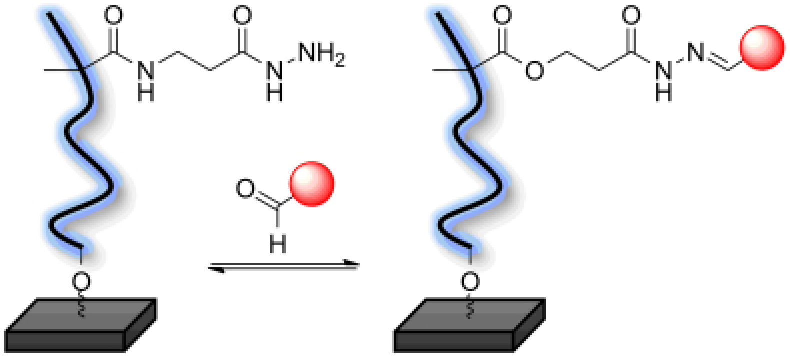
329 - Hydrazone-based dynamic covalent chemistry for reversible brush surface modification

Emily A Hoff, *emily.hoff@eagles.usm.edu, Will K Adkins, Ryan M Hensarling, Arthur LeBlanc, Derek L Patton. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

The development of surface modification techniques for “on-demand” control of surface properties is essential in order to engineer modular surface platforms with a high degree of control over complexity, functionality, and responsiveness to external stimuli. Most examples of surface modification are irreversible; however, “on-demand” reversible functionalization of surfaces would enable strategies such as “catch-and-release” and “reusable” surfaces important for advances in biosensors, self-healable materials, antifouling coatings, etc. Dynamic covalent chemistry (DCC) can be used to establish reversible covalent bonds that are responsive to external stimuli such as pH, UV light, and temperature. Dynamic covalent hydrazone linkages, which are formed through an imine reaction of a hydrazide moiety and an aldehyde or ketone, are responsive to changes in pH while still exhibiting reasonable product stability thus making this chemistry an ideal handle for controlling surfaces properties.



Dynamic Brush Surface Functionalization

In order to facilitate “on-demand” control of surface properties, pH-responsive, reversible hydrazone linkages were incorporated substituents on polymer brush surfaces via surface-initiated atom transfer radical polymerization (SI-ATRP) and subsequent post-polymerization modification (PPM). Reversible changes in wettability of substrates were achieved over multiple cycles through the formation of hydrazone linkages with various hydrophobic/hydrophilic aldehydes or ketones. This research also investigated changes in surface wettability via an *in situ* exchange, or transamination, reaction between surface bound aldehydes and aldehydes in solution were investigated enabling changes in functionalization without separate hydrazone formation and reversal steps.

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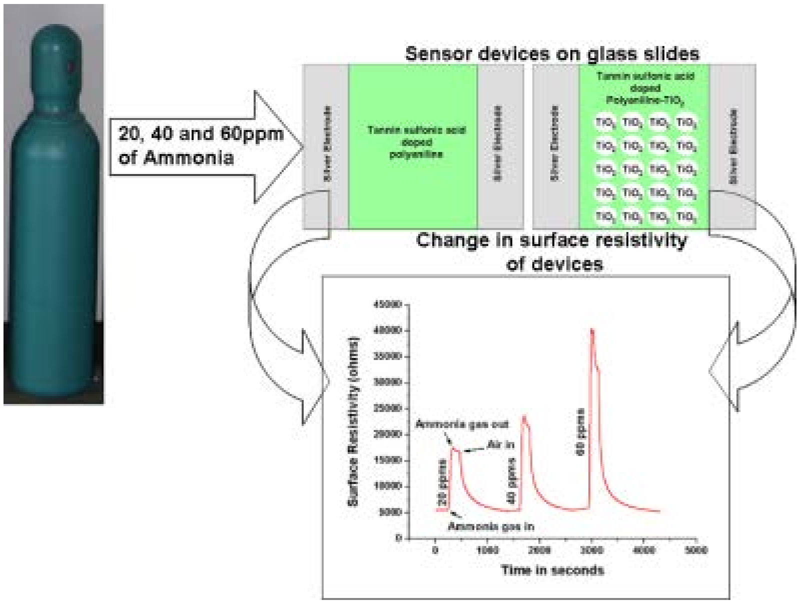
330 - Ammonia gas sensing applications of tanninsulfonic acid-doped polyaniline-titanium dioxide nanocomposites

Venu Gopal Bairi, *vxbairi@ualr.edu, Dev Nair, Shawn E Bourdo, Regis Viaud, Nicholas Sacre, Brian C Berry, Tito Viswanathan. Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72204, United States*

Tannin-sulfonic acid doped polyaniline-titanium dioxide nanocomposites were synthesized by *in situ* polymerization of aniline in the presence of varying amounts (10%-70%) of titanium dioxide nanoparticles. Incorporation and interaction of the titanium dioxide into polyaniline matrix was confirmed by the X-ray diffraction, thermogravimetric analysis and infrared spectroscopy. Ammonia gas sensing behavior of different nanocomposites films were analyzed by recording the change in surface resistivity of these films with time, when exposed to different concentrations (20ppm, 40ppm and 60ppm) of ammonia gas. All the nanocomposites showed better response and shorter recovery times when compared to the tannin-doped polyaniline alone. Ammonia gas sensing plots showing a) response versus content of TiO_2 in polymer-nanocomposites and b) recovery times versus content of TiO_2 in polymer-nanocomposites will be presented.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

Location: Morial Convention Center

Room: Hall E

331 - Novel bicyclic monomers provide alternating ROMP copolymers without backbiting

Li Tan, *li.tan@stonybrook.edu, Airong song, Jae chul Lee, Kathlyn A Parker, Nicole S Sampson. Chemistry, SUNY at Stony Brook, Stony Brook, NY 11790-3400, United States*

Copolymers are employed in applications ranging from the biomedical to the electronic. Previously, a series of cyclo butene derivatives with different electron densities were synthesized and studied for their ability to react with Grubbs catalysts in alternating ring-opening metathesis polymerization (AROMP). Methyl 1-cyclobutenecarboxylate and cyclohexene alternately react with ruthenium alkylidene catalyst to provide highly alternating copolymers. However, intramolecular back-biting of the enoic ruthenium carbene on the unstrained disubstituted olefinic bonds in the growing polymer chain reduces the molecular weight and increases the molecular weight distribution (PDI) of these polymers. To address back-biting, a series of new steric monomers were synthesized and employed in AROMP. Introduction of a cyclohexyl ring into one of the AROMP monomers to provide methyl bicyclo[4.2.0]oct-7-ene-7-carboxylate eliminated back-biting

. Therefore, perfectly alternating, linear polymers are now available through ruthenium-catalyzed AROMP.

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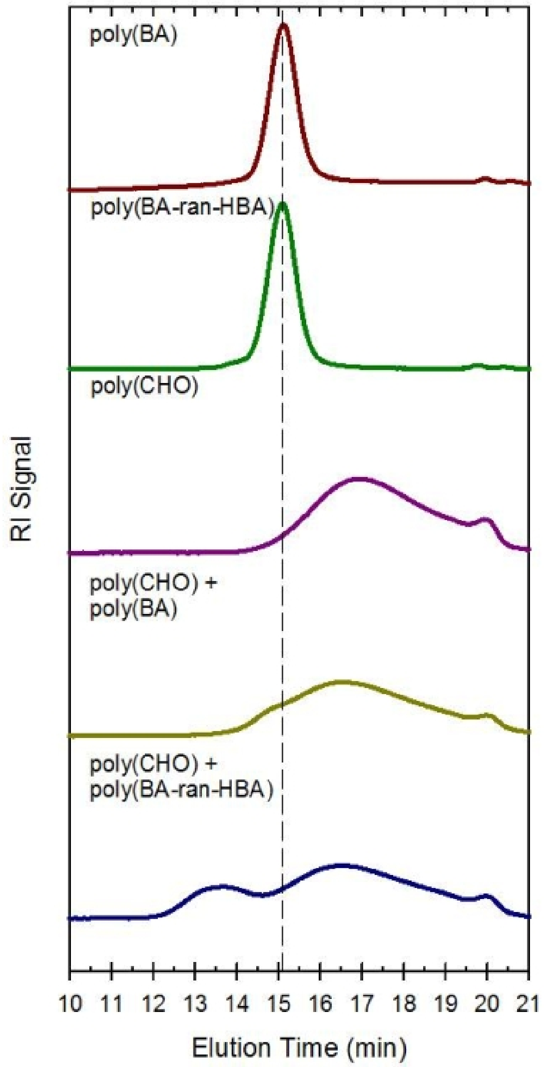
332 - Grafting epoxides: Using the activated monomer mechanism to decorate acrylate polymers

Brian Dillman, *brian-dillman@uiowa.edu, Julie L.P. Jessop. Chemical and Biochemical Engineering, University of Iowa, Iowa City, IOWA 52242, United States*

Photopolymerization is an important technology for coatings, films and adhesives industries. Cationically polymerizable monomers offer much less demanding reaction conditions in comparison to free radically polymerizable monomers. Epoxides may be polymerized by two parallel mechanisms one called the Active Chain End (ACE) mechanism, which is a chain-growth mechanism. The other is called the Activated Monomer (AM) mechanism, which is promoted by the addition of organic alcohols. In this work the physical effects of the AM mechanism are studied. Acrylate polymers were prepared via controlled radical polymerization and epoxide monomers were subsequently grafted from the pendant hydroxyl groups. Grafting was confirmed and quantified via Gel-Permeation Chromatography analysis.



The acrylate polymers and monomers were prepared in a crosslinking epoxy resin. The resins were photo-cured and analyzed via Dynamic Mechanical Analysis. The AM mechanism has profound effects in property modulation based on the relative concentration of hydroxyl to epoxide functional groups.

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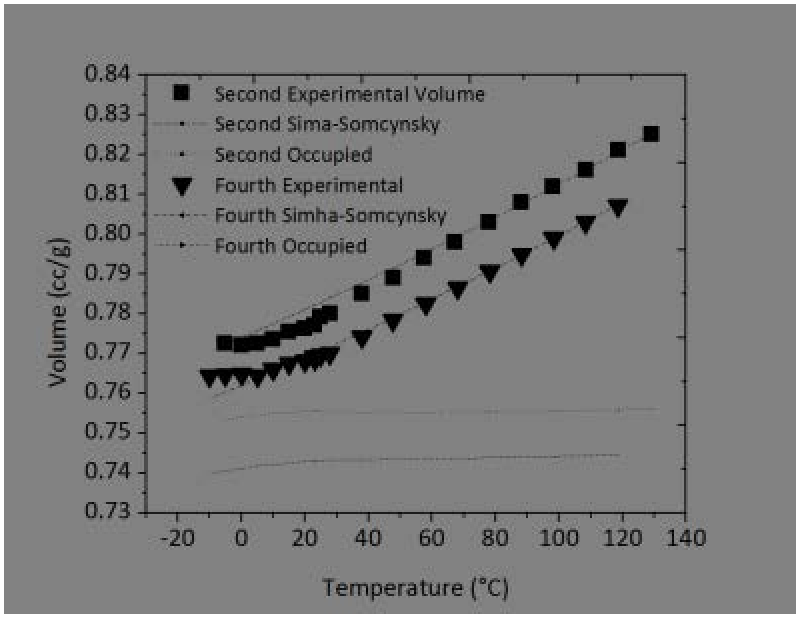
333 - Thermodynamic and volumetric comparison of second and fourth generation bis-MPA based hydroxylated hyperbranched polyesters: Free volume and structural ordering

***Maliha N Syed**, maliha.n.syed@gmail.com, Sergei Nazarenko. Department of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS - Mississippi 39406, United States*

Ubiquitous hydroxyl end groups and high branching densities lend hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) applications ranging from biodegradable drug carriers and nanocomposites to additives in coatings. The origins of hydrogen bond driven structural ordering in the second and fourth generations was explored. Positron annihilation lifetime spectroscopy yielded average-hole free volume while pressure-volume-temperature dilatometry obtained total specific volume, total free volume, occupied volume, and thermal expansion. Rheological data showed a viscosity build-up and also yielded free volume parameters.



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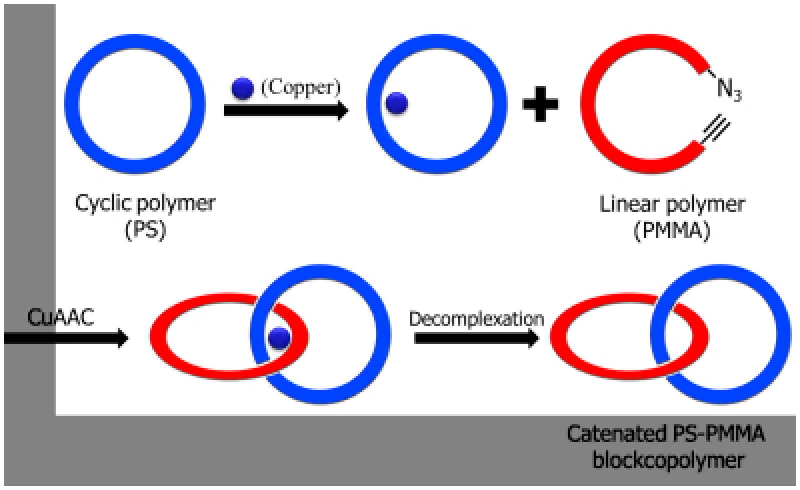
334 - Synthesis of polymer[2]catenane by azide-alkyne Huisgen cycloaddition

***Katrina Pangilinan**, kdp33@case.edu, Rigoberto Advincula. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States*

Polymers with different topologies such as linear, star, dendritic and brush have been widely studied. However, synthesizing entangled topologies such as catenanes and knots remains a challenge. Here, we report a synthesis method to obtain polymer[2]catenane through the active metal template approach. This strategy uses metal-mediated bond formations for the synthesis of catenanes, where the template assembly of a macrocyclic polymer and an acyclic polymer about the metal ion is followed by a covalent bond-forming reaction between the end groups of the acyclic polymer, catalyzed by the same metal ion. The linear polymer was designed with azide and alkyne terminal groups for the subsequent Copper-Assisted Azide-Alkyne Cycloaddition (CuAAC). In this study, Cu^{+1} was used to form the template between the cyclic and the linear polymer and to catalyze the "click reaction". Demetalation yields polymer[2]catenanes.



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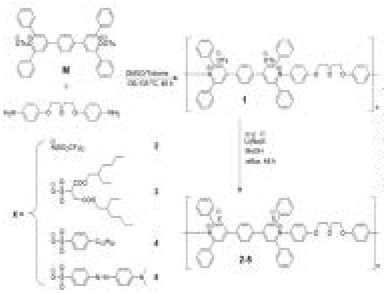
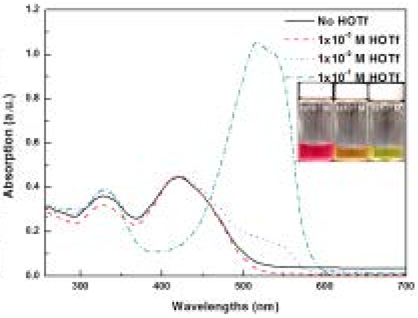
335 - Synthesis and characterization of poly(pyridinium salt)s containing dioxyethylene units in the main-chain and their sensing performance toward acids in organic solvents

Tae Soo Jo[1], ***Jung Jae Koh***[1], *kohj@unlv.nevada.edu, Alexi K Nedeltchev*[1], *Haesook Han*[1], *Pradip K Bhowmik*[1], *Hari D Mandal*[2]. *(1) Department of Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada 89154, United States, (2) Department of Biology and Chemistry, Texas A&M International University, Laredo, Texas 78041, United States*

A series of poly(pyridinium salt)s with dioxyethylene units were synthesized through the ring-transmutation polymerization reaction of bispyrylium ditosylate salt and the dioxyethylene containing diamine, and its counterions were exchanged to different organic anions via the metathesis reactions. Their chemical structures were confirmed from their ^1H and ^{13}C NMR spectra and elemental analysis. Their absorption and photoluminescent properties were measured by UV-Vis and luminescence spectrometer, respectively.





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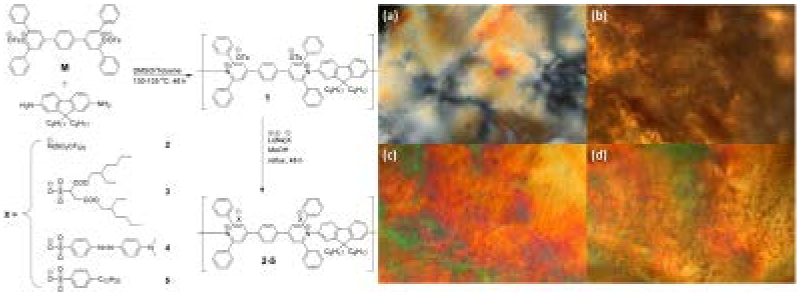
336 - Synthesis of poly(pyridinium salt)s containing fluorene moieties in the main-chain with various organic counterions

*Tae Soo Jo, **Jung Jae Koh**, kohj@unlv.nevada.edu, Haesook Han, Jongwon Park, Bidyut Biswas, Pradip K Bhowmik. Department of Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada 89154, United States*

A series of poly(pyridinium salt)s containing fluorene moieties in the main-chain and various organic counterions were synthesized through a ring-transmutation polymerization reaction of bispyrylium ditosylate salt and 9,9¢-dioctyl-9H-fluorene-2,7-diamine and metathesis reactions. Their chemical structures were characterized by FTIR, ^{1}H and ^{19}F NMR spectroscopy. They exhibited lyotropic liquid-crystalline properties in polar organic solvents. Their light-emission properties showed a positive solvatochromism, i.e., their l$_{em}$ peaks shifted bathochromically on changing the polarity of the solvents.



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

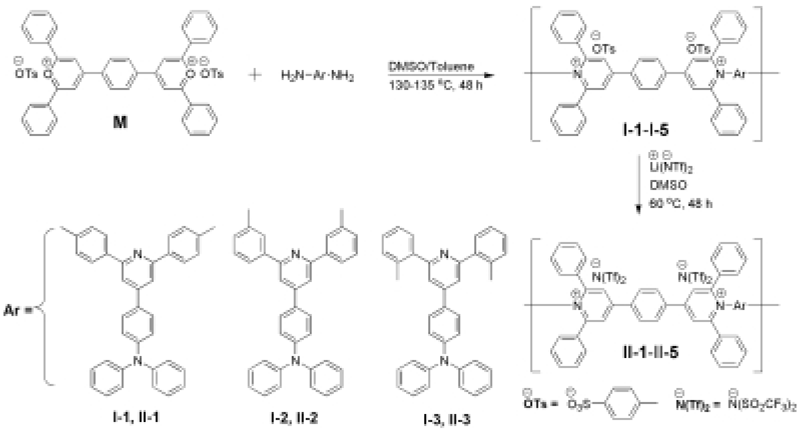
Location: Morial Convention Center

Room: Hall E

337 - Synthesis of poly(pyridinium salt)s containing heterocyclic pyridine and triphenylamine moieties in the main-chain and their solution, thermal and optical properties

*Tae Soo Jo[1], **Jung Jae Koh**[1], kohj@unlv.nevada.edu, Haesook Han[1], Pradip K Bhowmik[1], Hari D Mandal[2]. (1) Department of Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada 89154, United States, (2) Department of Biology and Chemistry, Texas A&M International University, Laredo, Texas 78041, United States*

A series of poly(pyridinium salt)s were synthesized by the ring-transmutation polymerization reaction of bispyrylium ditosylate salt with theheterocyclic pyridine and triphenylamine containing diamines on heating in dimethyl sulfoxide. From these tosylate polymers, the respective triflimide containing polymers were prepared via the metathesis reactions in a common organic solvent. Their chemical structures were confirmed by ^{1}H and ^{13}C NMR spectroscopic techniques and elemental analysis. Their absorption and emission properties were examined by using UV-vis and photoluminescence spectrometer, respectively.



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

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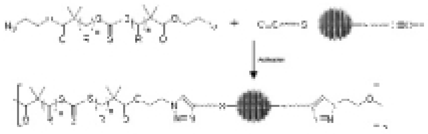
Room: Hall E

338 - Synthesis of gold nanoparticle chains via 1, 3-dipolar cycloaddition and reversible addition-fragmentation chain transfer (RAFT) polymerization

Eboni M Perkins, *eperkins@siu.edu, Daniel J Dyer, Colleen N Scott. Department of Chemistry and Biochemistry, Southern Illinois University-Carbondale, Carbondale, Illinois 62901, United States*

Our research is directed towards controlling the distance between gold nanoparticles in a nanoparticle chain. We envisioned a method that employs two facile techniques, 1, 3-dipolar cycloaddition (Click Chemistry) and reversible addition chain-transfer polymerization (RAFT) to prepare our nanoparticle chains. Our gold nanoparticles were functionalized with thiolated alkyne molecules which exposed alkyne moieties on the nanoparticle surface. Utilizing a new RAFT compound successfully synthesized in our laboratory, bis (2-azidoethyl)-2, 2'thiocarbonylbis (sulfaniyl) bis (2-methypropanoate), we were able to link the nanoparticles via the azide alkyne cycloaddition. To demonstrate the control of chain length and nanoparticle distance we varied the reaction times of each RAFT polymerization.



Tuesday, April 9, 2013 05:30 PM

General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

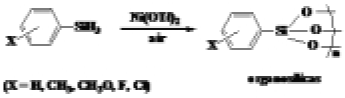
Location: Morial Convention Center

Room: Hall E

339 - Dry sol-gel polymerization of p-X-$C_6H_4SiH_3$ (X = H, CH_3, CH_3O, F, Cl) to organosilicas p-X-$C_6H_4SiO_{1.5}$ catalyzed by nickel(II) trifluoromethanesulfonate and nickel(II) hexafluoroacetylacetonate

Hyeonsook Cheong[1], *Jaeyoung Park*[1], *Ji Eun Noh*[2], ***Hee-Gweon Woo***[2], *hgwoo@chonnam.ac.kr, Myong-Shik Cho*[3]. *(1) Department of Biotechnology, Chosun University, Gwangju, Republic of Korea, (2) Department of Chemistry, Chonnam National University, Gwangju, Republic of Korea, (3) KFDA, Gwangju Regional Food and Drug Administration, Gwangju, Republic of Korea*

This work describes the dry sol-gel reaction of *p*-X-$C_6H_4SiH_3$ (X = H, CH_3, CH_3O, F, Cl) to *p*-$C_6H_4SiO_{1.5}$in high yield, catalyzed by nickel(II) salts such as acetate, triflate, hexafluoroacetylacetonate, which are then reduced to nickel(0) species. The highest yield, molecular weight, polydispersity index, and TGA residue yield were found for *p*-Cl-$C_6H_4SiH_3$. Some degree of unreacted Si-H bonds still remained in the gel probably because of obvious steric hindrance. X-ray powder diffraction patterns for all the insoluble gels were featureless, which suggests that the gels adopt an amorphous structure. SEM images of the gels exhibit a smooth surface regardless of the para-substituent. A plausible mechanism for the dry sol-gel reaction, mediated by Ni(0) catalytic species, was proposed based on the experimental results.



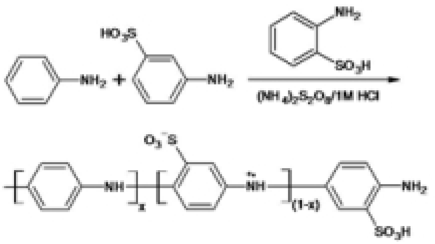
Tuesday, April 9, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

340 - Synthesis of end-group capped sulfonated polyaniline-based organic electrodes for human osteosarcoma cells

Yidong Liu[1], *yidong.liu@fangyuanyc.com, Yanyin Yang*[3]*, Yadagiri Poojari*[2]*, Derek Hansford*[3]*,* ***Yong Min***[1,2]*, yongm86@yahoo.com, Arthur Epstein*[2]*. (1) Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210046, China, (2) Department of Physics and Chemistry & Biochemistry, Ohio State University, Columbus, OH 43210, United States, (3) Department of Biomedical Engineering, Ohio State University, Columbus, OH 43210, United States*

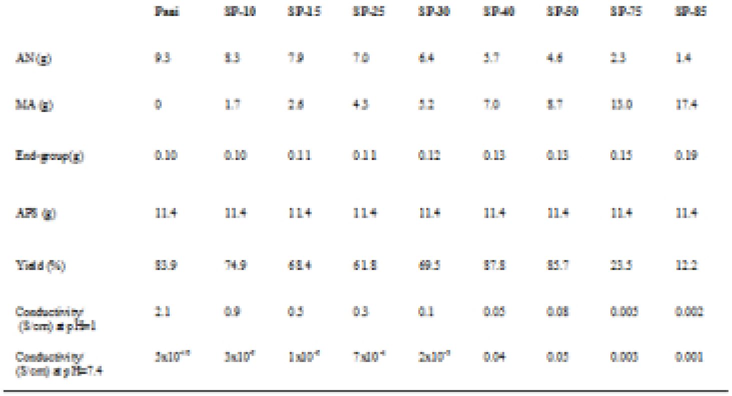
Electrically conducting polymers (CPs) were found to stimulate various cell types such as neurons, osteoblasts, fibroblasts in both *in vitro* and *in vivo*studies. Here we reported a facile method of synthesis and fabrication of self-doped sulfonated polyaniline (SPAN)-based interdigitating electrodes (SPAN-IDEs) with polymer chain terminator to control the length of polymer which might help us increasing the material's bio-degradability. Conductivity test showed they have the similar conductivity as the polymers without terminator which is much longer and harder to degrade. Increasing the degree of sulfonation was found to increase the SPAN conductivity as well.

Keywords: Sulfonated polyaniline; end-group capped.



Scheme 1. SPAN synthesis using aniline and metanilic acid (3-aminol-benzene sulfonic acid) monomers in 1M HCL with ammonium persulfate as an oxidant. 2-aminol-benzene sulfonic acid was used as a polymer chain terminator.

Table 1. Conductivity of the synthesized sulfonated polyaniline at pH ~ 1 and pH ~ 7.4, where PANI is polyaniline and SP-xx is SPAN with %xx indicating the degree of sulfonation.



	Pani	SP-10	SP-15	SP-25	SP-30	SP-40	SP-50	SP-75	SP-85
AN (g)	9.3	8.3	7.9	7.0	6.4	5.7	4.6	2.3	1.4
MA (g)	0	1.7	2.6	4.3	5.2	7.0	8.7	13.0	17.4
End-group(g)	0.10	0.10	0.11	0.11	0.12	0.13	0.13	0.15	0.19
APS (g)	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4
Yield (%)	83.9	74.9	68.4	61.8	69.5	87.8	85.7	23.5	12.2
Conductivity (S/cm) at pH=1	2.1	0.9	0.5	0.3	0.1	0.05	0.08	0.005	0.002
Conductivity (S/cm) at pH=7.4	$3x10^{-10}$	$3x10^{-6}$	$1x10^{-6}$	$7x10^{-4}$	$2x10^{-3}$	0.04	0.05	0.003	0.001

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341 - Biocompatibility studies of polyaniline-based materials by using osteosarcoma cells

Yidong Liu[1], *yidong.liu@fangyuanyc.com*, *Yadagiri Poojari*[2], *Yadagiri Poojari*[2], *Jen-Chieh Wu*[2], *Eason Hildreth*[3], *Tom Rosal*[3], ***Yong Min***[1,2], *yongm86@yahoo.com*, *Arthur Epstein*[2]. *(1) Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210046, China, (2) Department of Physics and Chemistry & Biochemistry, Ohio State University, Columbus, OH 43210, United States, (3) Department of Biomedical Engineering, Ohio State University, Columbus, OH 43210, United States*

Electrically conducting polymers (CPs) were found to stimulate various cell types such as neurons, osteoblasts, fibroblasts in both *in vitro* and *in vivo* studies. Here we report a facile fabrication method of self-doped sulfonated polyaniline (SPAN)-based interdigitated electrodes (IDEs) for controlled electrical stimulation of Osteosarcoma (OS) cells. Increasing the degree of sulfonation was found to increase the SPAN conductivity, which in turn improved the cell attachment and cell growth without electrical stimulation. We believe that these organic electrodes may find utility in electrical stimulation of cancer or tumour cells for therapy and research, and may also provide an alternative to the conventional metal based electrodes.

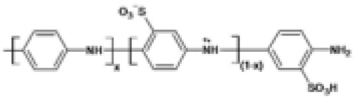

Figure 1. Structures of self-doped sulfonated polyaniline (SPAN)

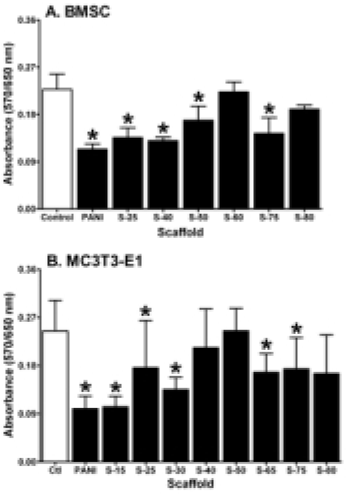

Figure 2. Assessment of SPAN biocompatibility by assessing the cellular proliferation of (a), BMSCs and (b), MC3T3-E1 cells, without electrical stimulation after 5 days of growth on SPAN with varying DS or control wells. *Denotes a statistically significant difference when compared to control ($P < 0.05$) as assessed with a 1-way ANOVA and a Dunnett's multiple comparison

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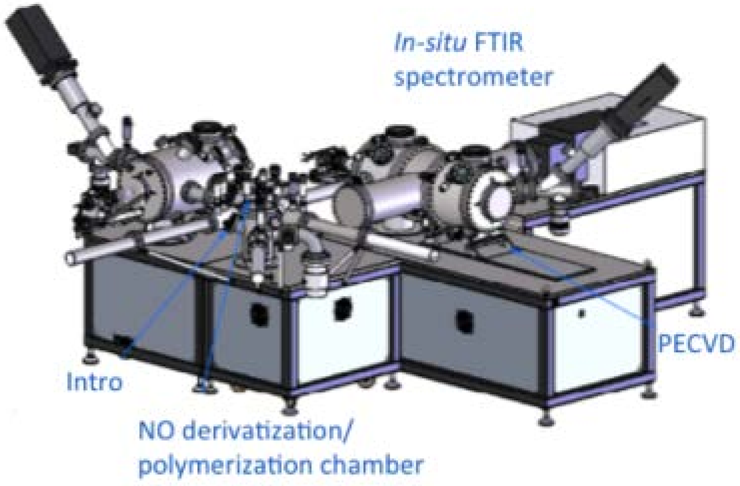
342 - Grafting of polymer brushes on free radicals generated during plasma polymerization deposition

***Farid Khelifa**, farid.khelifa@umons.ac.be, Sergey Ershov, Youssef Habibi, Rony Snyders, Philippe Dubois. Departement of Research in Science and Engineering of Materials, University of Mons, Mons, Mons 7000, Belgium*

Modern corrosion protective coatings for aluminum substrate are expected to present both strong barrier and self-healing properties. To fulfill these requirements, coating material is commonly comprised of several layers where at least one layer can be a highly cross-linked plasma polymerized film (PPF) deposited by plasma-enhanced chemical vapor deposition (PECVD). Depending on deposition parameters, this PPF might contain a certain amount of surface free radicals that can serve as initiation sites for conventional radical polymerization.

The aim of present work is to develop new multilayer coating materials using an isopropanol-based PPF from which free radicals were generated. Prior to the polymerization of the second polymeric layer, the optimal conditions to generate maximum density of free radicals on the PPF surface were determined using nitrogen monoxide (NO) as labeling agent. Successful polymerization of EHA was then carried out on the surface and optimized.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

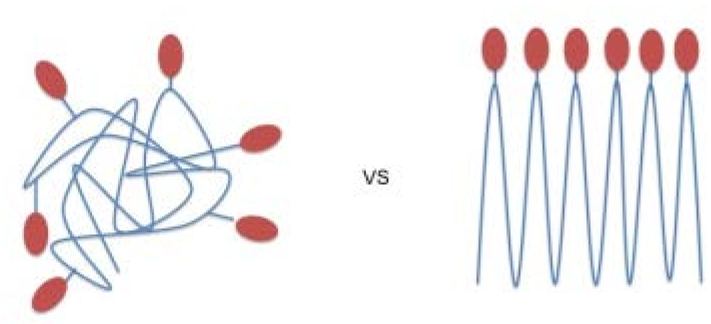
343 - Synthesis of siloxane branched polyolefins via ADMET polymerization for use as extruding aids

Pascale Atallah, *pascale@ufl.edu, Ken Wagener. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States*

Polyethylene, is one of the most widely used plastics because of its commercial and technical applications. Processing of polyethylene by extrusion can create meltfracture leading to defective products.

Silanes act as extrusion lubricants when used, by coating the inner surface of the extruder's cylinder as well as the screw and die.

ADMET chemistry will be used in order to synthesize precise siloxane branched polyethylene. The purpose being to find the right chain length, and number of siloxane units branched polymer that will improve the flow of polyethylene, leading to less melt-fractures during its processing. The rheological properties of the polymers synthesized will be studied and compared to the rheological properties of butyl branched polyethylene.



Random vs precise siloxane branches on polyethylene backbone

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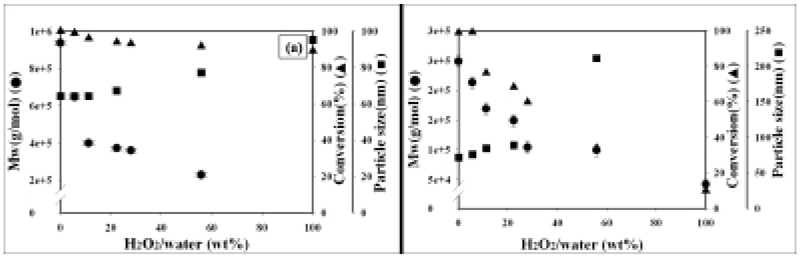
Room: Hall E

344 - Effect of H_2O_2 in emulsion polymerization of MMA

***Si Jung Lee**, sjtlwjddl@nate.com, Sung Eun Rhee, Soonja Choe. Department of chemical engineering, Inha university, Inchoen, Republic of Korea*

The emulsion polymerization of methylmethacrylate(MMA) and styrene(SM) was carried out using initiator, KPS, in the presence of SDS. As the amounts of hydrogen peroxide increased, the monomer conversion and molecular weight decreased, but the particle size increased. In addition, the surface tension of SDS showed CMC in water, resulting in the formation of micelle, but not in hydrogen peroxide. In order to verify the role of hydrogen peroxide in the medium mixture, the same polymerization of MMA was performed in the absence of KPS, and presence and absence of SDS. As a consequence, SDS was important to provide the polymerization site by forming a micelle and hydrogen peroxide was used as an initiator in the absence of KPS. In order to investigate the effect of surfactants, various surfactants, such as anionic, cationic and nonionic ones were used and discussed in terms of the monomer conversion, molecular weight and particle characteristics.

Polymerization(70 , 200rpm, 6hrs)		
Monomer	MMA, SM 10wt.%	MMA 10 wt%
Initiator	KPS	None
Medium	DI Water/H2O2 100/0, 94.4/5.6, 88.8/11.2, 77.7/22.3, 44.2/55.8, 0/100	
Surfactant(1.144mmol)	SDS(288.72g/mol)	SDS(288.72g/mol)
		Sodium 1-dodecanesulfonate(282.38g/mol)
		SDBS(348.48g/mol)
		Sodium Myristate(250.36g/mol)
		CPC Monohydrate(358.01g/mol)
		CTAB(364.46g/mol)
		TritonX-705(10,484g/mol)



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

Location: Morial Convention Center

Room: Hall E

345 - Synthesis and characterization of monodisperse carboxylated polystyrene microspheres

Ningning Ma, Chao Ma, ***Yongjun Tang****, tangyongjun32@163.com,* ***Nongyue He****, nyhe1958@163.com, Zhan Chen. State Key Laboratory of Bioelectronics, Southeast University, Nanjing, Jiangsu 210096, China*

Carboxylated polystyrene microspheres were synthesized via two methods: emuisifer-free emulsion polymerization method and dispersion polymerization method. In emuisifer-free emulsion polymerization research, at boiling status, potassium persulfate was used as initiator reagent to induce copolymerization of styrene and methacrylic acid. Scanning electronic microscope revealed that diameter increased with monomer concentration and decreased with initiator reagent concentration increased. Otherwise, diameter increased with temperature first then decreased. In dispersion polymerization process, micro-size carboxylated polystyrene were prepared via styrene and methacrylic acid, polyvinylpyrrolidone, azodiisobutyronitrile and ethanol as monomer, stabilizer, initiator reagent and medium. Finally, carboxylated polystyrene with smooth surface and dispersibility were obtained. The prepared microspheres were easily dissolve in non-polar or weak-polar solvents. In brief, uniform and controllable polystyrene have been effectively applied for several biofunctional carriers and the research on the interaction with cell membranes.

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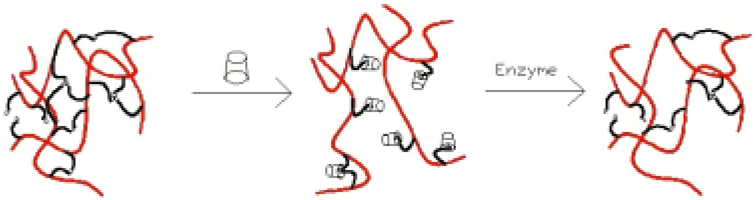
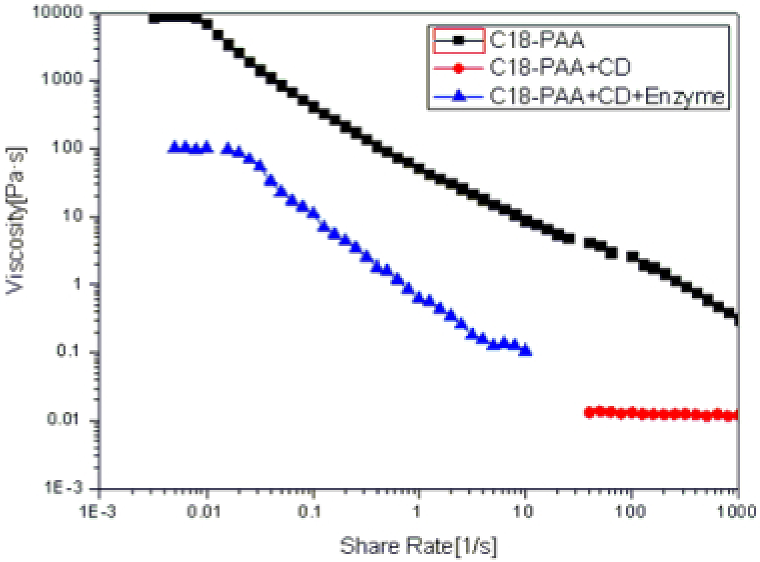
346 - Rheology modulation of hydrophobic associated polymeric networks by cyclodextrin inclusion and enzymatic degradation

*Weina Wang, Siyi Wang, **Xuhong Guo**, guoxuhong@ecust.edu.cn, Li Li. School of Chemical Engineering, East China University of Science and Technology, Shanghai, Shanghai 200237, China*

Systematic investigation on the rheology modulation of octadecyl (C18) modified poly(acrylic acid) (C18-PAA) by inclusive association between beta-cyclodextrin (CD) and C18 and the enzymatic degradation of CD was reported.



The hydrophobic association among C18 grafts in C18-PAA showed high viscosity over the critical concentration in waster. Upon addition of CD, the viscosity reduced dramatically because of the masking of C18 groups by CD with the inclusion association. After introduction of the enzyme a-amylase, the viscosity increased significantly due to the recovery of hydrophobic association by damaging a-1, 4 glycosidic bond of cyclodextrin.



In this way, the rheological properties of the hydrophobic associated polymeric networks can be tuned. This work opens a new way to prepare biodegradable polymeric networks for controlled drug delivery.

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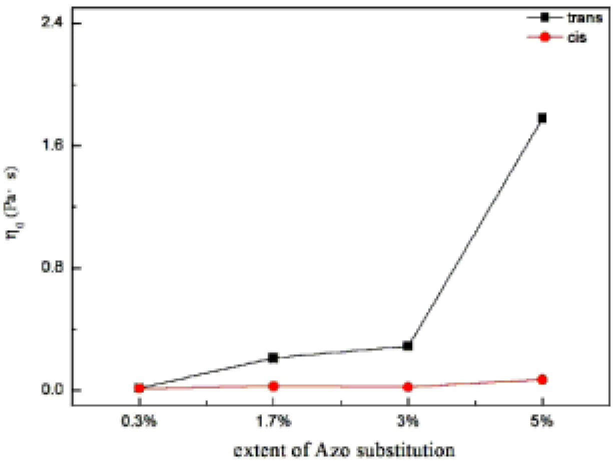
347 - Structural effect on viscosity of photoresponsive reversible hydrogel based on a-cyclodextrin and azobenzene polymers

Mingwei Wang, Li Li, Jie Wang, ***Xuhong Guo****, guoxuhong@ecust.edu.cn. School of Chemical Engineering, East China University of Science and Technology, Shanghai, Shanghai 200237, China*

Photo-responsive polymeric networks through host-guest complexation between the a-cyclodextrin (a-CD) substituent in poly(acrylic acid) (a-CD-PAA) and the azobenzene (Azo) derivative grafts in PAA (Azo-C_n-PAA, n = 0, 2, 6) were constructed. The UV-Vis spectrum showed that the complexation constant reached the maximum when n = 2. The rheology study showed that either increasing the mass concentration or the alkyl length, the zero-shear viscosity in both of Azo trans and cis configuration increased. With increasing the extent of Azo substitution, the zero-shear viscosity increased in Azo-trans configuration, while the kept constant in Azo-cis configuration



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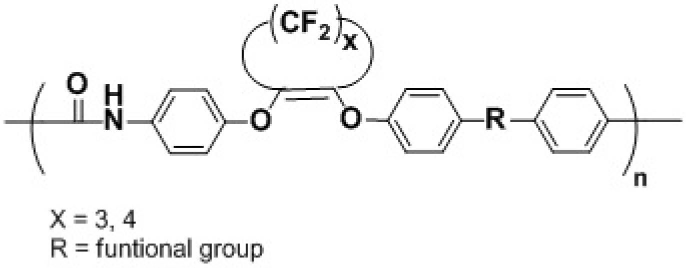
348 - Semi-fluorinated polyamide polymers

Babloo Sharma[1], *bsharma@utdallas.edu, Dennis W Smith*[1], *Shawna Liff*[2]. *(1) department of chemistry, University of texas at dallas, ichardson, texas 70580, United States, (2) components research, Intel Corporation, United States*

Here, we are reporting the synthesis of semi-fluorinated polyamide polymers containing perfluorocycoalkene (PFCA) moieties. Commercially available Octafluorocyclopentene (OFCP) and Decafluorocyclohexene (DFCH) are main constituents of PFCA family. We are demonstrating the synthesis of semifluorinated polyamide polymers via Polycondensation of dicarboxylic acids with PFCA containing diamine monomers (Scheme 1).



Scheme 1. Synthesis of Semifluorinated polyamides.

^{1}H, ^{19}F nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to characterize the polyamide polymers.

Keywords: Semi-fluoronated polymers, Polycondensation etc.

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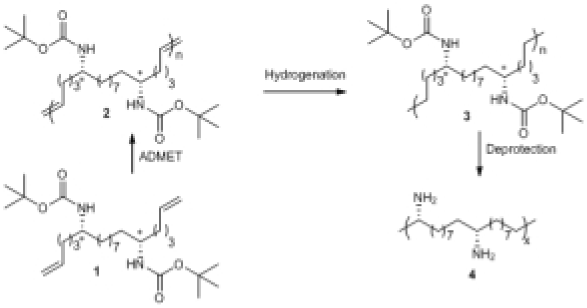
349 - Syndiotactic precision poly(ethylene-co-vinyl amine): Synthesis and thermal characterization

Chip Few, *chipfew@gmail.com, Henry Martinez, Ken Wagener. Chemistry Department, University of Florida, United States*

Tacticity control in polymers has been one of the most important challenges in the history of polymer chemistry. The work of Ziegler and Natta (1963 Nobel Prize) led to the production of isotactic polypropylene, one of the most widely used polymers in the world. While controlling the relative stereochemistry of branches on alternating carbons has a profound effect on polymer properties, we pose the question: “how far apart must the branches be before tacticity has no effect?” Herein we report the synthesis of tactic precision polymers bearing stereoregular amino groups on every ninth carbon on a polyethylene backbone.



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General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)

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350 - Preparation of high-k polyimide nanocomposite using plypyrrole-polyimide core-shell nanoparticles

Byoung Gak Kim, *byounggak@gmail.com, Ye Ji Hong, Young Seok Kim, Jong Chan Won. Division of Advanced Materials, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Republic of Korea*

Many approaches such as loading of PPy into polymer matrix for increased conductivity and for high capacitance have been attempted. However, conducting polymers have some of the drawbacks to the application such as their low environmental stability, poor mechanical properties and processability. To overcome these drawbacks, we designed a new high k dielectric material using core-shell (polypyrrole-polyimide) nanoparticles. It is expected that these show a low leakage current and dissipation factor because PI shells take a role of insulating layer. These PI shells can also improve dispersibility of particles due to compatibility between PI shells and polymer matrix. Therefore, high breakdown voltage and improved processability are also expected. In this presentation, we will describe the preparation of PPy@PI core-shell nanoparticles, the formation of all-polymer PI composite film using PPy@PI particles, and on the dielectric property and the mechanical property of PI composite film.

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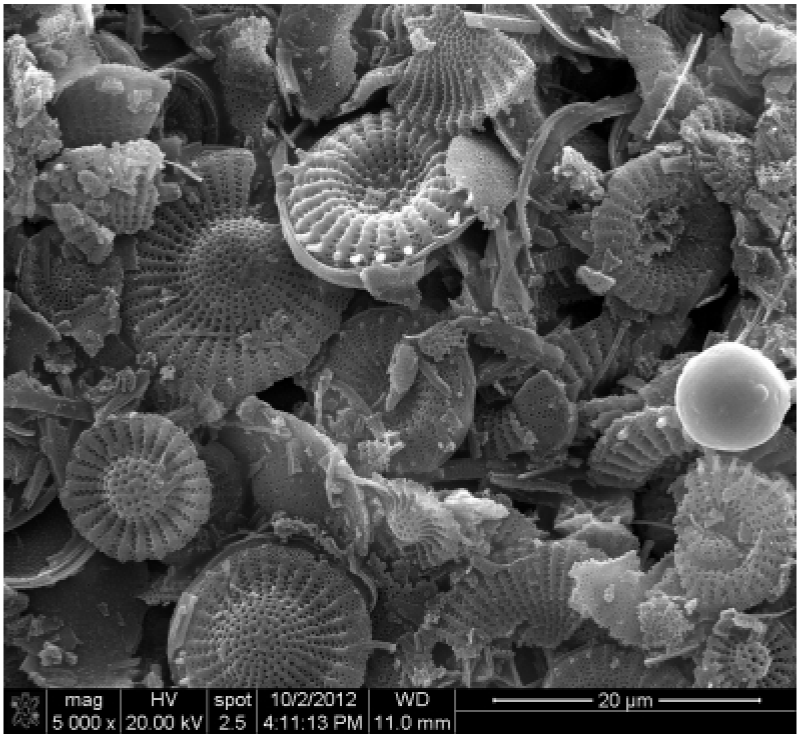
351 - Hydrophobic coatings from fluoro-silanated diatomaceous earth

*Bhishma R Sedai, **Bal K Khatiwada**, balika.khatiwada@okstate.edu, Frank D Blum, Abhijit Paul. Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States*

The surface properties of coatings of diatomaceous earth (DE) with polystyrene as a binder have been studied with the addition of modified and unmodified DE. The DE was modified with a fluorosilane coupling agent (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyltrimethoxysilane). The characterization of the coating was done with contact angle measurements of water droplet on surface and scanning electron microscopy (SEM). The contact angle measurement revealed that the hydrophobicity of the DE was improved with silanation of DE with the fluorosilane-coupling agent, which is consistent with lowering of surface energy of DE due to the fluorosilane coupling agent. The surface properties of coatings made with variation in composition of silanated DE with polymer was also studied. The contact angle increased with increased weight fraction of DE and then reached a maximum value. The SEM micrographs taken from top surface and from coating substrate interface (bottom of coating) have shown that more DE particles goes to the top surface, which is likely the cause of the increased contact angle with increased amounts of silanated DE.

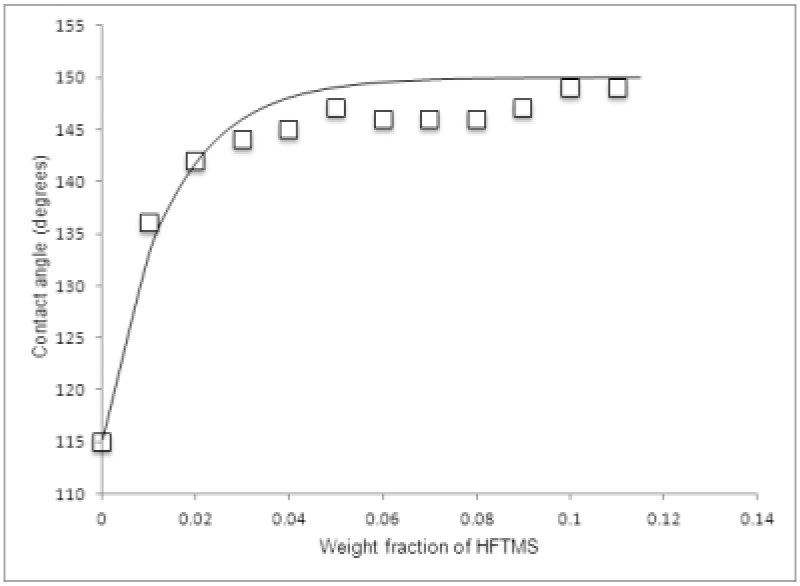


Tuesday, April 9, 2013 05:30 PM
Hybrid Materials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

352 - Hydrophobic polymer surfaces with silane-treated diatomaceous earth

Helanka J Perera, *helanka.perera@okstate.edu, Balika Khatiwada, Abhijit Paul, Frank D Blum. Department of chemistry, Oklahoma State University, stillwater, OK 74078, United States*

We developed a simple and inexpensive highly hydrophobic coating with diatomaceous earth (DE) treated with heptadecafloro-1, 1, 2, 2-tetrahydrodecyltrimethoxysilane (HFTMS) and different polymers. Samples were prepared onto glass surfaces (microscope slide) using a simple coating procedure. The characteristic properties of the films were analyzed by contact angle measurements with water and scanning electron microscopy (SEM). The contact angles were studied as a function of the weight percentage of HFTMS on the DE, weight fraction of DE, and type of the polymeric material. For these systems, the contact angle approaches 150° as the amount of DE is increased. An example is shown below for the HFTMS-DE-epoxy system.



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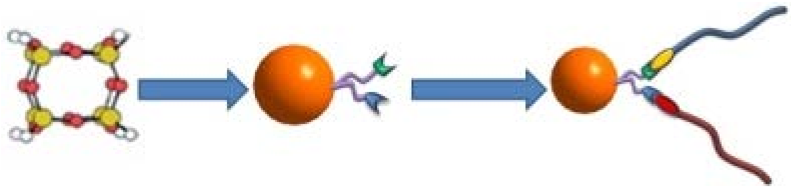
Hybrid Materials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

353 - Universal sequential “click” chemistry towards polyhedral oligomeric silsesquioxane-based miktoarm shape amphiphiles

***Hao Su**, hs61@zips.uakron.edu, Zhao Wang, Bo Ni, Yiwen Li, Stephen Z. D. Cheng. Department of Polymer Science, College of Polymer Science and Polymer Engineering,, The University of Akron, Akron, OH 44325-3909, United States*

Recently, a new class of amphiphiles named “shape amphiphiles” has emerged as hybrids of nano-building blocks that are incommensurate in terms of shapes and interactions. Especially, the design, synthesis and self-assembly of polyhedral oligomeric silsesquioxane (POSS)-based two-component shape amphiphiles, including “giant surfactants” (one POSS head tethered with one polymer tail), “giant lipids” (one POSS head tethered with two polymer tails) and “giant gemini surfactants” (two POSS heads tethered with two polymer tails) have been reported by our group. It was found that not only could they self-assemble into diverse hierarchical supramolecular structures, but also distinct self-assembly behaviors could be observed based on tiny differences in the shape and symmetry of POSS heads, as well as the geometry and topology of the tethered polymer tails. Herein we strive to expand the scope of POSS-based shape amphiphiles toolbox to the family of multiple-component miktoarm shape amphiphiles using sequential “click” reactions. The versatile vinyl POSS-based tri-functional precursor was employed to orthogonally design and synthesize miktoarm shape amphiphiles by three-step “click” reactions, such as one POSS head tethered with two asymmetric polymer tails, or two asymmetric POSS heads tethered with one polymer tail. And the POSS head and polymer chain composition could thus be tuned separately in a modular and efficient way.



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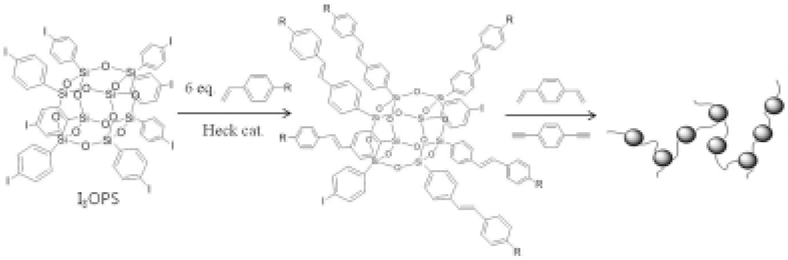
354 - Synthesis of conjugated beads on chain (BoC) type silsesquioxane (SQ) polymers from octaiodophenylSQ (I_8OPS) and their photophysical properties

Jae Hwan Jung[1], *jaehjung@umich.edu, Joesph Furgal*[2], *Sarah Clark*[3], *Matthew Schwartz*[4], *Kathleen Chou*[4], *Richard M Laine*[1,4]. *(1) Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, MI 48109, United States, (2) Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States, (3) Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States, (4) Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States*

Silsesquioxane based beads-on-chain (BoC) oligomers and polymers are synthesized from OctaiodophenylSQs by reaction with bridging organic units using a variety of catalytic coupling methods. Here we describe two different routes to conjugated BoC polymers and their photophysical properties. The first approach involves the direct reaction of $[p\text{-}IC_6H_5SiO_{1.5}]_8$ (I_8OPS) with divinylbenzene. The second approach begins with the synthesis of two/three iodophenyl SQs using partial Heck coupling of I_8OPS with *p*-R-styrene followed by Heck or Sonogashira coupling reaction with divinylbenzene or diethynylbenzene.



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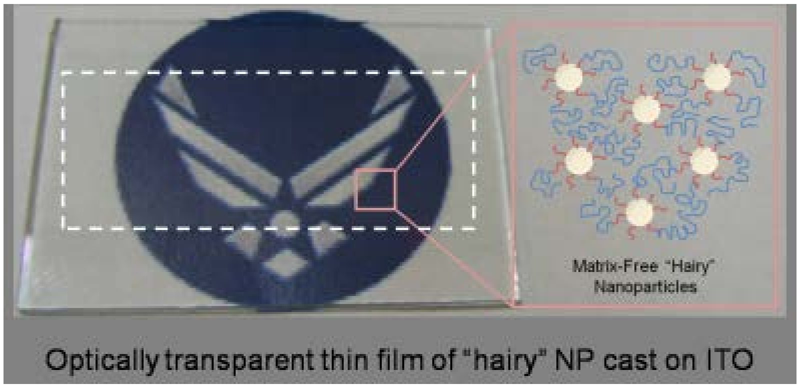
355 - Synthesis, stability, and dielectric properties of polymer-functionalized SiO_2 nanoparticles

Elizabeth Opsitnick, *elizabeth.opsitnick.ctr@wpafb.af.mil, Chris Grabowski, Hilmar Koerner, Larry Drummy, Richard Vaia. Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433-7750, United States*

Neat (matrix free) assemblies of polymer-functionalized inorganic nanoparticles have gained attention for their potential applications in high performance dielectrics, ceramic green bodies, multifunctional composites, and meta materials. Combining low-graft density (<0.1 chains/nm^2) with a high molecular weight polymer, chain entanglement between the hairy nanoparticle (HNP) coronas can be preserved while maximizing the hybrid's inorganic fraction. While a “grafting from” technique can provide hairy nanoparticles with a broad range of grafting density, the surface polymerization is often difficult to control, leading to different molecular weight polymers on the surface. Alternatively, a “grafting to” approach facilitates the modular synthesis of HNP. A series of solvents and catalysts for optimal nanoparticle dispersion and yield were determined for coupling azide-terminal polystyrene to alkyne functionalized silica via “click” reaction. Size exclusion chromatography (SEC) provided insight on the reaction process as well as the stability of the HNP after being subjected to extreme temperatures and shear mixing. The corona height depends on grafting density and polymer size, and has a profound effect on the morphology, processibility and thermomechanical properties of these materials. After casting thin films of neat HNP, their dielectric properties were measured and compared to polystyrene and polystyrene - HNP mixtures to understand the impact of dispersion state, volume fraction and dielectric contrast of the nanoparticle on the dielectric breakdown process of the hybrid.



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Hybrid Materials (05:30 PM - 07:30 PM)
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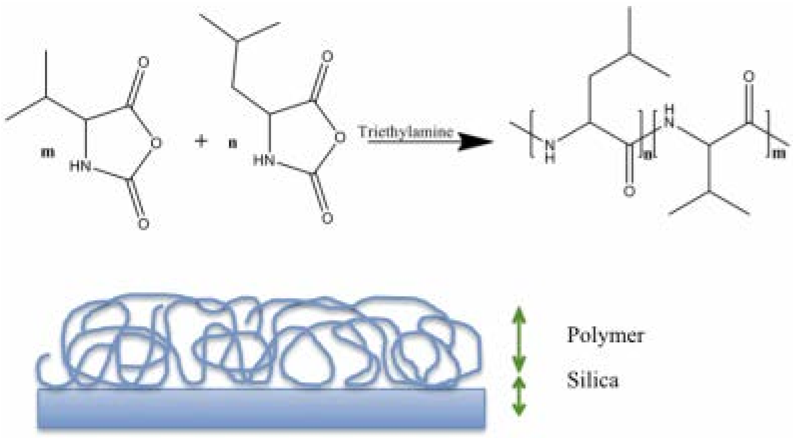
356 - Heat capacity of a co-poly(amino acid) in bulk and on silica

Charmaine Munro, *charmaine.munro@okstate.edu, Bal Khatiwada, Frank D Blum. Department of Chemistry, Oklahoma State U, Stillwater, OK 74078, United States*

The ring-opening *co*-polymerization of L-leucine *N*-carboxyanhydride (Leu-NCA) and L- valine *N*-carboxyanhydride (VAL-NCA) in a 1:1 ratio synthesized using triphosgene was carried out in solution by using triethylamine (TEA) as an initiator. The copolymers of valine and leucine were adsorbed on fumed silica and studied using differential scanning calorimetry (DSC). Heat capacity measurements of the polymer and polymer-composites were made using DSC in the temperature range of -80 °C to 280 °C. The heat capacities (C_p) of the polymers in the composites were lower than those of the bulk copolymer. The lower C_ps indicated that the polymer chains in the composite had lower flexibility due to the strong interactions between the amide moiety of the polyamino acids and the charged silanol groups, resulting in a polypeptide on the silica which is likely largely tightly bound.



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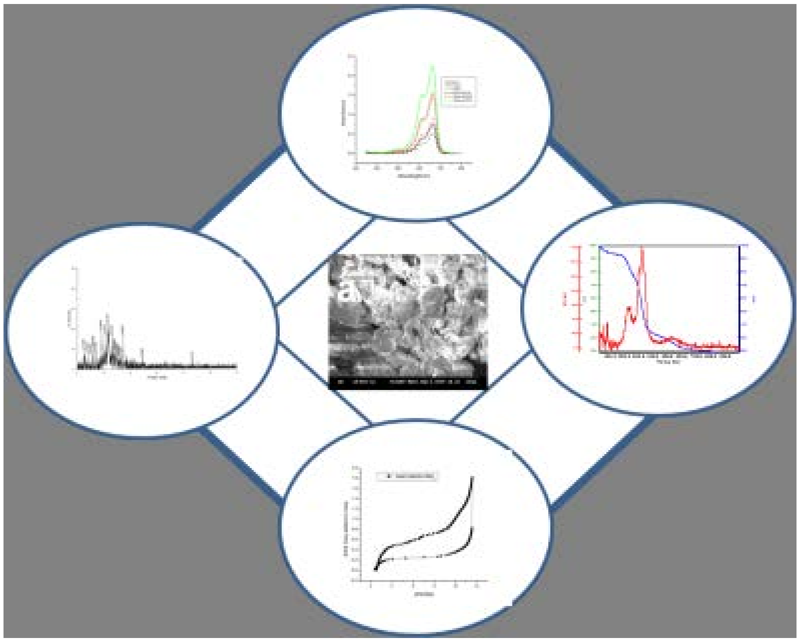
357 - Synthesis and characterization of 5-sulphosalicylate doped tetraethoxysilane composite material by sol-gel method

***Altaf Hussain Pandith**, altafpandit23@gmail.com, Suhai-ul H Rehman. Department of Chemistry, The University of Kashmir, SRINAGAR, Jammu&Kashmir 190006, India*

We report the synthesis and characterization of a new sulphosalicylate doped tetraethoxysilane composite material by sol-gel method. The material has an ion exchange capacity of 0.64meq/g(dry) for sodium ions, 0.60meq/g(dry) for potassium ions, 1.84meq/g(dry) for magnesium ions, 1.08meq/g(dry) for calcium ions and 1.36meq/g(dry) for strontium ions. Its X-ray diffraction studies suggest that it is crystalline in nature. The material has been characterized by SEM, IR, TGA and DTG so as to identify the various functional groups and ion exchange sites present in this material. Further, studies such as elution behaviour, pH titration, distribution behaviour towards ion exchange and adsorption behaviour towards certain important dyes have been performed on this material. This material shows selectivity for Mg (II) among alkaline earth metal ions and Ni (II) among the transition metal ions in aqueous solutions. The material shows remarkable adsorption behaviour towards environmentally important representative dyes like malachite green and methylene blue.



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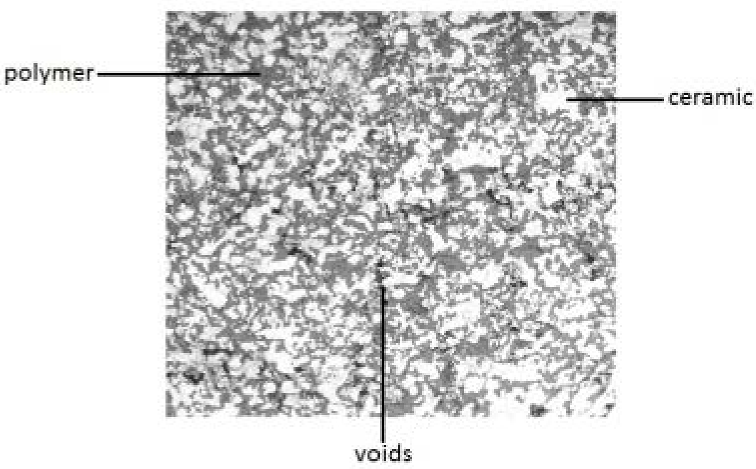
358 - Structure-property relationships of ceramic-polymer co-continuous composites for structural applications

Manuela Ocampo, *ocampom@corning.com, James W. Zimmermann, Patrick D. Tepesch. Science & Technology, Corning Incorporated, Corning, NY 14831, United States*

Ceramic-polymer co-continuous composites for structural materials were investigated. Structure-property relationships were studied for a variety of polymer systems varying from thermal cure epoxy-amine to UV-curable acrylates. Moreover, this study specifically investigated the mechanical properties of mullite-cordierite/epoxy co-continuous ceramics. These composites have strength similar to heat strengthened glass but with significantly lower Young's modulus and density. These materials have shown to be easily scaled to large sizes, easily machined, impermeable to water and aesthetically pleasing making them suitable for structural applications.



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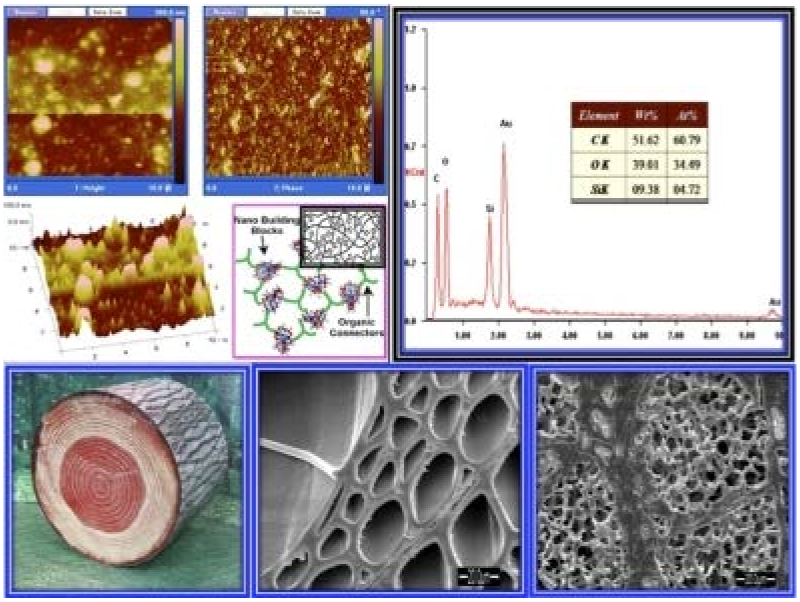
Room: Hall E

359 - Preparation and structure characterization of wood-organic-inorganic hybrid nanocomposite

*Dongxiao Ying[1], **Yongfeng Li**[1], lyf288@yahoo.com.cn, Lijun Ma[2]. (1) Forestry College, Shandong Agricultural University, Taian, China, (2) Research Institute of Forest Industry, Jilin Academy of Forestry, Changchun, China*

Wood as a natural and renewable biomass material possesses special porous structure and unique chemical components, which impart it high strength-to-weight ratio, popular texture and smart environmental benign nature capable of absorbing and releasing moisture response to environment. Consequently, wood has been desirable as an essential material for human survival since the primitive state. However, the shortcomings of wood including vulnerability to degradation when exposed to fire and microorganisms, and susceptibility to change in dimension under humidities, often result in it to be a less effective material for long-term utilization. Under such background and inspired from the characteristics of wood, wood-organic-inorganic hybrid composite (WOIC) was created by in-situ formation of organic-inorganic hybrid polymer (OIP) within wood porous structure via a sol-gel process. Glycidyl methacrylate (GMA) was first copolymerized with a vinyl-containing trialkoxysilane outside wood and then undergone a hydrolysis-condensation process (sol-gel process) with tetraethyl orthosilicate (TEOS) in wood cellular structure. Under the employed conditions, a transparent OIP was synthesized, and AFM proved that the OIP has controlled morphology with nanometer phase separation. And the resulted OIP filled up the porous structure of wood which was confirmed by SEM-EDX. FTIR further proved that OIP seems bonding to wood substance. Such formed OIP can theoretically reinforce wood as filler, which may impart good mechanical properties and durability to wood capable of being used in a broad variety.



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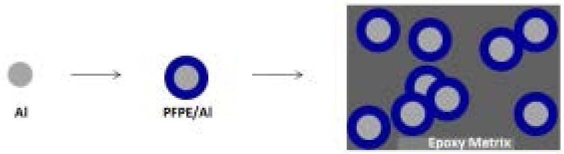
360 - Partially fluorinated bisphenol-A epoxy aluminized composite materials

Hannah A Miller, *hannah.miller.ctr@usafa.edu, James W Neat, Sharon C Kettwich, Scott T Iacono. Department of Chemistry/ Chemistry Research Center, USAF Academy, USAF Academy, Colorado 80840, United States*

Perfluoropolyethers (PFPEs) are used as coatings to passivate micro- and nanometer-sized aluminum particles. PFPEs are known to have low volatility, minimal shear thinning, and viscosity that is mostly independent of temperature. These properties enable them stable in extreme processing conditions. Recent efforts have been focused on trying to optimize the energetic behavior of the accelerated thermal degradation of these PFPEs facilitated by exothermic metal-mediated oxidation. We explore the processing of this aluminum-PFPE core-shell formulation as an additive in the bisphenol-A epoxy matricies. This presentation will discuss the preparation structural components, thermal properties, and characterization of this particular composite system.



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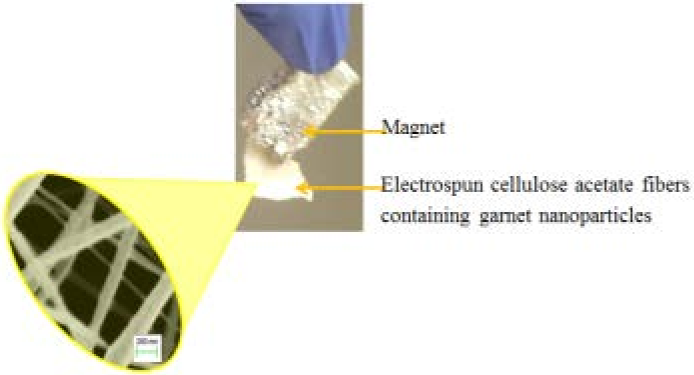
Room: Hall E

361 - Electrospun cellulose acetate: Garnet nanocomposite fibers with magnetic properties

Imalka Munaweera, *msm110020@utdallas.edu, Kenneth J Balkus Jr.. Department of Chemistry and the Alan G. MacDiarmid Nanotech Institute, University of Texas at Dallas, Richardson, Texas 75080, United States*

Cellulose acetate fibers with magnetic properties have recently attracted much attention due to their potential novel applications in biomedicine, textronics, security papermaking, packaging and reprographic applications such as magnetographic printing substrate as well as for specialty uses such as electromagnetic shielding. In my research, garnet nanoparticles have been used as magnetic additives where the magnetic properties mainly depend on composition, crystal structure and temperature. Yttrium iron garnet and gadolinium substituted yttrium iron garnet nanoparticles were synthesized using a hydroxide coprecipitation method and characterized by PXRD, SEM, TEM and superconducting quantum interference device magnetometer. Garnet nanoparticles dispersed in cellulose acetate polymer solutions were electrospun on an aluminum foil substrate to prepare free standing nonwoven mat as well as on paper substrates in order to prepare a magnetic paper. The resulting cellulose acetate nanofibers containing garnet nanoparticles are pale yellow in color and exhibit magnetic properties, i.e they can be picked up with a magnet.



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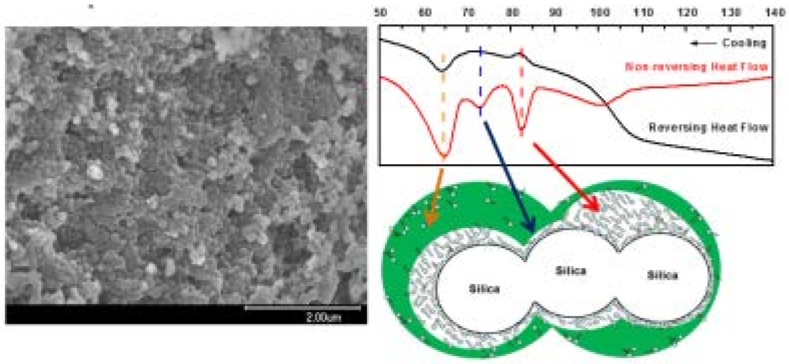
362 - New room-temperature approach to hybrid materials: Polystyrene/silica from emulsion gels

Tan Zhang[1], *tan.zhang@okstate.edu, Gu Xu*[2], *Zhe-Fei Li*[3], *Oren Regev*[4], *Madhubhashini Maddumaarachchi*[1], *Frank D Blum*[1]. *(1) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States, (2) Brewer Science Inc., Rolla, MO 65401, United States, (3) Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409, United States, (4) Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel*

Emulsion gels are systems which are similar to emulsions in composition, but also similar to gels in viscosity and stability. In the presence of the cationic surfactant CTAB, emulsion gels of styrene and fumed silica formed with water. *In-situ* free radical polymerization was carried out in emulsion gels at room temperature by surfactant-assisted initiation. Roughly mono-dispersed spherical nano-particles were obtained. Thermal analysis showed that the silica particles were covered by a thin layer of CTAB, followed by CTAB multilayers and then a mixed PS-CTAB coating. The stabilized emulsion gels made it possible to obtain hybrids of uniform composition without stirring.



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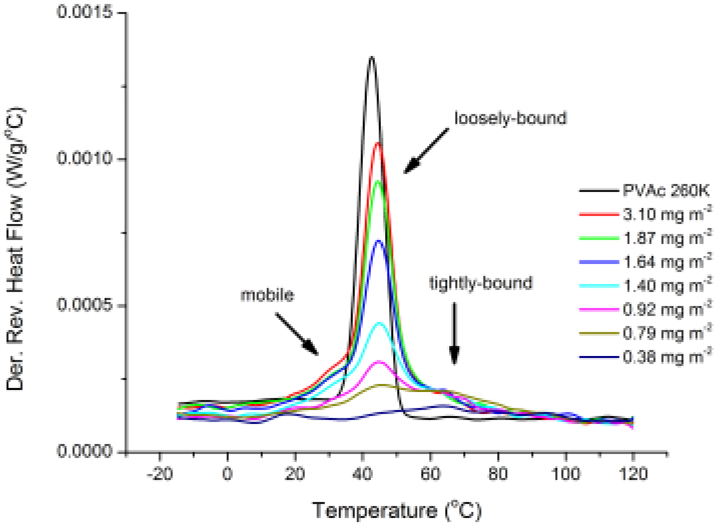
363 - Thermal analysis of adsorbed poly(vinyl acetate) on silica

Hamid Mortazavian, *hamid.mortazavian@okstate.edu, Frank D Blum. Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States*

The thermal behavior of adsorbed poly(vinyl acetate) (PVAc) on silica was investigated using temperature-modulated differential scanning calorimetry (TMDSC). Samples were prepared using three different molecular masses of PVAc and silica. Loosely and tightly-bound polymers showed slightly and significantly higher glass-transition temperatures (T_g) than that of bulk polymers, respectively. The amount of tightly bound polymer was quantified with a two-component model using relative intensities of the transitions. It was found that after a minimum amount, the amount of tightly-bound polymer was constant as additional polymer was added. For the first time, we have also been able to observe polymer at the air interface that has a T_g lower than that of bulk, which we refer to as the mobile fraction.



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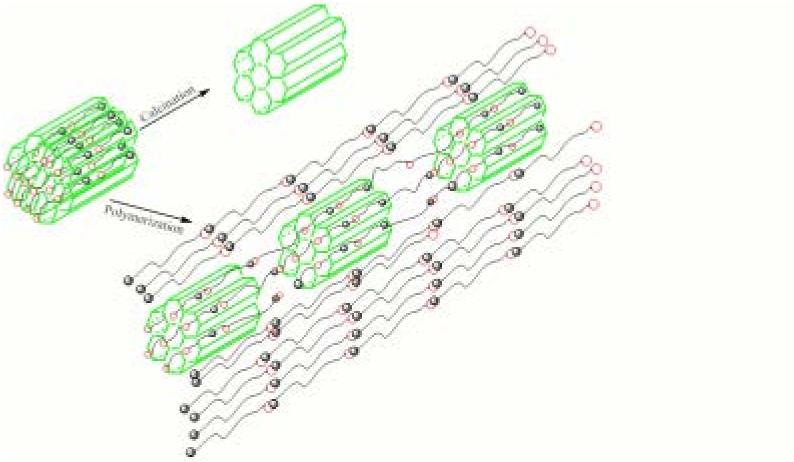
364 - Polymerizable structure-directing agents for in-situ synthesis of nanocomposite networks

Nitin V Patil, *nitin.patil@okstate.edu, Jeffery L White. Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States*

SBA-15 silica because of ordered mesostructure finds application in catalysis, sensors, and semiconductor devices. In this work, we synthesize self-assembled polymer nanocomposites wherein the meso-pores of silica are filled with polymer as well overall high organic content resulting in unique physical properties of composites due to space restriction effect. Polymerizable tri-block copolymer is synthesized using end group chemistry which possesses two functions: a) directs structure of silica and b) polymerize inside the pores connecting silica particles forming in-situ polymer nanocomposites.



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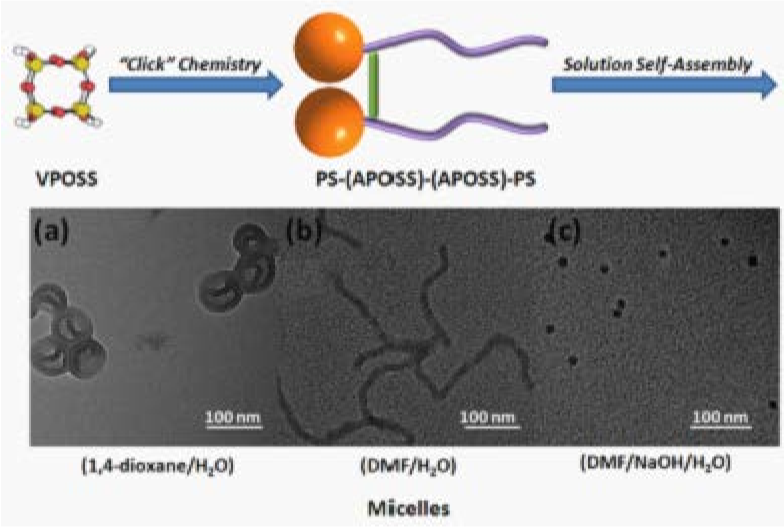
365 - Giant gemini surfactants based on polystyrene hydrophilic polyhedral oligomeric silsesquioxane shape amphiphiles: Sequential click chemistry and solution self-assembly

Zhao Wang, *zw11@zips.uakron.edu, department of polymer science, university of akron, akron, oh 44325, United States*

The synthesis, assembly and applications of gemini surfactants, a new family of two-faced molecular surfactants consisting of two conventional surfactants chemically connected together by a rigid spacer, have significantly intensified in the past decades. It was found that the nature of the spacer group (length, rigidity, chemical composition) greatly affect the solution self-assembly behaviors of aqueous gemini surfactants. Due to the intrinsic attractive properties and promising applications of gemini surfactants, a new triple “click” chemistry method is applied to synthesize POSS-based “giant gemini surfactant” (PS-(APOSS)-(APOSS)-PS). Interestingly, the PS tails are much less stretched in micelle cores than those in the micelles formed by APOSS end-capped polystyrene(APOSS-PS). With further decreasing the length of the linker, the PS tail become shorter.



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366 - Imprinting hydrogels with metal ions for metal nanoparticle preparation and use in hydrogen production as catalysis media

Fahriye Seven[1], *fahriyesvn89@gmail.com, Berkant Yetiskin*[1], *Tugce Turhan*[2,3], *Elif Karacan*[1], ***Nurettin Sahiner***[1,2], *sahiner71@gmail.com. (1) Department of Chemistry, Canakkale Onsekiz Mart University, Canakkale, Turkey, (2) Nanoscience and Technologhy Research and Application Center, Canakkale Onsekiz Mart University, Canakkale, Turkey, (3) Department of Chemical Engineering, Istanbul Technical University, Maslak, Istanbul 34469, Turkey*

Poly(2-Acrylamido-2-methyl-1-propanesulfonic acid) hydrogel (p(AMPS)) containing metal ions such as Co(II), Ni(II) and Cu(II) was prepared from the aqueous solution of AMPS monomer and metal ion mixtures at 1:1 mole ratios. The prepared hydrogels already contained metal ions were washed with DI water and treated with aqueous $NaBH_4$ for in situ metal nanoparticle formation within hydrogel matrices. The hydrogels imprinted with M ions (M: Co(II), Ni(II), and Cu(II) etc) were used in the hydrogen generation from the hydrolysis of $NaBH_4$ after metal nanoparticle formation. Bare hydrogels without imprinting metals ion were also prepared and their catalytic performances were compared with M ion imprinted hydrogels. Furthermore, bare and metal ion imprinted hydrogels (MIPH) were employed in several metal ion loading and reduction cycles to increase the amounts of metal nanoparticles and their H_2 production rates were compared. The MIPH seems viable for various metal nanoparticle preparation and catalysis of different reactions.

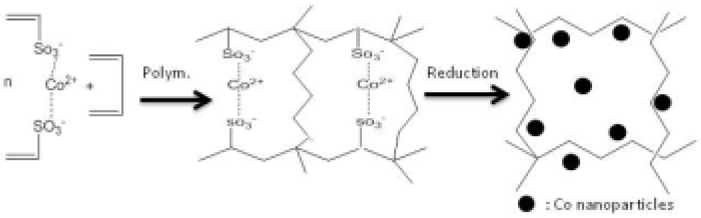

Figure 1. Metal ion imprinted hydrogel for in situ metal nanoparticle synthesis

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367 - Spray-deposited superhydrophobic coatings via photopolymerization of hybrid thiol-ene polymer networks

Li Xiong, *Li.Xiong@eagles.usm.edu, Bradley J. Sparks, Ethan F. T. Hoff, Derek L. Patton. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Engineering the chemical and physical structure of surfaces to achieve tailored wettability has attracted a great deal of attention in recent years. Surfaces with extreme wetting properties such as superhydrophobicity are of interest for self-cleaning, anti-fouling, and anti-fogging applications. Development of simple fabrication methodologies that yield robust coatings is important for widespread implementation of such applications. In this work, we present a simple technique for fabrication of superhydrophobic coatings based on photopolymerization of hybrid thiol-ene resins. Thiol-ene resins containing hydrophobic silica nanoparticles were sprayed onto a variety of substrates (i.e. glass, aluminum, paper, cotton cloth) and cured under UV light.

Coatings exhibited water contact angles greater than 156° with low contact angle hysteresis and low sliding angles (< 5°). Scanning electron microscopy images show the typical nano- and micro-scale roughness required for superhydrophobicity. Strategies toward achieving superhydrophobic/superoleophobic thiol-ene coatings will also be presented.

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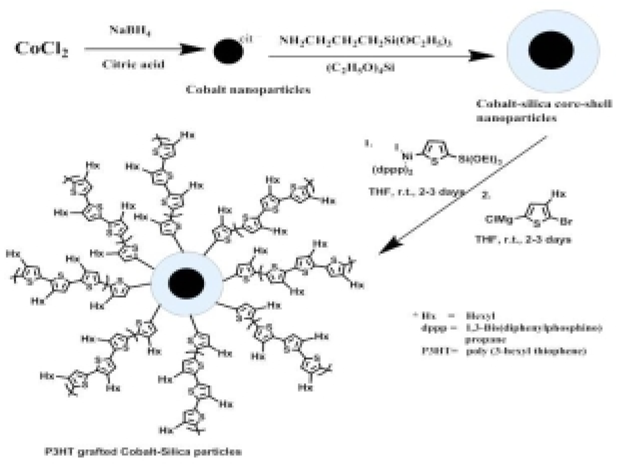
368 - Stimuli-responsive superparamagnetic nanoparticles functionalized with surface-immobilized fluorescent conjugated polymers

***Sourav Chatterjee**, schatt1@tigers.lsu.edu, Evgueni E. Nesterov, Paul S. Russo. Department of Chemistry and Macromolecular Studies Group, Louisiana State University, Baton Rouge, LA 70803, United States*

Controlling sensitivity of fluorescent chemo- and biodetection devices can be potentially achieved by varying magnetic field applied to the hybrid nanoscale systems consisting of fluorescent conjugated polymers (such as polythiophenes) and superparamagnetic (SPM) nanoparticles. In this study, we introduce a novel model to study this magneto-optical phenomenon. The model is based on SPM cobalt@silica nanoparticles as well as bare cobalt nanoparticles modified with covalently attached fluorescent conjugated polymer shell. The shell was prepared via surface-initiated chain-growth polycondensation. Formation of the conjugated polymer shell was confirmed by electron microscopy and fluorescence spectroscopy studies. Preparation of SPM cobalt nanoparticles with and without outer silica layer and their surface modification with covalently attached conjugated polymer shell will be addressed in this presentation. We will also report on the effect of magnetic and electromagnetic fields on photophysical properties of conjugated polymers at the nanoscale

Synthesis of P3HT grafted cobalt-silica particle .



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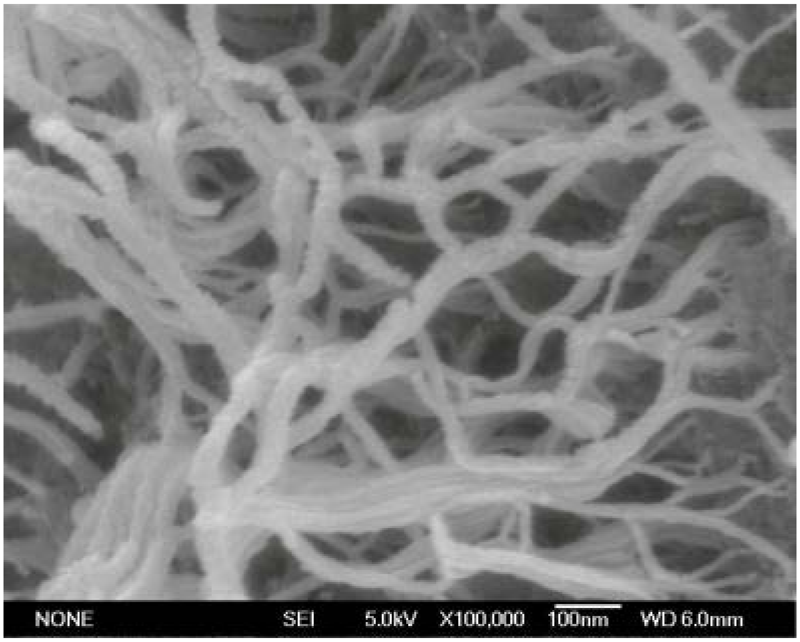
369 - Polyaniline nanofibers supported $FeCl_3$ heterogeneous catalyst synthesized by a one-step strategy

Hangjun Ding[1], *dinghangjun@163.com, Huai Yang*[2], *Zhou Yang*[1], *Hui Cao*[1]. *(1) School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, Beijing 100083, China, (2) Department of Materials Science and Engineering, Peking University, Beijing, Beijing 100871, China*

This article exposed a one-step self-assembly method to synthesize highly effective and recyclable PANI nanofiber-$FeCl_3$ catalysts by using $FeCl_3$ as binary oxidant and Lewis acid dopant with inducing the catalytic properties at the same time. It is very simple for not only omitting the reagents but also simplifying the reaction. It has been demonstrated that PANI nanofiber-$FeCl_3$ could be used as heterogeneous catalyst in acetalilzation model reaction with high conversion of ~96% and reused several times without leaching of $FeCl_3$



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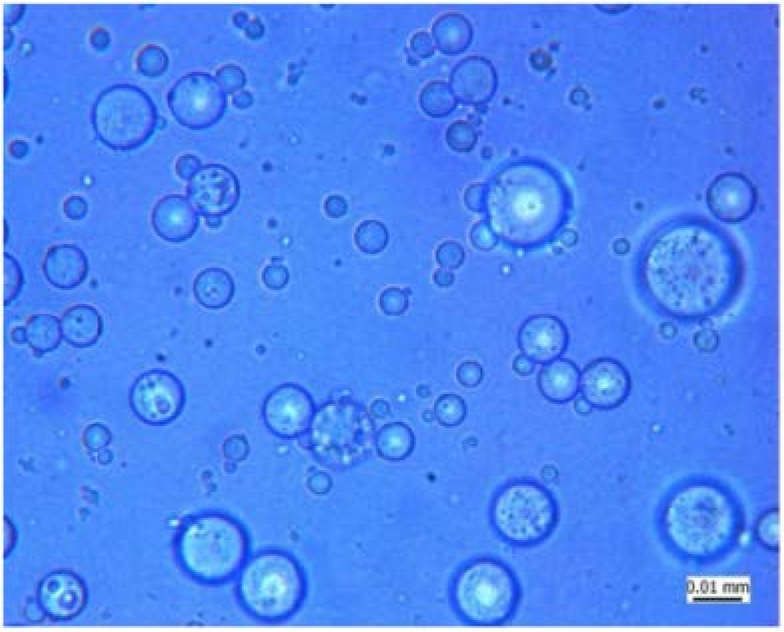
Room: Hall E

370 - Smart antimicrobial coating to against adenovirus

*Yan Li[1,3], **Qing Chang**[1], changqing@ust.hk, Joseph K C Kwan[2,4], King Lun Yeung[1,2]. (1) Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region of China, (2) Division of Environment, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region of China, (3) Bioengineering Graduate Program, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region of China, (4) Health, Safety & Environment Office, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region of China*

The most common route for transmission of infectious diseases is by indirect contact with surfaces contaminated with infectious droplets produced by human coughing, sneezing or talking. This work report a smart antimicrobial coating prepared from polymer-encapsulated chlorine dioxide (ClO_2). The ClO_2 was encapsulated by water-in-oil-in-water (w/o/w) double emulsion which consists of dispersed oily globules containing smaller aqueous droplets.



Touch and infectious droplets can trigger an increased release of the biocides at the sites of contamination, resulting in rapid disinfection. Low concentration copper (500ppm) and ascorbic acid (100ppm) were added to provide “contact-killing” property to coating. The desinged coating is effective against the DNA virus—adenovirus. A greater than 96.02% virucidal reduction activity was obtained in a short contact time of 1 min, and over 97.21 % and 98.92 % were obtained in the contact time of 3 min and 5 min, respectively.

Tuesday, April 9, 2013 05:30 PM
Hybrid Materials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

371 - Hybrid hydrogel films with antimicrobial properties

Mehtap Sahiner[1]*, mehtap_gez@hotmail.com,* ***Duygu Alpaslan***[2]*, alpaslanduygu@gmail.com, Behzat O Bitlisli*[1]*. (1) Department of Leather Engineering, Ege University, Bornova, Izmir 35100, Turkey, (2) Department of Chemistry, Yuzuncu Yil University, Van, Van 65080, Turkey*

Hydrogels films containing different amounts of collagen from different monomers such as N-vinyl pyrrolidone, acrylamide, and hema were prepared as shown below

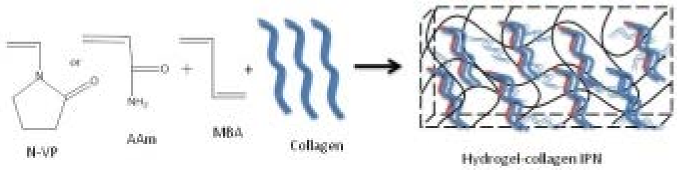


Figure 1. Collagen containing hybrid hydrogel films.

The hydrogel films were loaded with Cu(II) and Ag(I) ions from their aqueous solutions and then reduced to metallic nanoparticle to provide antimicrobial properties. The amount of metal ions was determined by Atomic Absorption Spectroscopy (AAS). It was found that metal nanoparticle containning hydrogels have good antimicrobial properties against E. Coli. Furthermore, the prepared hydrogels films were also loaded with gallic acid, an antioxidant agent and its in vitro release studies were carried out using UV-Vis spectrophotometer.Collagen containing hydrogel films antimicrobial properties were tested against E. Coli using Astm 2149 and agar well diffusion methods. The prepared material in this investigation are resourceful and can have great potential application in biomedical fields as biocompatible drug delivery devices, and antimicrobial wound dressing materials and so on.

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Hybrid Materials (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

372 - Facile route for the synthesis of organic dye embedded “smart” nanogel for optical detection of glucose

Yingyu Li[1,2], *yingyu.li@csi.cuny.edu, Shuiqin Zhou*[1,2]. *(1) Department of Chemistry, College of Staten Island, City University of New York, Staten Island, NY 10314, United States, (2) Department of Chemistry, Graduate Center, City University of New York, New York, NY 10016, United States*

An easy way for fabrication of “smart” nanogels for optical detection of glucose can be achieved. Bordeaux, a commercially available fluorescent dye, was adopted as a model of optical code. A copolymer microgel template poly(N-isopropylacrylamide-*co*-acrylic acid-*co*-acrylamide) [p(NIPAM-AA-AAm)] was synthesized *via* free radical precipitation copolymerization. PAA segments were designed to couple with boronic acid derivatives for glucose sensitivity, and PAAm segments were to tether with organic dye molecules for optical property

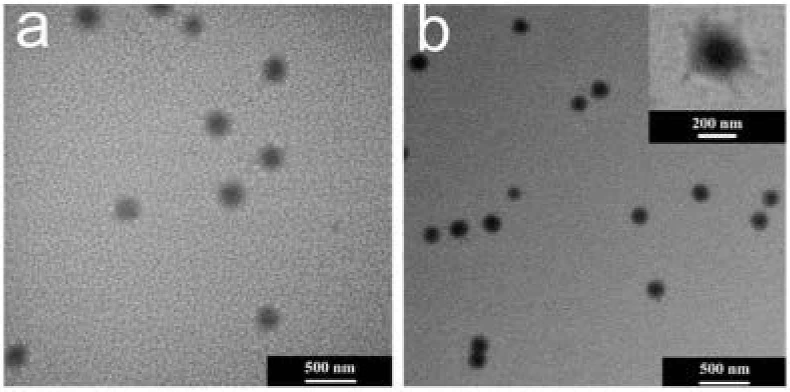

figure 1. Typical TEM images of (a) p(NIPAM-AAm-PBA) and (b) p(NIPAM-AAm-PBA)-Bordeaux R dye composite microgels.

. The glucose-induced swelling/shrinking of the microgel network regulated the fluorescence of embedded dye molecular assemblies, being able to convert chemical changes into optical signals. The dye composited microgels demonstrated good stability, as well as high selectivity to glucose over the potential interferences of lactate and human serum albumin under physiologically important glucose levels, which may have potential applications in biosensing.

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Hybrid Materials (05:30 PM - 07:30 PM)
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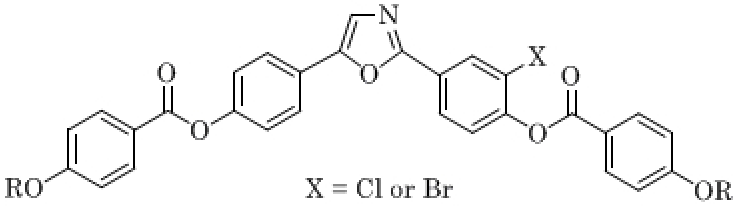
373 - Towards a low temperature biaxial nematic phase: Synthesis and phase behavior of oxazole based liquid crystals

Katie M. Gulliford[2], *kgulliford@tacomacc.edu*, ***Eric Scharrer***[1], *escharrer@pugetsound.edu*, *Mary Packard*[1]. *(1) Chemistry, University of Puget Sound, Tacoma, Washington 98416, United States, (2) Chemistry, Tacoma Community College, Tacoma, Washington 98466, United States*

In 2004, oxadiazole based liquid crystals were shown to possess the elusive biaxial nematic at high temperatures. Our group has been successful in lowering the nematic onset temperatures in this class of compounds by incorporating lateral groups on the benzene rings. In order to further reduce the onset temperatures, we have prepared the less polar oxazole-based derivatives possessing a lateral halogen group (1). Synthetic details and phase behavior of these compounds will be discussed.



X = Cl or Br

1

Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Morial Convention Center
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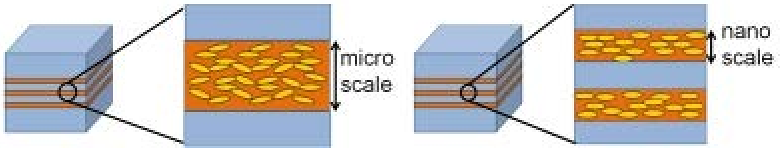
Tuesday, April 9, 2013 05:30 PM
Liquid Crystals and Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

374 - Effects of nano-confinement on the structure and properties of liquid crystalline polymers

Paola A. Gonzalez Garza[1], *paola@che.utexas.edu, Zhenpeng P. Li*[1]*, Eric Baer*[2]*, Christopher J. Ellison*[1]*. (1) Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States, (2) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

Semi-crystalline polymers have shown increased crystalline order and size when confined in multilayered films made by coextrusion[1]. The resulting large crystals lead to dramatic improvements in gas barrier properties. Ordered polymers whose characteristics are between that of the liquid phase and the crystalline phase are known as liquid crystalline polymers. The highly ordered mesogens in liquid crystalline polymers contribute to their exceptional bulk properties. In this research, main-chain and side-chain liquid crystalline polymers were confined in multilayered films with a non-liquid crystalline polymer, made by either multilayer coextrusion or spin coating, in an attempt to improve the ordering of the liquid crystalline mesogens. The liquid crystalline behavior and morphology was studied to understand the correlation between the structure and the properties of the multilayer films.



(1) Wang, H.; Keum, J. K.; Hiltner, A.; Baer, E.; Freeman, B.; Rozanski, A.; Galeski, A. *Science* **2009** , *323*, 757-760.

Monday, April 8, 2013 08:00 PM
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Location: Morial Convention Center
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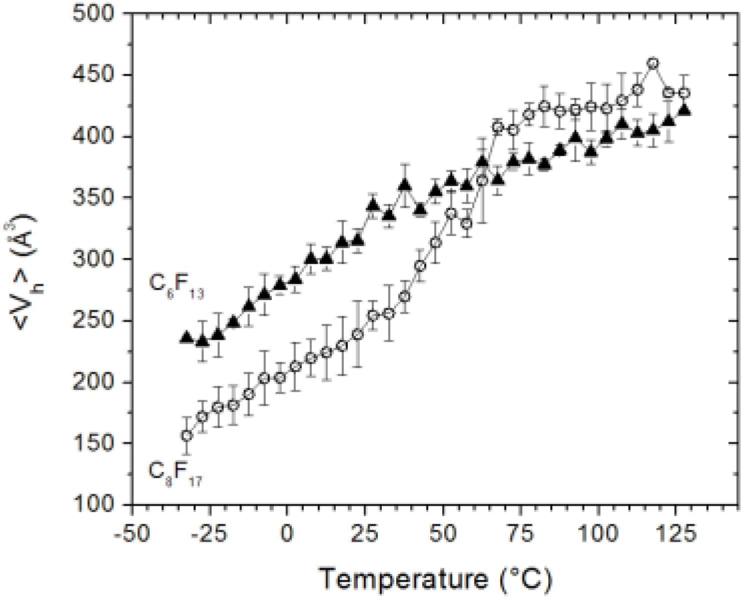
Tuesday, April 9, 2013 05:30 PM
Liquid Crystals and Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

375 - Perfluorinated side chain liquid crystals: Transport and free volume behavior in UV-cured acrylate networks

James Goetz, *james.goetz@eagles.usm.edu, Sergei Nazarenko. Department of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MISSISSIPPI 39406, United States*

Stimuli-responsive materials such as thermotropic liquid crystalline polymers show sharp property changes through the smectic-LC transition induced by a change in temperature. Lightly crosslinked, UV-cured amorphous C_6F_{13} and mesogen containing C_8F_{17} perfluorinated side chain acrylate network films were prepared. Thermal and morphological characterization indicated a restructuring of the liquid crystalline phase through the isotropic transition giving rise to increase in transport and free volume properties. The amorphous film showed no dramatic change in transport or free volume properties.



Tuesday, April 9, 2013 05:30 PM
Liquid Crystals and Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

376 - Smart liquid crystalline polymers: Tuning gas permeability with external stimuli

Robinson Anandakathir[1,2], *Bridgette_Budhlall@uml.edu, Margaret J Sobkowicz*[1], *Joey Mead*[1,2], *Syed Hassan*[1,2], *Bridgette M Budhlall*[1,2]. *(1) Department of Plastics Engineering, University of Massachusetts, Lowell, MA 01854, United States, (2) NSF Center for High-Rate Nanomanufacturing, University of Massachusetts, Lowell, MA 01854, United States*

Liquid crystalline polymers (LCP) are considered to be smart polymers which can change their phases in response to external stimuli. Incorporation of an azobenzene into a LCP adds advantageous features for fabricating photoresponsive systems. Several studies have shown photoisomerization of azobenzene changes the permeation of the polymer. Here we describe the synthesis and characterization of a smart LCP with tunable permeability. A series of azobenzene side-chain LCPs with flexible spacer lengths were synthesized with an acrylate backbone and characterized with FTIR and NMR techniques. The thermal properties and phase transition temperatures were studied with TGA, DSC and the polymer morphology was characterized by XRD. The gas permeation properties of these polymers were measured using oxygen permeation analyzer. Fast switching of gas permeation is demonstrated by alternative heating and cooling cycles, which results in a 50% difference in the permeability of the originally non-porous film.

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Liquid Crystals and Polymers (05:30 PM - 07:30 PM)
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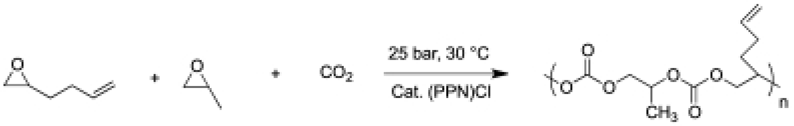
Room: Hall E

377 - From CO_2 to multifunctional poly(carbonate)s with controlled number of functional groups for grafting via click chemistry

Jeannette Geschwind[1,2], *geschwij@uni-mainz.de, Frederik Wurm*[1,3], *Holger Frey*[1]. *(1) Department of Organic Chemistry, Johannes Gutenberg University, Mainz, Germany, (2) Graduate School Materials Science in Mainz, Mainz, Germany, (3) Max Planck Institute for Polymer Science, Mainz, Germany*

Copolymerization of CO_2 and epoxides resulting in polycarbonates has been employed to generate functional materials. The introduction of reactive double bonds at a poly(propylene carbonate) (PPC) backbone has been realized by copolymerization of aliphatic alkene epoxides (epoxy hexene and epoxy decene) with propylene oxide (PO) and carbon dioxide (CO_2). Facile transformation of the pending double bonds was verified by a thiol-ene reaction with thioglycolic acid and mercaptoethanol, resulting in quantitative conversion of the double bonds.



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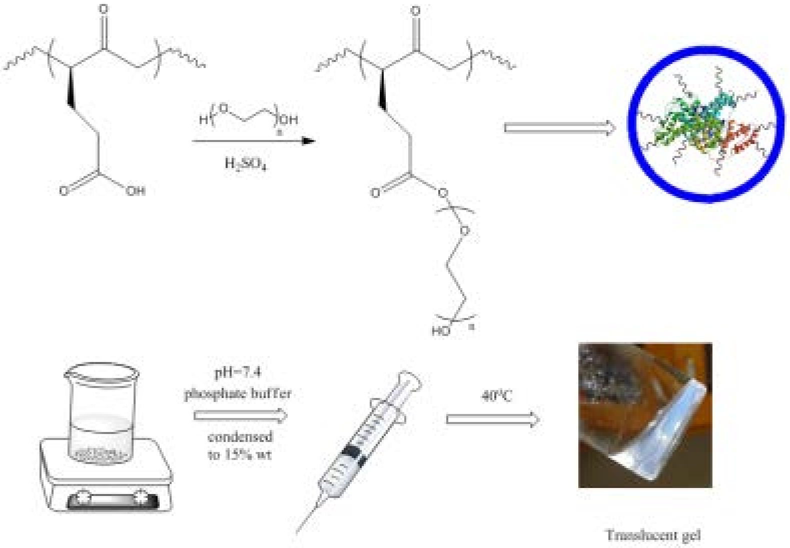
Tuesday, April 9, 2013 05:30 PM
Natural and Renewable Polymers (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

378 - Pegylated protein injectable hydrogel from bovine serum albumin and polyethylene glycol

Kai Wang[1], *kzw0012@tigermail.auburn.edu, Gisela Buschle-Diller*[1], *Yonnie Wu*[2]. *(1) Department of Polymer & Fiber Engineering, Auburn University, Auburn, AL 36849, United States, (2) Department of Chemistry & Biochemistry, Auburn University, Auburn, AL 36849, United States*

Bovine serum albumin (BSA) and polyethylene glycol (PEG) were reacted in a one-step pegylation reaction to synthesize a thermo-responsive injectable hydrogel. A physically cross-linked network of BSA-PEG micelles was formed. The sol-gel transition was initialized by a change in the size and shape of these micelles and exhibited heat responsiveness in the range of body temperature. The translucent BSA-PEG hydrogel showed a highly porous structure.



The BSA moiety remained in its native folded conformation, thus maintaining the capacity of binding to small and medium-sized drugs. The drug delivery was assessed with 5-Fluoreracial by a discontinuous model in vitro. This novel material holds promise for biomedical applications, such as a drug carrier and for tissue engineering scaffolding.

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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379 - Soy-based surface active copolymers as safer replacement for low molecular weight surfactants

*Samim Alamam[2], **Olena Kudina**[1], olena.kudina@my.ndsu.edu, Harjyoti Kalita[2], **Andriy Popadyuk**[1], andriy.popadyuk@my.ndsu.edu, Bret J. Chisholm[1,2], Andriy Voronov[1]. (1) Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58108, United States, (2) Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota 58108, United States*

Novel environmentally friendly and efficient soybean-based polymeric surfactants for personal-care applications were developed. Our approach combines benefits from using soybean oil, as a starting material, with an ability of amphiphilic polymeric macromolecules to self-assemble into micelles at a specific concentration and solubilize hydrophobic molecules. Fabricated macromolecules can be used as both a surface active agent and an additive that enhances the surface activity of low molecular weight surfactants (e.g. sodium dodecyl sulfate) in personal-care products.

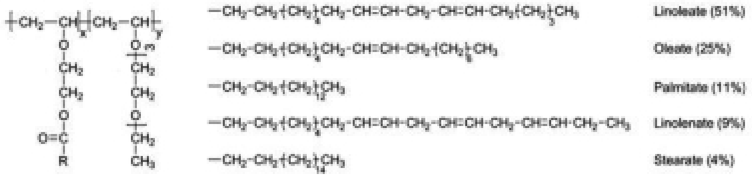

Figure 1. General structure of 2-(vinyloxy)ethyl soyate -ran- triethylene glycol copolymer.

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)

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Room: Hall E

380 - RAFT polymerization of sustainable triblock copolymers for applications as thermoplastic elastomers

Shu Wang, *s.yuki.wang@gmail.com, Megan L Robertson, Kim M Le. Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States*

Polymers derived from agricultural sources offer benefits to society of a reduced environmental impact and utilization of an annually renewable resource. Reversible addition fragmentation chain transfer (RAFT) polymerization has been utilized to prepare fully sustainable triblock copolymers. The middle block is fatty acid-derived polyacrylate which is rubbery and amorphous at room temperature. The outer blocks are glassy and semi-crystalline polylactide, which is derived from plant sugars. These triblock copolymers are being investigated for utility as fully sustainable thermoplastic elastomers.

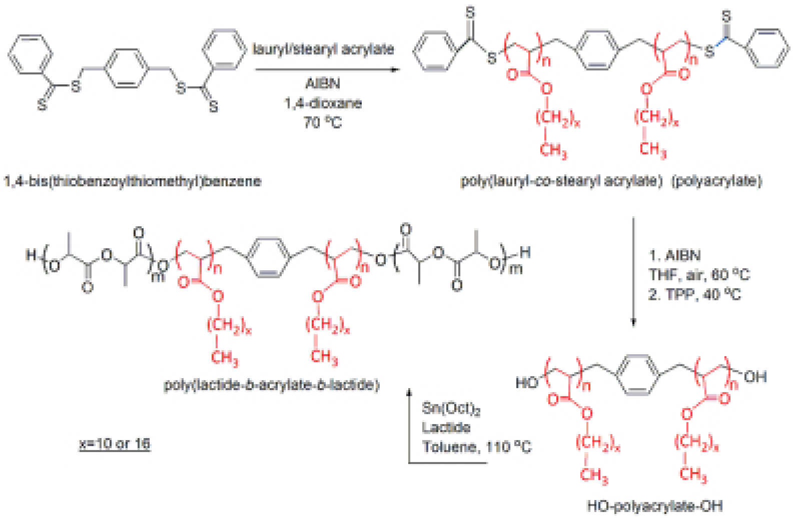

figure1: Synthesis of poly(lactide-*b*-acrylate-*b*-lactide) triblock copolymer

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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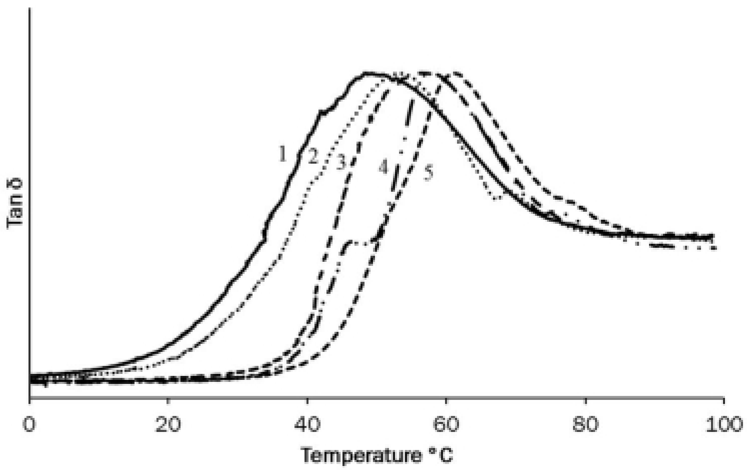
Room: Hall E

381 - Blending synergies of succinate bio-based PVC plasticizers

Amanda Stuart, ***Dale J LeCaptain***, *lecap1dj@cmich.edu, Choon Y Lee, Dillip K Mohanty. Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48640, United States*

Chemical synergism can occur when the interaction between two materials is enhanced by the addition of a third component. This concept of synergism was applied to plasticizers within a polymer matrix. The blending of 3 succinate based plasticizers into PVC are reported. Mixtures of these succinate di-esters and previously reported ones are discussed for plasticizing poly(vinyl chloride) (PVC). Mixtures of di-decyl and di-octyl succinate as well as di-decyl, di-octyl, and di-hexyl succinate exhibit potentially higher efficiency than any of the components was used individually. All components were blended with PVC between 7.5% and 27.5% by weight.



Tan d Peaks Normalized for PVC Films Plasticized with 7.5% by Weight DOS & DDS (1); DHS, DOS, & DDS (2); DES & DDoDS (3); DES & DDS (4); DES & DOS (5)

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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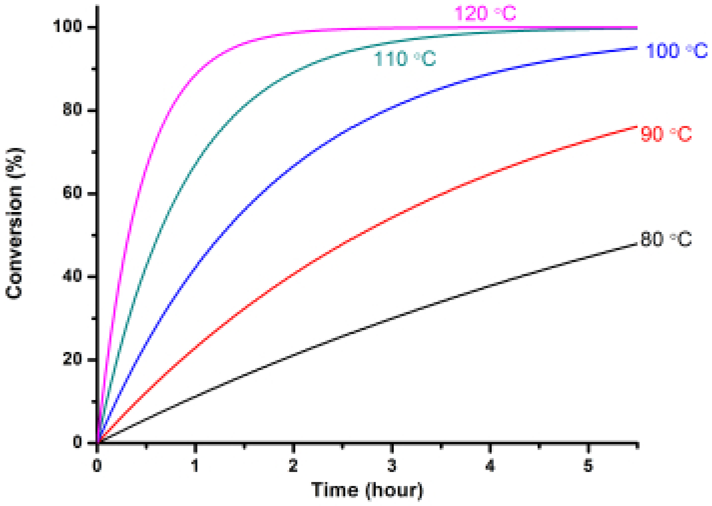
382 - Biobased epoxy-anhydride thermosets for biocomposite matrix resin systems

Adlina Paramarta[1], *Adlina.Paramarta@my.ndsu.edu, Dean Webster*[1], *Chris Taylor*[2], *Chad Ulven*[2]. *(1) Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58102, United States, (2) Department of Mechanical Engineering, North Dakota State University, Fargo, North Dakota 58102, United States*

Biocomposites are often formed using petroleum-based resins with natural fiber as reinforcement agent. Increased biobased content in the biocomposites can be achieved by using a biobased resin such as epoxidized sucrose soyate. This epoxy resin crosslinked with cycloaliphatic anhydride has been previously shown to have high modulus and tensile strength; higher than its epoxidized sucrose soyate counterpart and comparable to current petrochemical epoxy and polyurethane technologies (Pan, et al., 2011). The objective of this research is to explore the effect of composition variables on the performance of the novel binder system. Differential scanning calorimetry (DSC) is used as a rapid tool for obtaining kinetic information in order to predict the curing schedule of the matrix resin so that optimum properties can be achieved. The attached figure shows the conversion percent as a function of time and tempearature for curing schedule optimization in which the graph was generated fromt he DSC kinetic data. Furthermore, the structure-property relationships of the matrix resin system are studied as a function of different epoxy functionality, anhydride crosslinker, catalyst type and molar ratio of chemical constituents.



References:

Pan, X., Sengupta, P. and Webster, D.C., (2011). 'High biobased content epoxy-anhydride thermosets from epoxidized sucrose ester of fatty acids'. *Biomacromolecules*, 12:2416-2428.

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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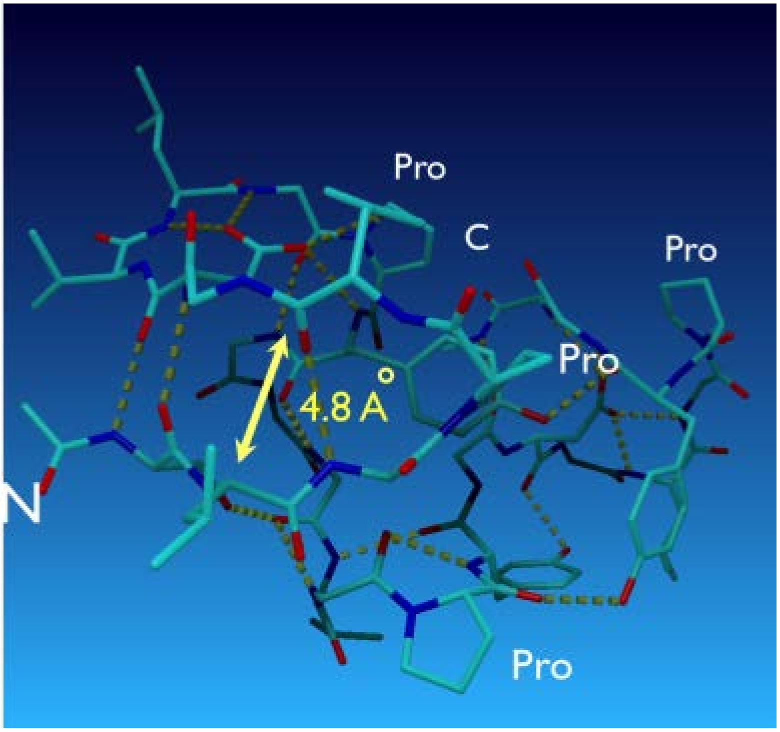
Room: Hall E

383 - Characterization and nanofiber fabrication of underwater silk protein from *Stenopsyche marmorata*

Kousaku Ohkawa, *kohkawa@shinshu-u.ac.jp, Takaomi Nomura, Ryoichi Arai, Koji Abe, Masuhiro Tsukada, Kimio Hirabayashi. Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano Prefecture 386-8567, Japan*

Larval silk proteins from *Stenopsyche marmorata* was isolated as a protein mixture of Smsp-1, 2, 3 and 4. The Smsp-1 is a giant polypeptide and occupies at least 45%-mass of the mixture. The proteins are fabricated into a thin film, which is high extensible in water. Polarized FT-IR and wide-angle X ray diffractometry suggested that the backbone adopts two different conformations, one of which was assigned as b-turn-like conformer. A proline-rich segment of Smsp-1 was subjected to conformer search calculation, and the b-turn-like conformers were generated as predominant chain structures



. The silk proteins can be also fabricated into a nanofibrous non-woven via electrospinning process. There results indicated that the caddisfly silk is one of promising as a novel tissue engineering material.

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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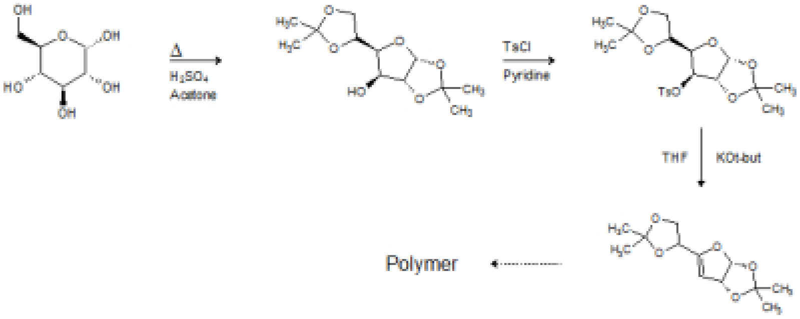
384 - Diacetone glucose derived polyolefins

Patrick S. Corrigan, *pcorrigan@monmouthcollege.edu*, ***Mitchell L Heuermann***, *mheuermann@monmouthcollege.edu*, *Eric M Todd*. *Department of Chemistry and Biochemistry, Monmouth College, Monmouth, Illinois 61462, United States*

1,2:5,6-Di-*O*-isopropylidene-a-D-glucofuranose, diacetone glucose (DAG), is commercially available and can be easily prepared from glucose in high yield. Tosylation of the remaining alcohol followed by elimination yields an olefin monomer in 50% yield. Here we report initial efforts to polymerize the DAG derived olefin using a variety of methods, including radical and cationic mechanisms.



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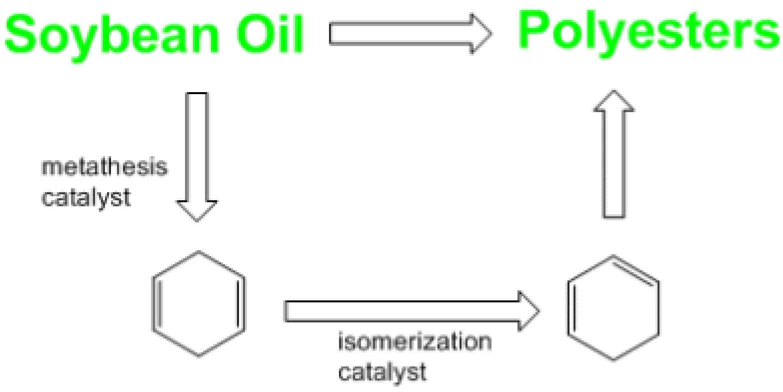
Natural and Renewable Polymers (05:30 PM - 07:30 PM)

Location: Morial Convention Center

Room: Hall E

385 - Renewable polyesters based on soybean oil

*Michael P Cavazza, Aaron Hoover, Stewart P Lewis, **Robert T Mathers**, rtm11@psu.edu. Department of Chemistry, The Pennsylvania State University, New Kensington, PA 15068, United States*



Renewable polyesters based on soybean oil provide alternatives to petroleum-based chemicals. These polyesters contain 1,4-cyclohexadiene (1,4-CHD) synthesized using ruthenium-catalyzed cyclization of alkenes in polyunsaturated plant oils of soybean oil. The polyesters were characterized with GPC, DSC, TGA, and FTIR.

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386 - Synthesis and characterization of liquefied switchgrass-based epoxy resin

__Nan Wei__[1], nzw0003@auburn.edu, Brian K. Via[2], Maria L. Auad[3], Yifen Wang[1]. (1) Biosystems Engineering, Auburn university, Auburn, AL 36832, United States, (2) School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL 36832, United States, (3) Polymer and Fiber Engineering, Auburn University, Auburn, AL, United States

In this study, switchgrass was converted to bio-oil through a liquefaction process, and then liquefied switchgrass was utilized as a feedstock for epoxy resin synthesis. The aim of this study was to synthesize and characterize the liquefied switchgrass-based epoxy resin. This study was composed of three steps, (1) liquefaction, (2) epoxidation and curing, and (3) characterization. Three different ratios of diglycidyl ether of biphenol A (EPON 828) to bio-oil (1:1, 1:2, and 1:3) were investigated. FTIR analysis proved that epoxy functionality wassuccessfully introduced into the liquefaction oil. Through the results of DSC,TGA, extraction and three point bending tests, the ratio of 1:2 (EPON 828:bio-oil) exhibited the highest properties which could be used for many common applications.

Sample (Epon:liquefiedswitchgrass)	Glass Transition Temperature (°C)	Decomposition Temperature (°C)	Modulus of Rupture (GPa)
1:1	46.27	260	3.874
1:2	51.68	300	11.628
1:3	41.21	275	5.029

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Natural and Renewable Polymers (05:30 PM - 07:30 PM)
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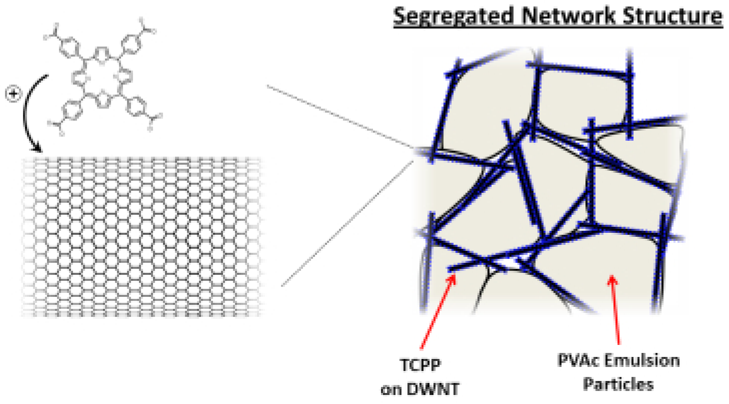
387 - Enhancing power factor of polymer composites containing porphyrin-stabilized nanotubes

*Gregory Moriarty[2], **Bart Stevens**[1], bartstevens@tamu.edu, Jaime Grunlan[1,2]. (1) Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, United States, (2) Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3123, United States*

Poly(vinyl acetate) copolymer latex-based composites were prepared with multi-walled carbon nanotubes (MWNT), stabilized with sodium deoxycholate (DOC) or meso-tetra(4-carboxyphenyl) porphine (TCPP). SEM images show that a segregated MWNT network developed during drying, which resulted in relatively low percolation thresholds (1.62 and 2.17 wt% MWNT for DOC and TCPP, respectively). The electrical conductivity of TCPP-stabilized composites is very similar to that of DOC-stabilized, while the thermopower (or Seebeck coefficient) is five times as large (5 to 25 µV/K, respectively). This enhanced thermopower suggests the MWNT:TCPP composite will have an order of magnitude greater thermoelectric efficiency. The thermal conductivity also remains comparable to typical polymeric materials (< 0.30 W/(m·K)) due to numerous tube - tube connections that act as phonon scattering centers. The universality of this approach was confirmed using double-walled carbon nanotube-filled composites that showed similar improvement with TCPP stabilization. The tailorability of the Seebeck coefficient with different stabilizing agents is an important tool for increasing the thermoelectric efficiencies of polymer composites.



Tuesday, April 9, 2013 05:30 PM

Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)

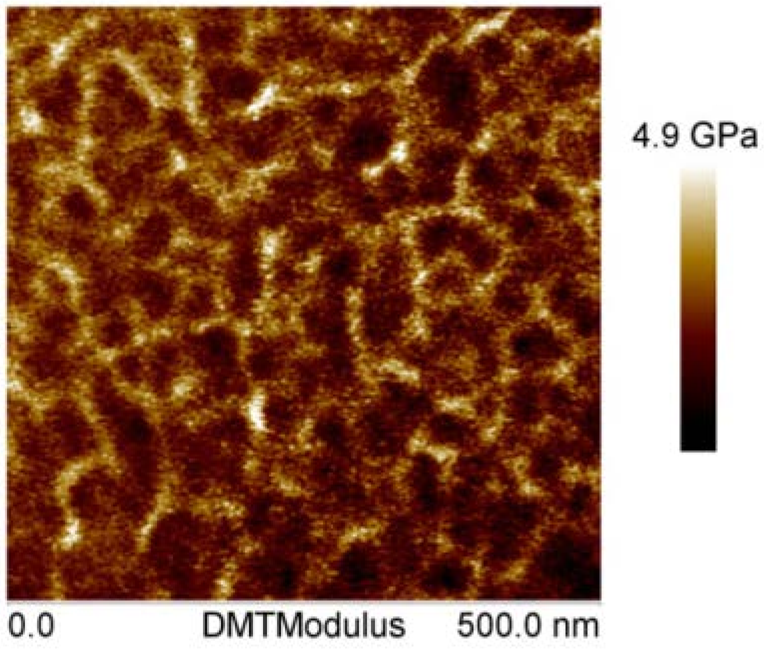
Location: Morial Convention Center

Room: Hall E

388 - Improved morphology control in organic photovoltaic (OPV) cells through incorporation of polyhedral oligomeric silisesquioxane (POSS)

Qi Wu, *wuqiqingdao@gmail.com, Mithun Bhattacharya, Sarah Morgan. School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Polymer OPV cells have distinct advantages over silicon-based solar cells due to their ease of fabrication, low-weight, flexibility and lower cost. A disadvantage of OPVs is their low conversion efficiency, which is directly related to the morphology and phase separation in the active layer. Nanomechanical mapping (NM) AFM allows simultaneous evaluation of mechanical properties and topography, providing increased information about composition and morphology. POSS modified P3HT/PCBM OPV cells were analyzed by NM and conductive AFM and their conversion efficiency quantified.



Tuesday, April 9, 2013 05:30 PM

Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)

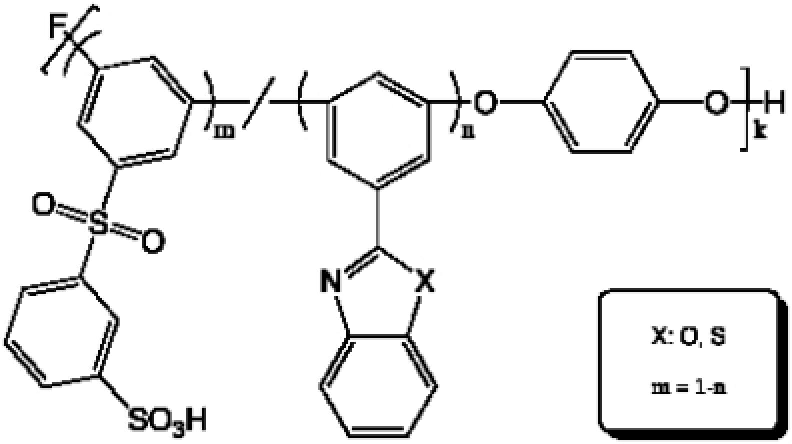
Location: Morial Convention Center

Room: Hall E

389 - Hydroquinone-based poly(arylene ether)s with pendant benzothiazole and 3-sulfonated phenyl sulfonate groups

***Huong Hoang**, hoang.7@wright.edu, Eric Fossum. Department of Chemistry, Wright State University, Dayton, OH 45435, United States*

A series of hydroquinone-based poly(arylene ether) copolymers, with truly pendent sulfonated phenylsulfonyl and either benzothiazole or benzoxazole groups, was prepared via *meta*activated nucleophilic aromatic substitution polycondensation reactions. The ratio of 3,5-difluoro-3'-sulfonated diphenylsulfone to 2-[3,5-bis-(4-hydroxyphenoxy)]benzothiazole was varied to afford ion-exchange capacities ranging from 0.31-1.63 meq. The copolymers displayed low water uptake values, moderate glass transition temperatures, and excellent thermal stability. These materials are promising candidates for use as proton exchange membranes under low relative humidity conditions.

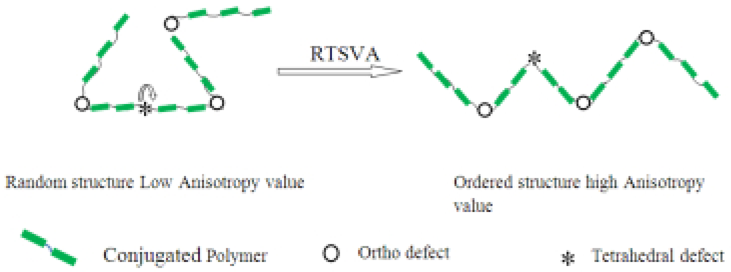


Tuesday, April 9, 2013 05:30 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

390 - Nanoscale morphology repairing of defected polymers by room temperature solvent vapor annealing

Subhadip Ghosh[1], *sghosh@niser.ac.in, Paul F Barbara*[2]*. (1) School of Chemical Science, National Institute of Science Education and Research, Bhubaneswar, Odissa 751005, India, (2) Center for Nano & Molecular Science & Technology, The University of Texas at Austin, Austin, Texas, United States*

During the spin coating process of conjugated polymers solvent evaporates rapidly and polymer segments are kinetically trapped with high energy conformations within the host matrix. In this work the morphological reorganizations ("equilibration") of polymer chains have been restored by using room temperature solvent vapor annealing (RTSVA). This solvent (toluene) vapor induced equilibration process substantially depends on the nature of defects present in the polymer backbone. Conjugated PPV type (poly phenylenevinylene) polymers where the linearity of backbone structure is enforced by defect molecules are usually trapped within the host matrix with nearly equilibrated conformations. RTSVA induces the modest tuning of morphology for these nearly equilibrated structures. Rigid defects that are bent and saturated defects that provide rotational freedoms in the polymer backbone tend towards more folded and compact structures after RTSVA.



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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)

Location: Morial Convention Center

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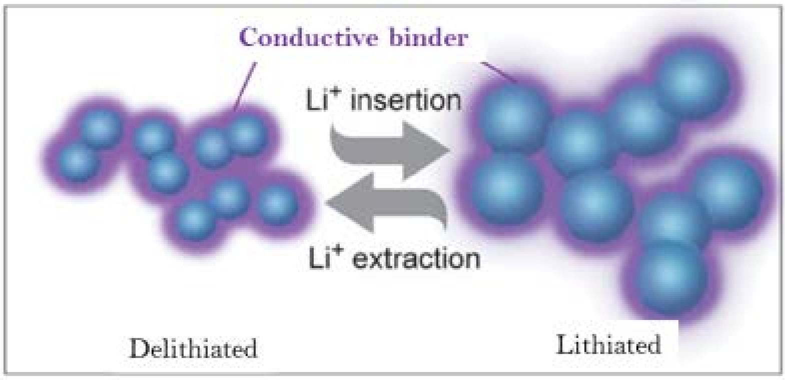
391 - Conductive polymer binder for high capacity lithium battery electrodes

Mingyan Wu, *mingyanwu@lbl.gov, Xiangyun Song, Shidi Xun, Vincent Battaglia, Gao Liu*. Environmental Energy Technologies Division (EETD), Lawrence Bekeley National Laboratory, Berkeley, CA 94720, United States*

A new conductive polymer binder is developed for solving the long-standing volume change issue for high capacity materials in lithium battery electrodes. Through synthesis modification, spectroscopy, and simulation techniques the electronic structure and polarity of the polymer was tailored favorably to enable in situ lithium doping. The composite electrodes based on Si particles and this polymer, without any conductive additive, exhibit so far the best performance in several critical aspects for commercial applications, including high capacity, long-term cycling, low over potential between charge and discharge, and good rate performance.



Tuesday, April 9, 2013 05:30 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

392 - Thermal and mechanical properties of biodegradable epoxy resins derived from epoxidized soybean oil

***Guozhen Yang**, gyang5@uh.edu, Megan L. Robertson. Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204-4004, United States*

Epoxy resins play an important role in wind power, an attractive alternative to fossil fuel. However, traditional epoxy resins, derived from petroleum, have two deficiencies: brittleness and lack of recyclability. In the present work, epoxidized soybean oil (ESO), derived from high-yield and low-price soybean oil, is a component of the epoxy resin to improve toughness and supply biodegradable cleavage points throughout the network. The thermal, mechanical, and biodegradation properties of epoxy resins with varying concentrations of ESO have been characterized.

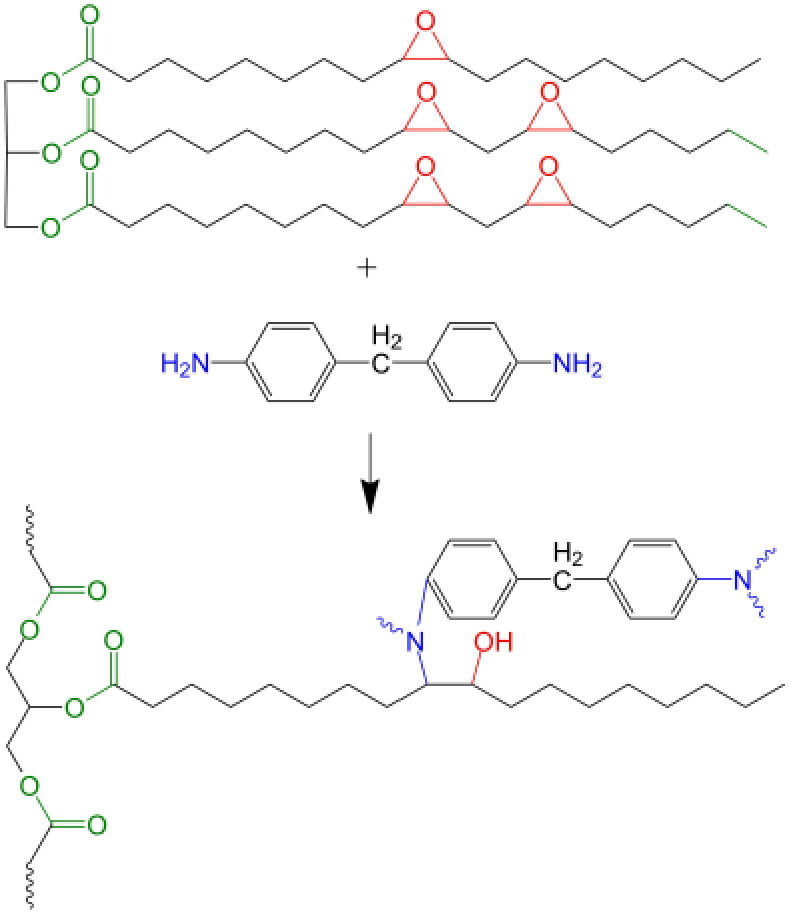


Figure1 Curing Reaction of Epoxidized Soybean Oil (ESO) and Methylene Dianiline (MDA)

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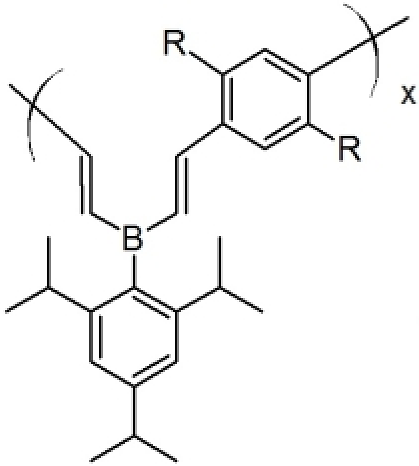
Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

393 - Properties of conjugated organoborane polymers prepared by hydroboration polymerization of substituted dialkynes

Reid A Lennon[2], Graham A Goulding[1], John H Huckans[2], Diane M Hinkens[1], ***Mark A Tapsak[1]****, mtapsak@bloomu.edu. (1) Department of Chemistry and Biochemistry, Bloomsburg Univ of Pennsylvania, Bloomsburg, Pennsylvania 17815, United States, (2) Department of Physics and Engineering Technology, Bloomsburg Univ of Pennsylvania, Bloomsburg, Pennsylvania 17815, United States*



Where R = H, OCH_3 or F

It is known that incorporating boron into the main chain of a conjugated polymer results in an electron deficient material that may behave as an n-type semiconductor.[1, 2] The semiconducting properties of organoborane polymers were measured when the aryl group was fluorene.[3] This current work builds upon prior studies by incorporating electron-donating or withdrawing groups onto the phenyl ring. To this end, a series of conjugated organoborane polymers, where R was H, OCH_3, or F, were synthesized and characterized. In addition, optical and electrical conductivity measurements were completed with the intention that these materials will be fabricated into organic solar cells. The results of these measurements will be presented in the context of their potential use as n-type organic semiconductors.

1. Nagai, A.; Murakami, T.; Nagata, Y.; Kokado, K.; Chujo, Y., *Macromolecules* **2009,** 42, (18), 7217-7220.

2. Cataldo, S.; Fabiano, S.; Ferrante, F.; Previti, F.; Patane, S.; Pignataro, B., *Macromol. Rapid Commun.* **2010,** 31, (14), 1281-1286.

3. Sato, N.; Ogawa, H.; Matsumoto, F.; Chujo, Y.; Matsuyama, T., *Synth. Met.* **2005,** 154, (1-3), 113-116.

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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
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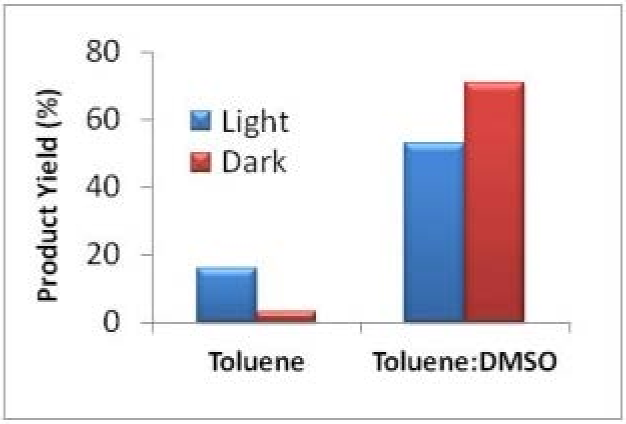
394 - Effect of light on the synthesis of polymer-tethered fullerenes in binary solvent mixtures

Amy M. Alexander-LeCroy, *amalexander@ualr.edu, Brian C. Berry. University of Arkansas at Little Rock, United States*

Polymer tethered fullerenes (PTFs) are useful for a variety of energy related applications. This study shows that an increase in reaction rates and product yields was observed in the presence of a co-solvent. With toluene alone, results indicate the presence of light increases reaction rates and yields as expected for an SET process. However, in the presence of DMSO, light hinders the reaction yields and leads to a different substitution pattern than reactions carried out in the dark.



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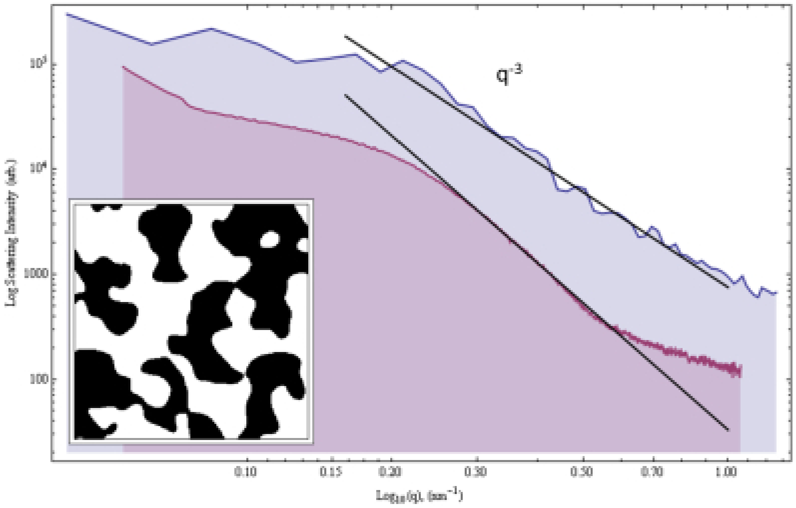
Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

395 - Quantitative characterization of two-phase morphologies for organic photovoltaics

***Jacob W Mohin**, jmohin@cmu.edu, Tomasz Kowalewski. Department of Chemistry, Carnegie Mellon university, Pittsburgh, Pennsylvania 15213, United States*

This presentation will discuss quantitative methods for characterizing two-phase morphologies such as bulk heterojunctions for organic photovoltaics. It will focus on the use of the well-known Porod law to determine the length of inhomogeneity and the interfacial area-to-volume ratio from grazing incidence small angle scattering patterns of thin films of polymer-fullerene blends used in organic solar cells. Extension of Porod's law to two dimensions, and its use to infer the actual dimensionality of nanoscale phase separation will also be described.



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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)

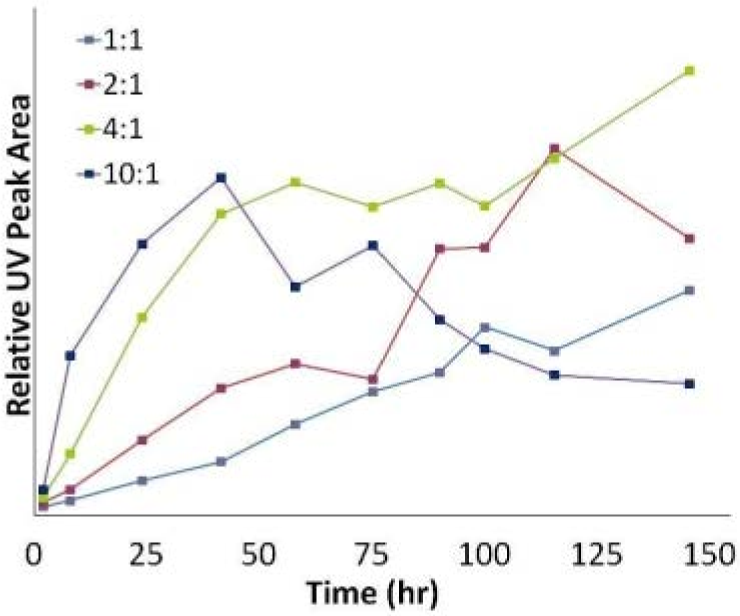
Location: Morial Convention Center

Room: Hall E

396 - Mechanochemical synthesis of polymer-tethered fullerenes

Steven E. Baker, *sebaker1@ualr.edu, Brian Berry. Department of Applied Science, University of Arkansas-Little Rock, Little Rock, Arkansas 72204, United States*

Mechanochemical synthesis is a green alternative to traditional organic syntheses. Using a simple laboratory-scale apparatus similar to the industrial action of a ball mill, polymer-tethered fullerenes (PTFs) were synthesized by reacting fullerene (C_{60}) with azide-terminated polystyrene (PS) of different molecular weights in varying ratios of C_{60}:PS. Gel Permeation Chromatography (GPC) was used to monitor the relative product yield as well as the number of tethers attached to each C_{60} over time.



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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)

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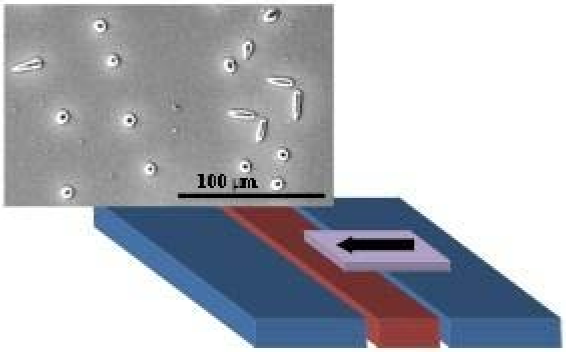
Room: Hall E

397 - Cold Zone annealing organic photovoltaics

Joshua A Moore, *jamoore1@ualr.edu, Department of Applied Science, University of Arkansas at Little Rock, Little Rock, Arkansas 72204, United States*

Poly(3-hexylthiophene)/PCBM composites are the most common materials for organic photovoltaics. In this study P3HT/PCBM bulk heterojunctions were annealed using cold zone annealing. SEM was used to determine PCBM domain size and orientation as a function of velocity, Tmax, and temperature gradient. In addition, IV curves were generated from the devices in order to determine efficiency, open circuit potential, short circuit current, and fill factor.



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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
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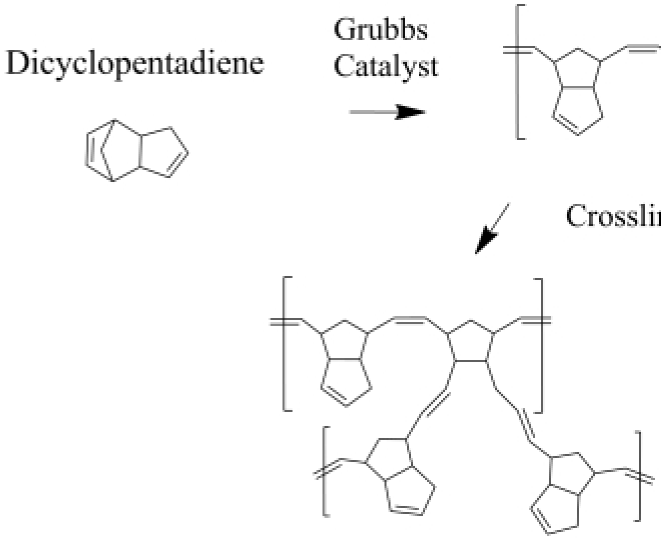
398 - Cure kinetics of dicyclopentadiene and 2nd generation Grubbs catalyst via ring opening metathesis polymerization

Brian J. Rohde, *br.rohde@gmail.com*, *Megan L. Robertson*. *Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States*

Dicyclopentadiene is a currently underutilized by-product of ethylene production and can create notoriously tough and stiff thermosets. The kinetics of ring opening metathesis polymerization (ROMP) of dicyclopentadiene with various Grubbs 2nd generation catalyst loadings were explored using differential scanning calorimetry and rheology.



The effects of the catalyst loading and methods of improving the catalyst solubility on the reaction kinetics and gelation time were probed. The tensile modulus, flexural modulus, and fracture toughness of the polymers were explored.

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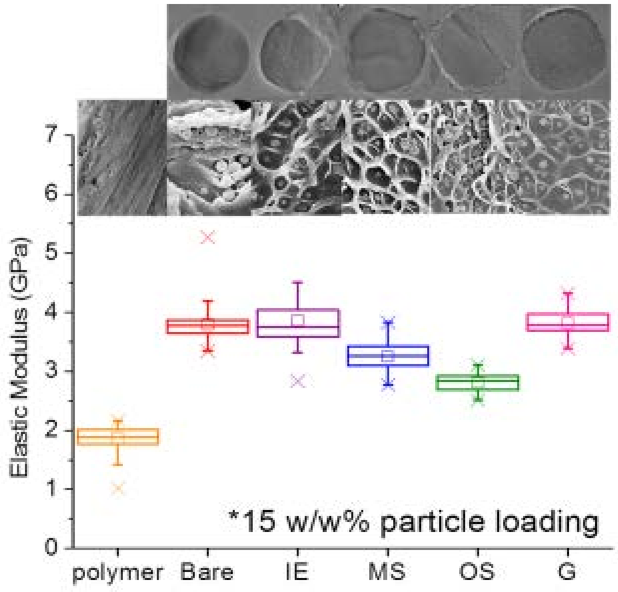
399 - Impact of zeolite LTA functionalization on polyimide nanocomposite membrane properties for use in natural gas separations

Megan E. Lydon[1], *melydon@gatech.edu, Christopher W. Jones*[1,2], *Sankar Nair*[2]. *(1) School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States, (2) School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

Natural gas is cleaner and safer than traditionally used energy sources and is an important transitional energy source; however, improvements in the efficiency and cost of purification are needed [1]. Nanocomposite membranes consisting of a bulk polymer phase and dispersed selective phase can improve gas selectivity compared to pure polymer membranes while avoiding the high costs of inorganic membranes. However, poor adhesion between the two phases leads to nonselective pathways for gas transport. Functionalization of the zeolite with MgO_xH_yinorganic surface nanostructures has been shown to eliminate or minimize the gap [2].

Four methods of inorganic surface roughening have been completed on aluminosilicate zeolite-LTA and characterized using HRTEM and nitrogen physisorption [3]. In this work, we show how these nanostructures impact properties of polyimide nanocomposite membranes including CO_2/CH_4 gas selectivity, nanoindentation mechanical properties, and phase compatibility by TEM imaging of cross sections. We show that all composite membranes show improved mechanical and gas separation properties compared to pure polymer, but one method, ion-exchange induced surface deposition, shows significantly improved mechanical and separation properties.[ol][li]Burnett, W. M.; Ban, S. D. *Science.* **1989** , *244*, 305-310.[/li][li]Shu, S.; Husain, S.; Koros, W. J. *J. Phys. Chem. C.* **2007** , *111*, 652-657.[/li][li]Lydon, M. E.; Unocic, K. A.; Bae, T.; Jones, C. W.; Nair, S. *J. Phys .Chem. C.* **2012** , *116*, 9636-9645.[/li][/ol]



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Polymer Composites for Energy Harvesting, Conversion and Storage (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

400 - Synthesis meso-micoporous carbons using PVDC block copolymer as a carbon precursor via RAFT

yongzhong Bao, *yongzhongbao@zju.edu.cn*, ***Jie Yang***, *11028038@zju.edu.cn. Department of Chemical and Biological Engineering, State Key Laboratory of Chemical Engineering, Hangzhou, Zhejiang 310027, China*

The work developed by our group has been focused on the use of vinylidene chloride (VDC) polymers as precursors to prepare porous carbon. Having established conditions for RAFT polymerization of VDC, serials of block copolymers, PS-b-PVDC, synthesize via RAFT. With thermal degradation characteristics, block copolymers exhibit subparagraph pyrolysis corresponding to the block structure of copolymers. As summarized in

Sample	S_{BET}(m^2/g)	S_{t-m}(m^2/g)	V_{total}(cm^3/g)	D_m(nm)	D_p(nm)
PS1-*b*-PVDC-carbon	1019.63	453.52	0.4835	0.52	3.63
PS2-*b*-PVDC-carbon	1219.36	487.38	0.9223	0.51	5.30
PS3-*b*-PVDC-carbon	1095.24	504.05	0.8019	0.52	12.10

S_{BET}: BET surface area; S_{t-m}: surface area of micropores calculated via the t-plot method; V_{total}: total pore volume; D_m: diameter of micropores; D_p: diameter of mesopores

, the S_{BET} of PS-*b*-PVDC-carbons increased from 1019m^2/g to 1219.36m^2/g with S_{t-m} decreased due to the increasing PS block amount and etching of the PS pyrolysis. This approach provide a satisfactory addition to the methods for the manufacturing of meso-microporous carbons from PVDC-containing block copolymers.

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Polymer Precursor-Derived Carbon (05:30 PM - 07:30 PM)
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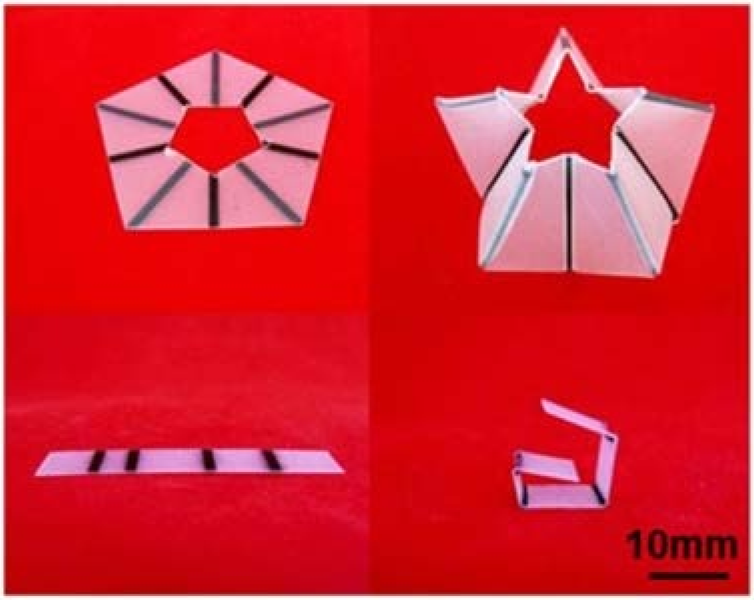
Room: Hall E

401 - Light responsive folding based on pre-stressed polymers

***Brandi Shaw**, blshaw@ncsu.edu, Ying Liu, Jan Genzer, Michael D. Dickey. Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States*

Self-folding is a self-assembly strategy that induces folding of a desired 3D structure based on a predefined 2D sheet. Self-folding can be applied in the fields of actuation, sensing, and packaging. We use a desktop printer to define ink 'hinges' on sheets of pre-stressed polymer. The ink absorbs light to heat the polymer underneath and causes folding. We demonstrate origami folding and study various light sources to trigger the folding effectively and sequentially.



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Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
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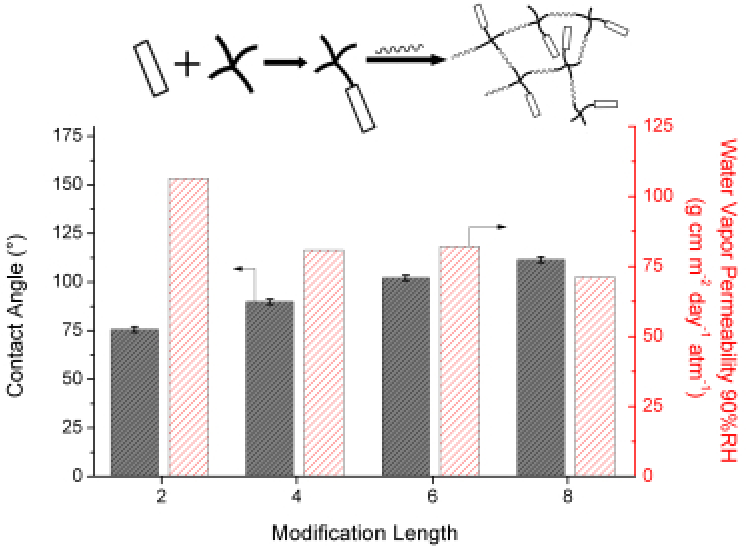
402 - Perfluorinated acrylate modified thiol-ene networks for highly water vapor breathable, waterproof materials

***Jacob M Schekman**, jschekman92@gmail.com, James Goetz, Sergei Nazarenko. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0001, United States*

Highly water vapor breathable materials are used in athletic apparel, military uniforms, medical clothing, and industrial dehydration processes. Increased water vapor permeability is targeted while retaining hydrophobicity on a breathable film's surface. Polyethylene glycol has been incorporated into various polymer systems to increase the water vapor permeation and fluorinated groups have been shown to decrease surface tension. Perfluoro n-alkyl acrylates of n = 2, 4, 6, and 8 carbons in length were used in a two stage process for the modification of thiol-ene networks to investigate the length effect on the water vapor permeability of highly crosslinked networks. Real time FTIR of the monomer mixtures showed near complete conversion of each monomer rapidly polymerized under a UV lamp. Fluoroalkyl acrylate modification of pentaerythritol tetrakis(3-mercaptopropionate) (4T) effectively increased water contact angle as the fluoroalkyl chain length was increased from a control (unmodified) to n = 8. The increase in water contact angle indicates that fluoroalkyl acrylates decrease surface energy of the thiol-ene film. Similarly, density of each film also increased with high fluorine content. Water-sorption uptake of the polymer showed increasing water-vapor permeation as it was subjected to environments of higher relative humidity. Highest permeation at 70% Relative Humidity was achieved with the n = 2 modified thiol monomer, with a permeation value of 114 (g*cm/m^2*day*atm).



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Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
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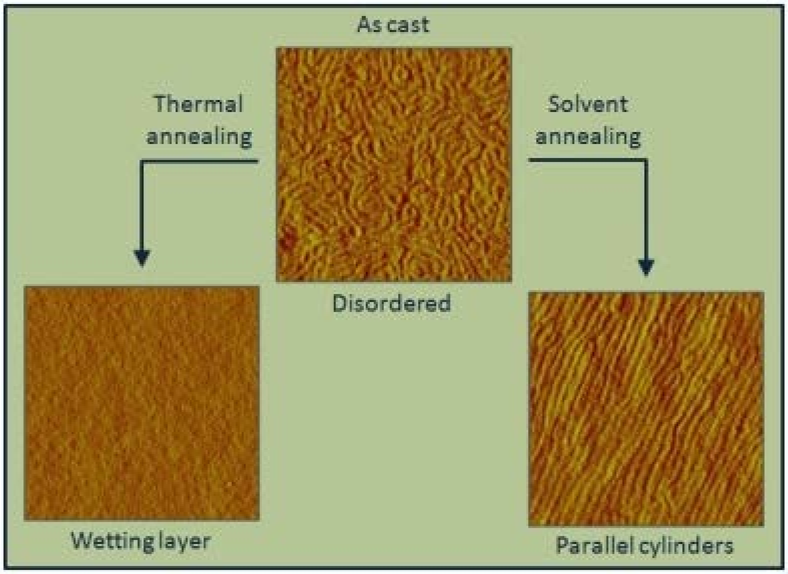
Room: Hall E

403 - Thin film morphology determination of poly(styrene-*b*-isoprene) diblock copolymer

Ronald L Lewis, III, *ronlewis@udel.edu, Thomas H Epps, III. Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19711, United States*



Our work focuses on using self-assembled poly(styrene-*b*-isoprene) diblock copolymer nanostructures in thin films for biomimetic applications. Thin films are created using gradient flow coating, a high throughput method, and are subject to various solvent and thermal annealing conditions to promote specific nanoscale morphologies. Solvent annealing with toluene for 4 hours produces a parallel-oriented cylindrical morphology, and thermal annealing for 8 hours at 200 °C creates an isoprene wetting layer at the surface of the film.

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404 - Formation and testing of xanthene-based mechanophores

Zoe Glick, *cjs@loyno.edu*, ***Farihah Haque***, *farihah3@gmail.com*, *Clifton Stephenson*. *Chemistry, Loyola University New Orleans, New Orleans, LA 70118, United States*

A mechanophore is a stress-sensitive material that undergoes selective bond breakage caused by physical stress. In many cases, this selective bond breakage causes changes in the colorimetric and/or fluorescent properties of molecules. Colorimetric mechanophores that are highly sensitive to mechanical stress could be useful for monitoring the relative stability of infrastructure and for testing the stress tolerance of materials. This research explores the potential of mechanophores formed from the spyrolactone xanthene dyes rhodamine and fluorescein. These dyes can change from a closed, colorless form to an open, colored, fluorescent form. These xanthene compounds offer much promise because they have a high quantum yield, are easy monitoring of bond breakage through changes in color and fluorescence, and have known facile derivatization routes. Described herein, is the development of new fluorescent monomers using rhodamine and fluorescein and the testing of the materials formed for their ability to function as mechanophore polymers.

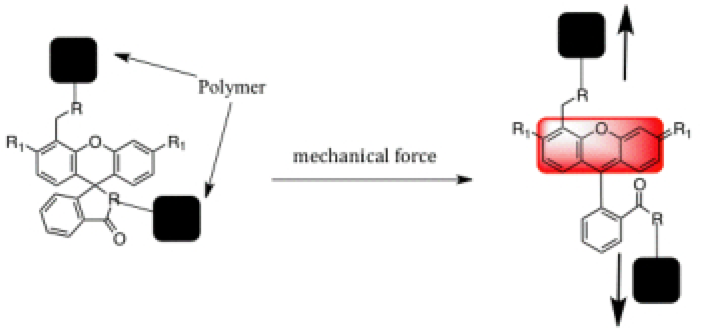

Figure 1: Cartoon showing how xanthene-based mechanophore will turn "on" when stretched

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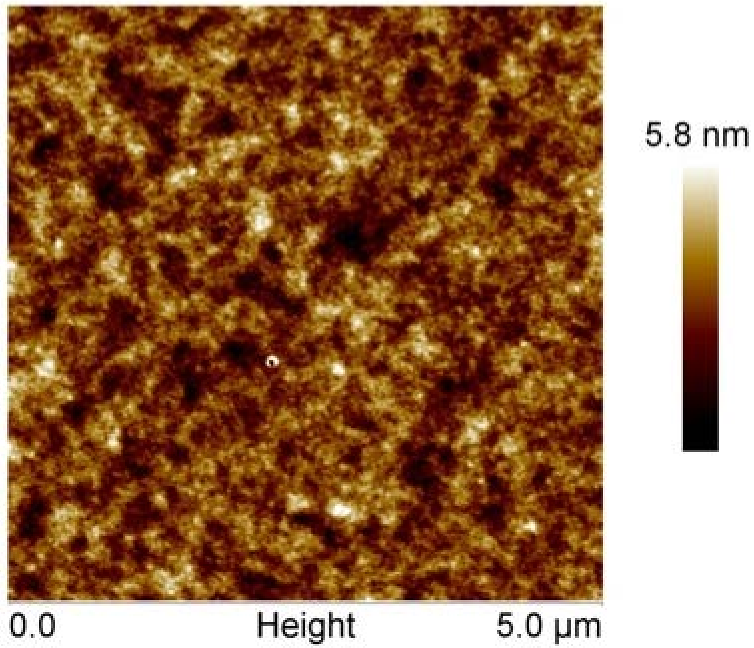
405 - Optimizing processing techniques to increase efficiency in P3HT/PCBM bulk heterojunction organic photovoltaic cells in different atmospheric conditions

Robert V Boswell, *robert.boswell@eagles.usm.edu, Qi Wu, Mithun Bhattacharya, Sarah E Morgan. School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Polymer OPV cells have several advantages when compared to silicon-based solar cells. Their low cost, flexibility, and ease of fabrication are superior to silicon-based solar cells. One of the main disadvantage of these OPVs is the lower conversion efficiency. Another disadvantage of OPVs is the requirement for an inert atmosphere during the construction of the cell. By understanding the performance of the P3HT/PCBM interactions using different solvent annealing techniques and atmospheric conditions the conversion efficiency can be quantified.



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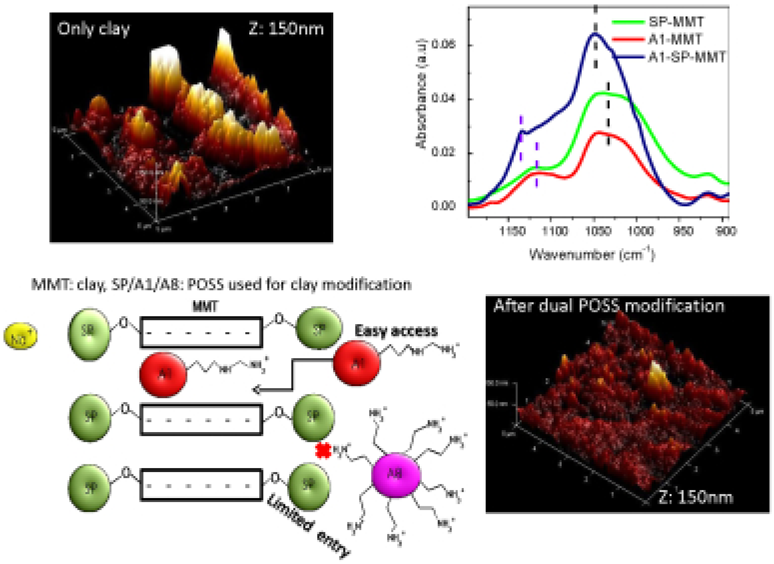
406 - Structure-property relationships of dual (tethered and intercalated) POSS modified montmorillonite in elastomeric nanocomposites

Harold Owens[1], *junior93@prodigy.net, Mithun Bhattacharya*[2], *Elana C Lewis*[2], *Sarah E Morgan*[2]. *(1) Department of Chemistry, Jackson State University, Jackson, MS 39217, United States, (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

POSS molecules have been reported to improve performance of clay nanocomposites through modification of the clay particles. Amine-functional POSS molecules are thought to intercalate and expand the clay gallery spacing, while silanol-POSS molecules preferentially attach at the edges of the clay layers. Rubber clay nanocomposites with mixed and multi-functional POSS molecules were prepared, and it was found that modulus of the nanocomposites was improved as much as 140%. Edge-tethered POSS, however, may limit intercalation of a second intercalant.



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Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
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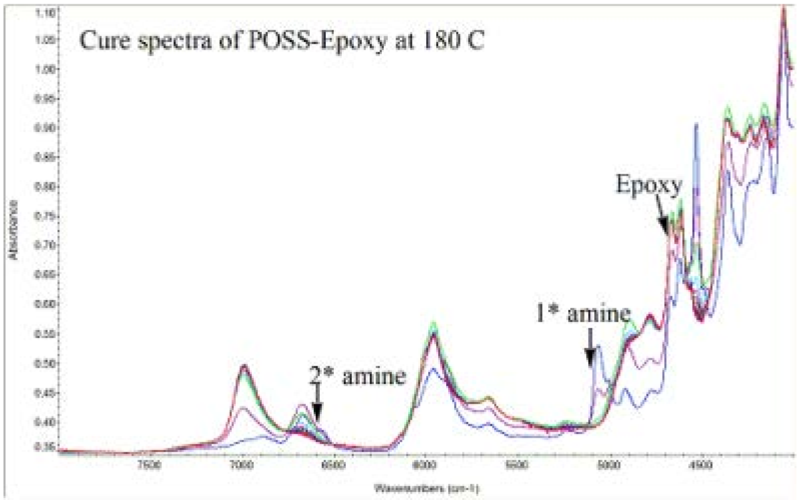
Room: Hall E

407 - Investigating cure kinetics of amine-functionalized polyhedral oligomeric silsesquioxane (POSS) in epoxy-amine networks

Travis L Thornell, *travis.thornell@eagles.usm.edu*, *Katherine L Frank*, *Jeffrey S Wiggins*. *School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Cure kinetics of polyhedral oligomeric silsesquioxane (POSS) with a single amine group functionality dispersed into epoxy-amine networks of diglycidyl ether of bisphenol-F (DGEBF) and 3,3'-diaminodiphenylsulfone (3,3'-DDS) were studied. POSS-modified samples were prepared in two ways: an in-situ reaction of all reagents, and a pre-reaction with the POSS and excess epoxy at high temperatures followed by reaction with remaining network components. The use of differential scanning calorimetry and near-infrared spectroscopy provided insight into how the network architectures are formed and altered through calculated activation energies and concentration of functional groups during the cure process.



Tuesday, April 9, 2013 05:30 PM

Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)

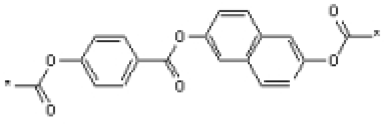
Location: Morial Convention Center

Room: Hall E

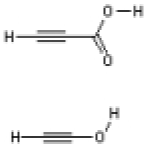
408 - End group effects on the curing temperature of liquid crystalline thermosets

Craig M Whitaker, ***Ryan Hickey***, *m133036@usna.edu*, ***Rebecca E Watson***, *m137140@usna.edu. Department of Chemistry, US Naval Academy, Annapolis, MD 21402, United States*

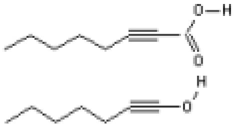
The goal of this project was to lower the reaction temperature for liquid crystalline thermosets (LCTs) using reactive end-caps attached to a Vectran backbone. In order to determine the optimal curing temperature for the LCTs, a systematic study of acetylene derivatives was initiated. The acetylenic derivatives potentially have the best processing window with a widely separated temperature at which the resin flows and the crosslinking temperature.



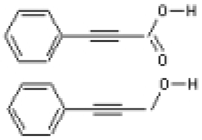
End-Cap



Propargyl



Octyl



Phenyl

Tuesday, April 9, 2013 05:30 PM

Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)

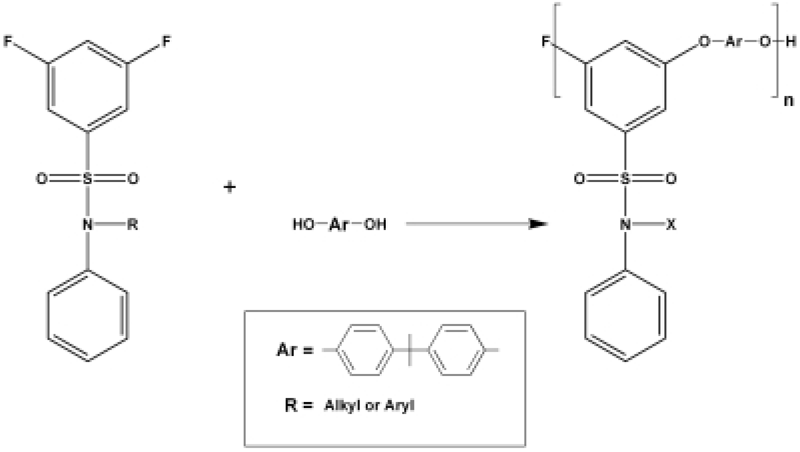
Location: Morial Convention Center

Room: Hall E

409 - Introducing chemical diversity to poly(arylene ether)s via N-phenyl-3,5-difluorobenzene sulfonamides

***Ryan Selhorst**, selhorst.16@wright.edu, Eric Fossum. Department of Chemistry, Wright State University, 3640 Colonel Glenn Hwy, Dayton, Ohio 45435, United States*

The synthesis of poly(arylene ether)s, PAE, is typically achieved via *para*-activated nucleophilic aromatic substitution of dihalo aromatic compounds, but the process can also be carried out with strong electron-withdrawing groups located in the *meta* position. The utilization of *N*-phenylbenzene sulfonamide as the activating group provides ready access to a wide array of functionalized PAE systems. The thermal properties and solubility characteristics can be tailored by a judicious choice of the R group as well as substitution on the phenyl ring.



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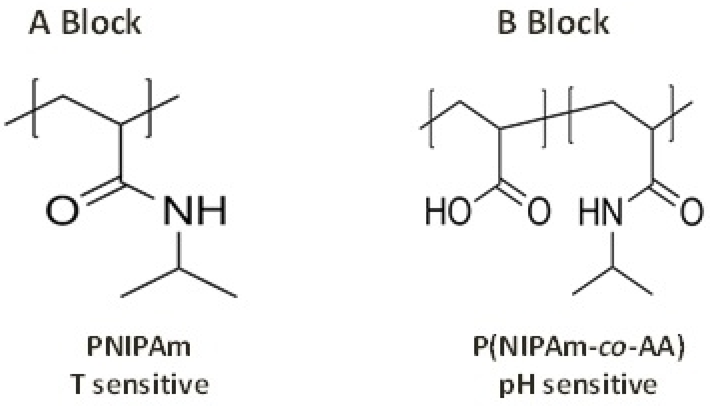
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

410 - Synthesis and characterization of dual pH/temperature sensitive block polymers

Allison M Siehr[2], *amsiehr@broncs.utpa.edu, Isha Koonar*[1], *Ron Siegel*[1]. *(1) Department of Pharmaceutics, University of Minnesota, Minneapolis, Minnesota 55455, United States, (2) Department of Chemistry, University of Texas Pan-American, Edinburg, Texas 78541, United States*

Stimuli-responsive block polymers can assemble into different morphologies depending on their composition, quantity of blocks, and environment. AB diblock and ABC triblock polymer solutions can form micelles or hydrogels, respectively. These structures are of increasing importance in biomaterials and drug delivery applications. In this work, micellization of AB block polymers, composed of N-isopropylacylamide and N-isopropylacrylamide-*co*-acrylic acid, was studied as a function of temperature and pH. The block polymers were analyzed to determine molecular weight, composition, structure, and phase behaviors.



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Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)

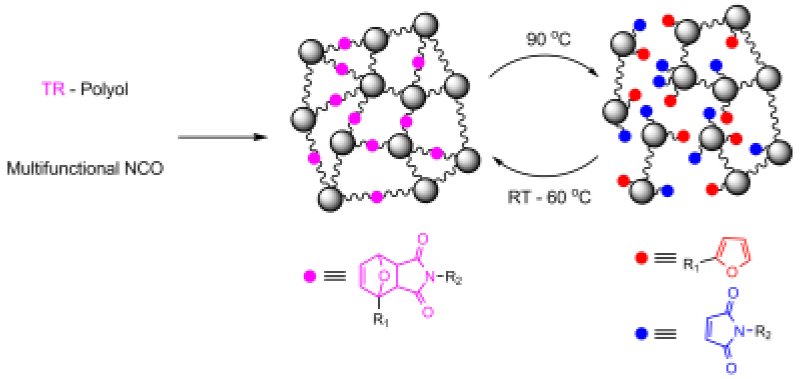
Location: Morial Convention Center

Room: Hall E

411 - Preparation of thermally-responsive polyurethanes based upon Diels-Alder chemistry

Craig A Machado, *pcostanz@calpoly.edu, Philip J Costanzo. Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407-0420, United States*

Diels-Alder (DA) chemistry is becoming increasing popular due to its simplicity and efficiency; however, one concept that has yet to be thoroughly explored is the incorporation of DA linkages to prepare polymeric phase change materials. This work details the preparation of various DA linkage systems and their subsequent incorporation into polyurethane systems.



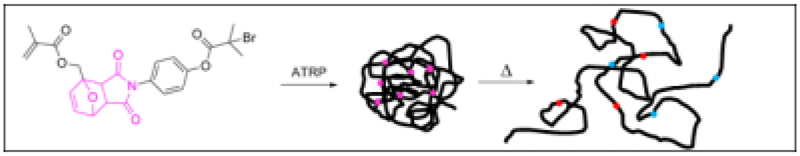
Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Morial Convention Center
Room: Hall D

Tuesday, April 9, 2013 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

412 - Dynamic topology of thermally-responsive materials via Diels-Alder chemistry

Tristan S Kleine, *pcostanz@calpoly.edu, Christopher D Roland, Alex E London, Philip J Costanzo. Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407-0402, United States*

Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry was employed to prepare an inimer compound to integrate DA linkages at branching points within a branched polymer backbone. Upon the application of a thermal stimulus, the retro-DA was induced and subsequent branch points were reduced to transform a highly branch architecture into a linear topology.



Tuesday, April 9, 2013 05:30 PM

Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)

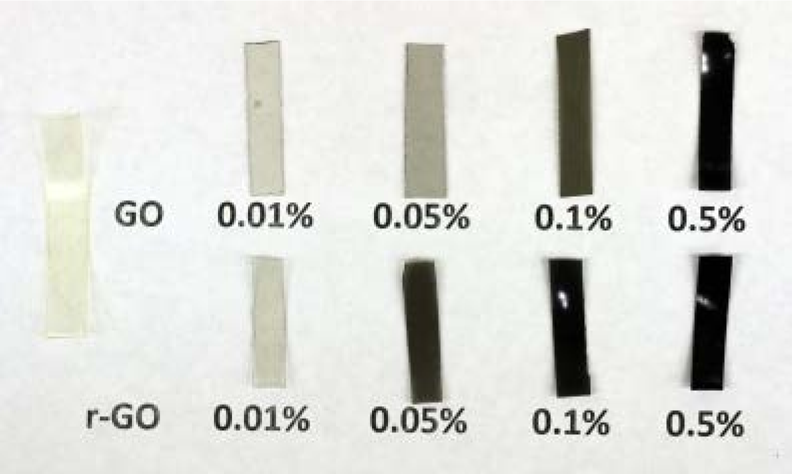
Location: Morial Convention Center

Room: Hall E

413 - Photopolymerization of thiol-ene/graphene nanocomposites

Ethan F. T. Hoff, *ethan.hoff@eagles.usm.edu, Bradley J. Sparks, LaTonya Hayes, Derek L. Patton. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

In this work, graphene materials were incorporated into thiol-ene resins at low loading percentages (0.01, 0.05, 0.1, and 0.5 wt. %) to determine the effect of graphene on the kinetic, thermomechanical, and mechanical properties of the graphene/thiol-ene nanocomposite materials. Combinations of alkenes (allyl isocyanurate (TTT) and pentaerythritol triallyl ether (APE)) and thiols (pentaerythritol tetra(3-mercaptopropionate) (PETMP) and trimethylolpropane tris(3-mercaptopropionate) (TMPMP)) were used to obtain networks with glass transition temperature ranging from 12 °C (APE-PETMP) to 68 °C (TTT-PETMP). The effect of the graphene materials on thermomechanical and mechanical properties were not uniform among the three thiol-ene resin systems.



The thermomechanical and tensile properties of the APE-PETMP resin system were relatively unaffected by the inclusion of the graphene materials. Graphene oxide (GO) did not have any notable effect on the thermomechanical properties of the TTT-TMPMP resin system, however, reduced graphene oxide (r-GO) enhanced the glass transition temperatures at low loading levels. Additionally, changes in the tensile properties were observed upon the incorporation of graphene materials. In the TTT-PETMP resin system, both the thermomechanical and tensile properties were affected with increasing weight percent of graphene materials. Dispersion of the graphene materials was characterized using optical microscopy.

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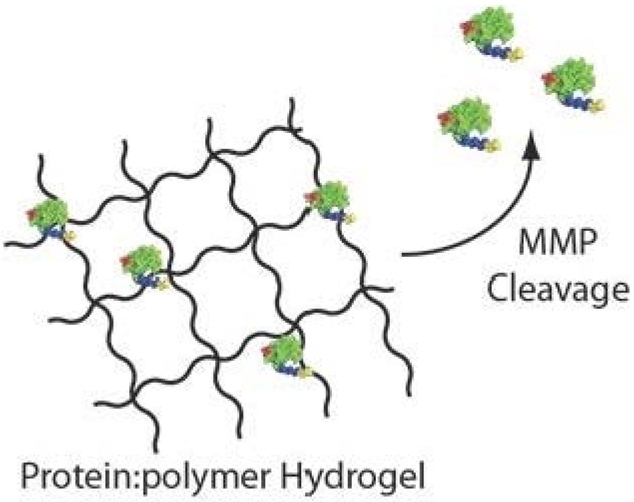
414 - Synthesis of genetically engineered epidermal growth factor for controlled release

__Kerry Martenis__, kgm31@case.edu, John Edelbrock, Si-Eun Kim, Jon Pokorski. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

During the healing phase, Epidermal Growth Factor (EGF) is released to help repair damaged tissue; EGF is the protein responsible for stimulating cell growth, proliferation, and differentiation. One approach to dermal tissue engineering would be to present EGF to the surrounding tissue in a way that accelerates the wound healing process. To this end, we have developed a genetically modified version of EGF that can be incorporated covalently into cross-linked polymer hydrogels. Our EGF variant contains a specific sequence designed to cleave the protein from the material scaffold for programmable release upon administration.

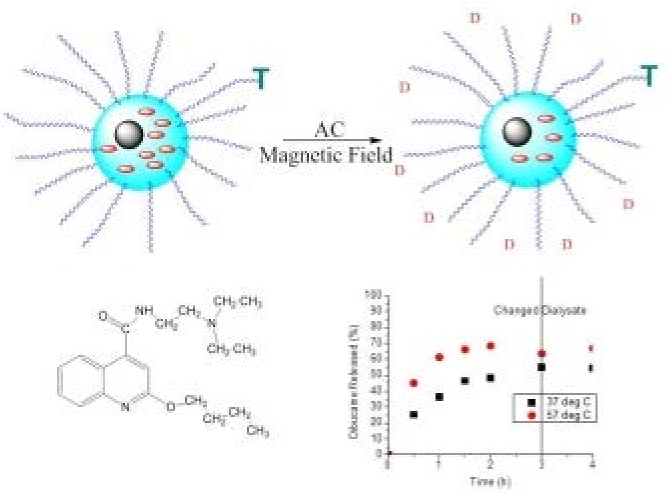


Tuesday, April 9, 2013 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

415 - Effectof formation conditions on the drug-loading capacity and thermally-triggered release for polymer micelles

Jerome S Arceneaux[1,2], *jarsen@uab.edu, Amanda L Glover*[1], *Jacqueline A Nikles*[2], *David E Nikles*[1]. *(1) Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States, (2) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240, United States*

Polymer micelles were made from a diblock copolymer poly(ethylene glycol-*b*-caprolactone), where the degree of polymerization for the poly(ethylene glycol) block was 45 and either 10 or 20 for the polycaprolactone block. The polycaprolactone in the micelle core was semicrystalline, and it was expected that the crystalline core would trap the cancer drug until the micelle core melted at temperatures above 45°C. 9-(Methylaminomethyl)anthracene was found to give disappointing encapsulation efficiencies of less than 1%. For the diblock copolymer, the best method was to load the drug at high temperatures, about 90°C, when the polycaprolactone core had melted. By loading at high temperatures, the encapsulation efficiency (21%) and loading (10%) of dibucaine was much higher. Thermally-triggered release experiments were carried out a 37°C and at 57°C showed a much high release rate when the temperature was above the melting point of the polycaprolactone core.



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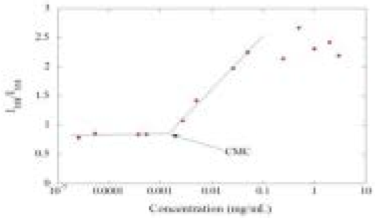
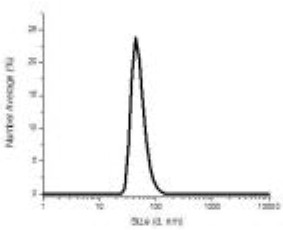
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

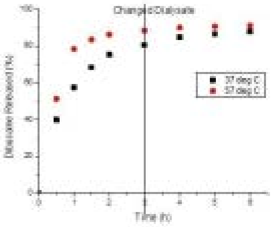
416 - Dibucaine encapsulation in polymer micelles having a semi-crystalline core made from a poly(ethylene-b-caprolactone) diblock copolymer

Lindsey N Cobb[1], *lncobb@crimson.ua.edu, Amanda L Glover*[1], *Jacqueline A Nikles*[2], *David E Nikles*[1]. *(1) Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States, (2) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240, United States*

The diblock copolymer, $CH_3O\text{-}(CH_2CH_2O)_{113}\text{-}(COCH_2CH_2CH_2CH_2CH_2O)_{99}\text{-}H$ was prepared by the tin-catalyzed, ring-opening polymerization of e-caprolactone from the alcohol terminus of poly(ethelene glycol) monomethyl ether, M_n ~ 5,000. Polymer micelles were made by dispersing the diblock in ultrapure water by solvent evaporation of THF. The critical micelle concentration was 1.44 mg/L and increased with increasing temperature. DSC showed that the polycaprolactone core was semi-crystalline with a melting point between 40 and 55 °C. Dibucaine was trapped in the core with a loading of 16% and an encapsulation efficiency of 28%. The rate of thermally triggered release of the dibucaine was determined isothermally at 37 °C, a temperature below the melting point of the polycaprolcatone core and at 57 °C, above the melting point, and pulse between 37 °C and 57 °C, to mimic heating that would be performed in the body. The release rate at 57 °C was higher and 90% of the dibucaine was released after 4 hours.







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Location: Morial Convention Center
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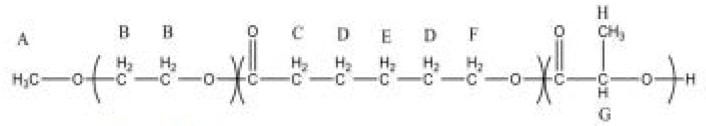
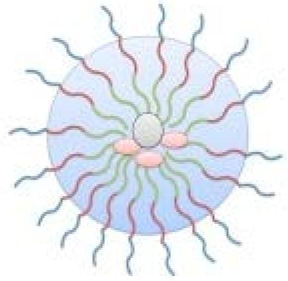
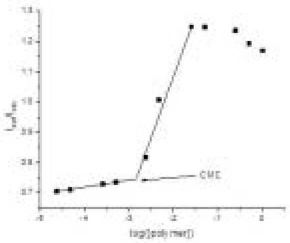
417 - Thermally triggered release of dibucaine from polymer micelles made from a poly(ethylene glycol-b-caprolactone-b-lactic acid) triblock terpolymer

Jesse A Gettinger[1], *jagettinger@crimson.ua.edu, Amanda L Glover*[1], *Jerome S Arceneaux*[1,2], *Jacqueline A Nikles*[2], *David E Nikles*[1]. *(1) Department of Chemistry, The University of Alabama, Tuscaloosa, Al 35487-0336, United States, (2) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240, United States*

The triblock terpolymer, $CH_3O\text{-}(CH_2CH_2O)_{120}\text{-}(COCH_2CH_2CH_2CH_2CH_2O)_{40}\text{-}(COCHCH_3O)_{37}\text{-}H$ was prepared in a two stage process. First, a poly(ethylene glycol-*b*-caprolactone) diblock copolymer was prepared by the tin-catalyzed, ring-opening polymerization of e-caprolactone from the alcohol terminus of poly(ethylene glycol) monomethyl ether, M_n~ 5,000, then the triblock was prepared by the tin-catalyzed ring-opening polymerization of L-lactide from the alcohol terminus of the caprolactone block. The critical micelle concentration was 1.35 mg/L. Loaded polymer micelles were made adding a solution of the triblock and dibucaine in THF to ultrapure water. Dibucaine was trapped in the core with a loading of 6% and an encapsulation efficiency of 9%. The rate of thermally triggered release of the dibucaine was determined at 37 °C, a temperature below the melting point of the polycaprolcatone core and at 57 °C, above the melting point. The release rate at 57 °C was higher and 68% of the dibucaine was released after 2 hours.







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418 - Modeling cilia inspired poly-acrylamide gel morphologies with a spiky ferrofluid

Daniel Hulgan, *danielhulgan@yahoo.com, Cornelia Rosu, Sourav Chatterjee, Paul S Russo. Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

Poly(acrylamide) gels were patterned into microbeaker arrays by conducting gelation at the interface with a ferrofluid in the presence of a strong magnetic field. The nature of the magnetic fluid was investigated with several techniques such as TEM, FTIR and SPME.

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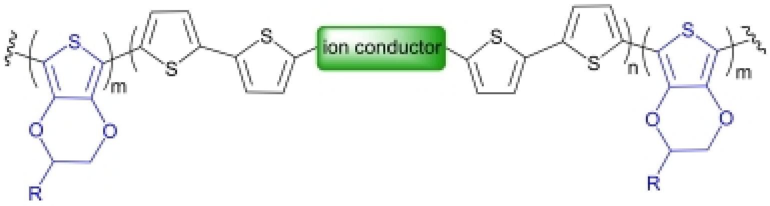
419 - Synthesis and characterization of thiophene-based conducting polymers for use as artificial muscles

Emily Lasselle[1], *lassele@students.wwu.edu, Celia Whelan*[2], *Amanda R. Murphy*[1]. *(1) Chemistry, Western Washington University, Bellingham, WA 98225, United States, (2) Chemistry, Western Kentucky University, Bowling Green, KY 42101, United States*

Biocompatible materials capable of conducting electricity have numerous biomedical applications including use as electrodes for neurological stimulation and recording, artificial muscles, and stimuli-responsive sensors. Conducting polymers such as poly(pyrrole) and poly(thiophene) are advantageous for these applications as they are biocompatible, and their chemical and physical properties can be easily tuned. We are synthesizing a family of thiophene-based conducting polymers designed for use as artificial muscles that contain linear or cyclic polyether segments in order to enhance the mechanical durability and increase the ion mobility through the polymers. Here we will present the synthesis, characterization and initial actuation performance of these polymers.



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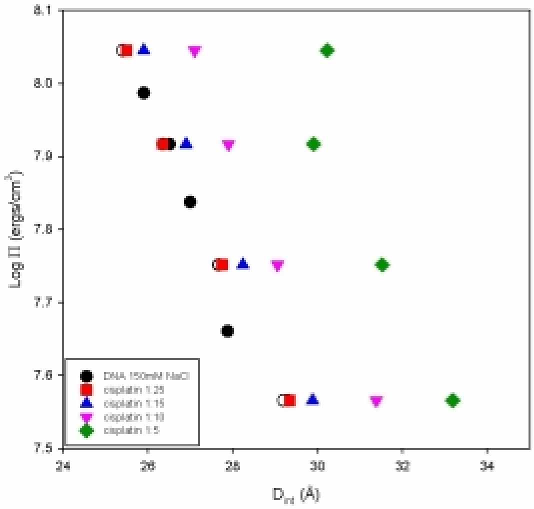
420 - Cisplatin adduct affects on DNA-DNA interactions

James M Hutchison, *matthew.hutchison@uky.edu, Jason DeRouchey. Department of Chemistry, University of Kentucky, Lexington, KY, United States*

Small drug molecules that bind directly to DNA are known to influence vital cell functions such as transcription and DNA replication. Cisplatin is a well-studied anti-tumor drug which has been used extensively to fight various forms of cancer. The high rate of cell apoptosis incurred has been attributed to the 1,2 intrastrand adducts formed between DNA and cisplatin. Currently, little is known about how cisplatin interacts with highly packaged DNA that is typically found within cells. We use osmotic stress coupled with x-ray scattering to study fundamental molecular scale interactions in DNA arrays. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to monitor unreacted cisplatin concentrations. DNA-DNA forces were measured as a function of cisplatin concentration. Large disruptions of the DNA-DNA spacings are observed with increasing cisplatin. These studies begin to shed light on how cisplatin interacts with condensed DNA.



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Location: Morial Convention Center
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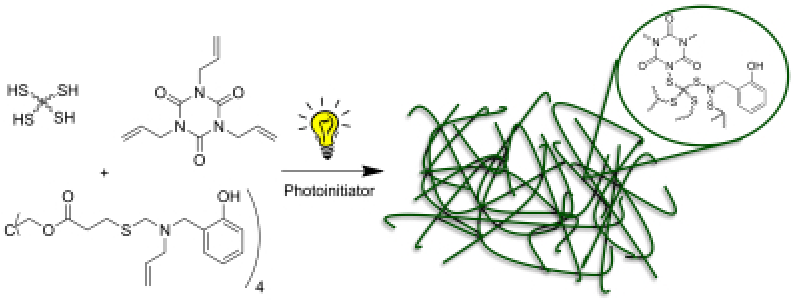
421 - Ternary thiol-ene photopolymerizations using multifunctional monomers derived from the thiol-benzoxazine reaction

Jared S. Cobb, *jaredscobb@gmail.com, Matthew J. Jungman, Jananee Narayanan, Derek L. Patton. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

The synthesis and subsequent thiol-alkene photopolymerization of a tetrafunctional alkene monomer based on a thiol-benzoxazine reaction is reported. An allyl-functional benzoxazine was reacted with pentaerythritol tetra(3-mercaptopropionate) (PETMP) to form a tetrafunctional alkene monomer (PETMP-4ene) with pendent phenols.



The effect of the PETMP-4ene monomer concentration on the thermomechanical properties, tensile properties and thermal stability of a ternary thiol-alkene system consisting of PETMP and triallyl isocyanurate (TTT) was evaluated using DMA, tensile testing and TGA, respectively. Photopolymerization kinetics were monitored using real-time FTIR. Increasing the loading concentration of PETMP-4ene led to a decrease in glass transition temperature, a decrease in initial thermal stability, an increase in char yield and an increase in toughness. The changes in thermomechanical properties are presented in terms of crosslink density and functional group conversions.

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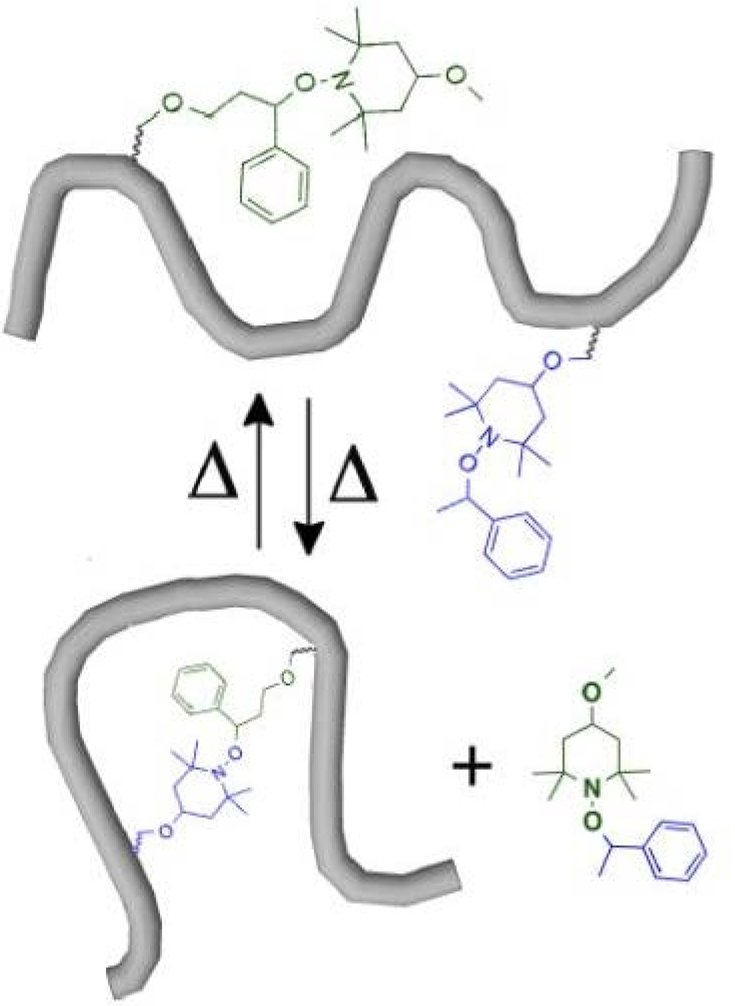
422 - Folding of synthetic polymer chains using radically exchangeable alkoxyamines

Odin Achorn, *obz2@wildcats.unh.edu, Danming Chao, Erik Berda. Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States*

We report the synthesis of single-chain polymer nanoparticles using radically exchangeable alkoxyamine cross-links. Cross-linking is achieved by complementary interactions between two different alkoxyamine functionalized monomers. Heat cleaves the two alkoxyamines homolytically, leaving nitroxide radicals and benzylic radicals along the backbone. Coupling of the radicals causes the polymer to fold. Crosslinking is confirmed by an increase in GPC retention time, by DLS, and spectroscopically. This is a step toward future efforts at using multiple, orthogonal chemistries to achieve hierarchical assemblies.



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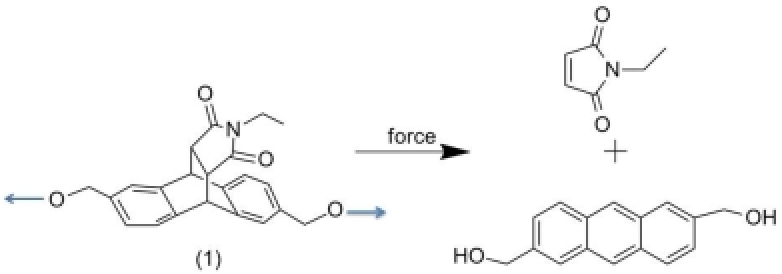
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

423 - Probing Diels-Alder adducts of anthracene and maleimide as mechanically active functional groups

Meredith G Hyatt[2], *hyattmer@email.meredith.edu, Zachary S Kean*[1], *Bobin Lee*[1], *Stephen L Craig*[1]. *(1) Department of Chemistry, Duke University, Durham, North Carolina 27708, United States, (2) Department of Chemistry, Physics, and Geoscience, Meredith College, Raleigh, North Carolina 27607, United States*

The mechanochemical response of an anthracene and maleimide Diels-Alder adduct (1) was investigated for the purpose of demonstrating small molecule release and unveiling masked fluorescence under applied force. The synthesis of 1 began with the reaction of 2,6-bis(hydroxymethyl) anthracene and n-ethylmaleimide through the Diels-Alder reaction. Polymer handles were necessary for the transduction of force under pulsed ultrasound, so a difunctional initiator was synthesized from 1 via esterification of hydroxyl groups to create 2-bromoisobutyrate esters and polymer chains were grown with ATRP.



GPC-UV analysis after pulsed ultrasound indicated polymer chain scission, but did not reveal an increase in UV absorbance at 365 nm as expected.

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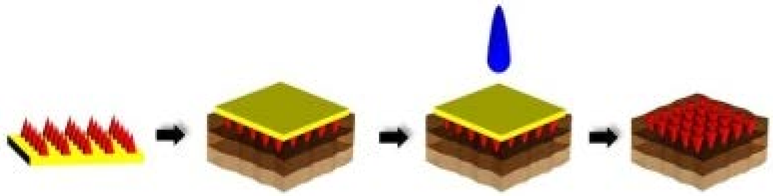
424 - Rapidly-dissolvable microneedle patches via a highly scalable and reproducible soft lithography approach

Christine F Archuleta, *archulet@live.unc.edu, Katherine A Moga, Lissett R. Bickford, Robert D Geil, Ashish A Pandya, Yapei Wang, Adrian T O'Neill, Joseph M DeSimone. Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States*

Transdermal drug delivery methods, particularly microneedles, effectively transport therapeutics locally and systemically. Microneedles of biocompatible components loaded with drug surrogate were fabricated using the Particle Replication in Non-wetting Templates (PRINT ®) process. Penetration and dissolution in *ex vivo* murine and human skin samples were evaluated; the stratum corneum barrier of the epidermis was breached and drug surrogate was delivered from the patches. PRINT microneedles could serve as a valuable transdermal delivery method for vaccines and the treatment of skin-related diseases.



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Location: Morial Convention Center
Room: Hall E

425 - Synthesis and characterization of "sweet" salicylic acid drugtrees

Darnell T. Wims, *wims1dt@cmich.edu, Minghui Chai. Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, United States*

NSAIDs normally require large doses to have therapeutic effects because of low water solubility, which induces adverse side effects long-term use. Small molecular drugs like NSAIDs also need to be taken several times daily in order to sustain their remedial effects during the treatment of illness. This research attempts to improve the solubility of salicylic acid, by conjugating galactose with it to make so called “sweet” salicylic acid. Dendritic architecture has been used to incorporate multiple salicylic acid molecules into a drugtree to give a slow controlled release of the drugs. A synthetic protocol has been developed to put the “sweet” salicylic acids on the surface of the salicylic acid dendrimers to make “sweet” salicylic acid drugtrees in attempt to overcome the solubility issue. Currently, the glycosylated core (Gal-SA G0) has been successfully synthesized. The structure of the product has been fully characterized using multidimensional NMR Spectroscopy.

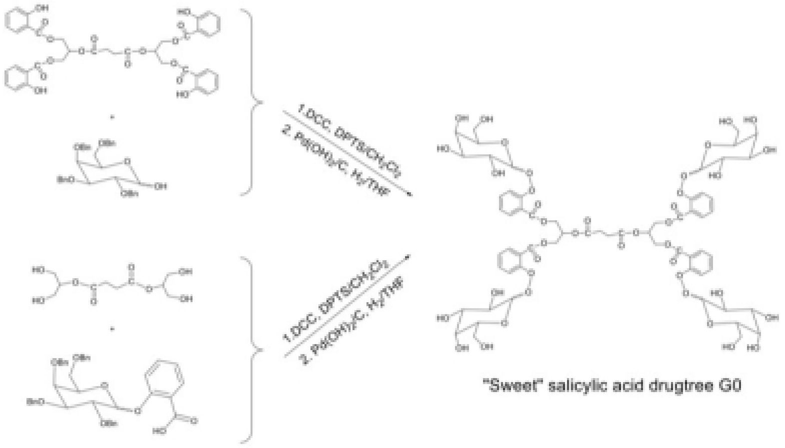

figure 1. Sythesis of Gal-SA G0 using two alternative methods.

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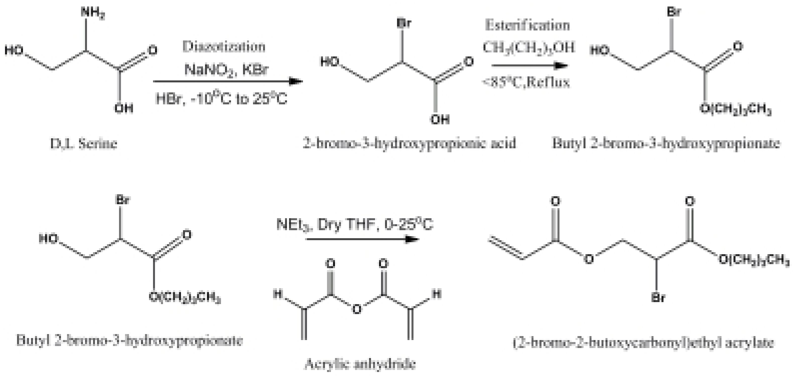
426 - Synthesis and polymerization of (2-bromo-2-butoxycarbonyl)ethyl acrylate using D,L-serine

Abegel Freedman, *freedmana@my.hiram.edu, Mina Garcia, Coleen Pugh. Polymer Science, University of Akron, Akron, OH 44313, United States*

In order to explore the potential of utilizing naturally occurring chemicals in industrial applications, D,L-serine was investigated as the initial reagent involved in the synthesis of a (2-bromo-2-butoxycarbonyl)ethyl acrylate inimer. The methods employed included a diazotization reaction of D,L-serine, which substituted the amine group with a bromine group to yield 2-bromo-3-hydroxypropionic acid, which was then esterificatied with butanol to yield butyl 2-bromo-3-hydroxypropionate. In the final step of the reaction, butyl 2-bromo-3-hydroxypropionate was reacted with acrylic anhydride to yield the (2-bromo-2-butoxycarbonyl)ethyl acrylate inimer. We have polymerized this inimer by self-condensing vinyl polymerization using various ATRP methods.



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Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
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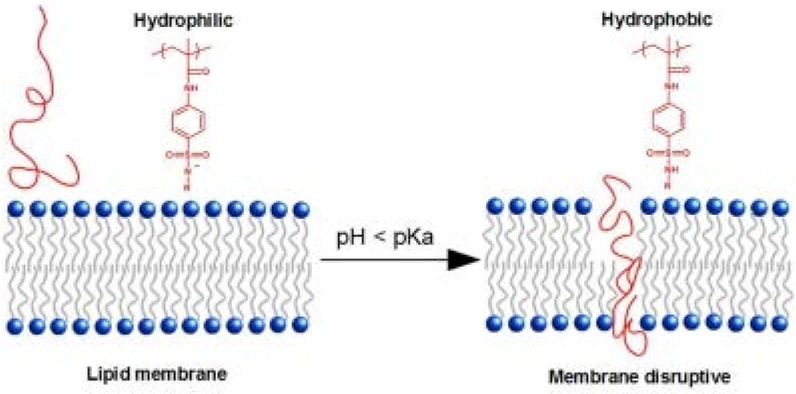
427 - Tunable pH-responsive sulfonamide-based polymers via RAFT as potential mediators of endosomal drug release

Michael B. Sims[1], *michael.b.sims@eagles.usm.edu, Brooks A. Abel*[1], *Charles L. McCormick*[1,2]. *(1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States, (2) Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406, United States*



Targeted delivery of cancer therapeutics offers an exciting new opportunity for utilization of controlled polymerization techniques. However, a major obstacle in achieving the desired therapeutic effect is facilitating endosomal release of active agents following endocytosis. Peptides and pH-responsive polymers have been utilized as a means of triggering endosomal release via phase transition-induced membrane disruption. Unfortunately, the fidelity by which the pK_a of these polymers/peptides can be varied is limited, such that it reduces their versatility in altering the phase transition point to best match the endosomal pH of a particular cell-type. Herein, we report the controlled polymerization of a library of methacryloylsulfonamide derivatives via reversible addition-fragmentation chain transfer (RAFT) polymerization that exhibit a range of physiologically relevant pK_a's. Polymerization control was observed by noting the low polydispersity indices of the polymers along with the linear progression of Mn with time during the polymerizations. The pH-dependent phase transition behavior of the polymers was tunable by varying the “R-group” of the sulfonamide, thus altering the $pK_a$of the resulting polymer. Future work includes pH-dependent hemolysis studies to determine which sulfonamide derivatives promote endosomal disruption under physiological conditions.

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428 - Recognition of mannose- and glucose-derived polymers

Bianca A Ulloa, *bau1@williams.edu, Lauren L. Agoubi, Michelle M. McRae, Olivia W. Foley,* ***Sarah L. Goh***, *sgoh@williams.edu. Department of Chemistry, Williams College, Williamstown, MA 01267, United States*

Polymers, as inert drug carriers, offer the possibility of effectively directing drugs to malignant cells by exploiting a tumor's leaky neovasculature induced through angiogenesis. Chemotherapy treatments that otherwise lack tumor specificity have limited efficiency and often negative side effects. Tumor-associate macrophages (TAMs) are known to accumulate in tumor's low oxygen supply regions and also present mannose-specific receptors. Thus, a glycopolymer carrier that directly targets these receptors would greatly improve a chemotherapeutic's delivery. Homopolymers poly(2-(b-D-glucosyloxy)ethyl methacrylate) (pGlucHEMA) and poly(2-(a-D-mannosyloxy) ethyl methacrylate) (pMannHEMA) were synthesized using both free radical and the reversible addition-fragmentation chain transfer (RAFT) polymerization techniques. Free mannose and pGlucHEMA did not result in aggregation of the lectin concanavalin A (ConA), as measured by optical density (Figure 1). In contrast, pendant mannose units of pMannHEMA were successfully recognized by ConA and the polymer's multivalency resulted in the formation of aggregates. Drug delivery carriers comprised of pMannHEMA have the potential for receptor recognition. By developing effectively cell-recognized glycopolymers, we propose a potent shepherding approach for chemotherapy drugs to further enhance our ability to target and treat malignant tumors.

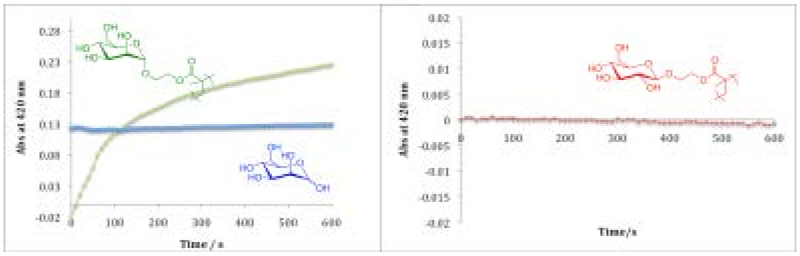

Figure 1. Time course of optical density at 420 nm of pMannHEMA (left, green), free mannose (left, blue), and pGlucHEMA (right, red).

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429 - Synthesis of oligo(2,3,4-tri-O-acetyl-a/b-D-galactopyranose)

***Emily Franckowiak**, franc1ea@cmich.edu, Lingyao Li, Yi Xu, Wenjun Du. Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48858, United States*

We are developing a convenient yet efficient glycosylation method for the synthesis of oligosaccharides. A di-functional AB monomer, 2,3,4-tri-*O*-acetyl-a-D-galactopyranosyl bromide was synthesized from the simple sugar galactopyranose. This monomer is weakly reactive and gave low conversion, low molecular weight and low yield under room temperature, regular heating, and even low microwave energy (65 and 150 watts) irradiation.

However, both the molecular weights of the oligosaccharides and the reaction efficiency can be significantly increased when the microwave energy reached to 300 watts. The kinetic GPC data of the glycosylation illustrated that at 300 watts, the glycosylation occurred rapidly with a fast formation of oligosaccharides within 30 min. Thereafter the reaction went smoothly with a continuous growth of the molecular weight. Oligosaccharides with molecular weights of 21 kDa can be conveniently synthesized quantitatively.

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430 - Synthesis of poly(2,3,4-tri-O-acetyl-a/b-D-glucopyranose)

Liye Fu, *fu1l@cmich.edu, Yi Xu, Lingyao Li, Wenjun Du. Department of Chemistry, Central Michigan Uniersity, Mount Pleasant, Michigan 48858, United States*

Polysaccharides are important bio-macromolecules that play important roles in biological systems. They are also ideal biomaterials for a variety of applications due to their inherent biodegradability and biocompatibility. However the chemical synthesis of polysaccharides has been very challenging.

In this poster, 2,3,4-tri-O-acetyl-a-D-Glucopyranosyl bromide was designed as a di-functional AB monomer, which is stable at ambient temperature however can be triggered to polymerization when tetrabutylammonium iodide (TBAI) was added as a promoter. The polymerization was conducted under different solvent and temperature, and we found that the best result was obtained when using dichloromethane as the solvent at reflux temperature. To our delight, oligosaccharides with molecular weight of 3.0 kDa can be obtained, as determined by 1H NMR and GPC.

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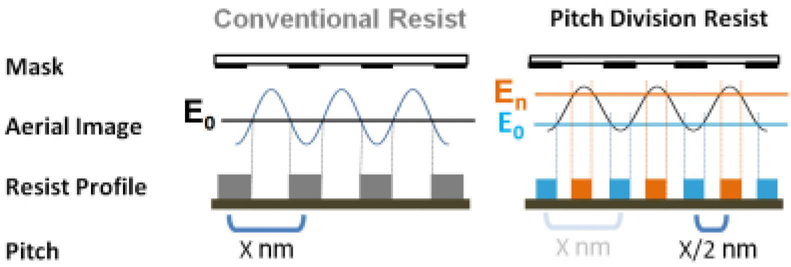
431 - Synthesis and characterization of novel two-stage photobase generators for pitch division lithography

Wade Wang[1], *wadewang@cm.utexas.edu, Ryan A Mesch*[1], *Takanori Kawakami*[1], *Yuji Hagiwara*[1], *Taeho Kim*[1], *Nicholas Turro*[2], *James Blackwell*[3], *C. Grant Willson*[1]. *(1) Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78705, United States, (2) Department of Chemistry, Columbia University, New York City, New York 10027, United States, (3) Intel Corporation, United States*

Pitch division lithography is a resolution enhancing technique that doubles the resolution of the photolithography process without imposing costly additional steps or requiring new manufacturing equipment. Upon exposure, a pitch division resist generates acid at medium doses while neutralizing that acid at higher doses, effectively crossing the response threshold twice, thereby producing two features instead of one. This behavior is accomplished by incorporating an excess of photobase generator with slower kinetics than the acid generator into the resist.

Pitch division lithography is a resolution enhancing technique that doubles the resolution of the photolithography process without imposing costly additional steps or requiring new manufacturing equipment. Upon exposure, a pitch division resist generates acid at medium doses while neutralizing that acid at higher doses, effectively crossing the response threshold twice, thereby producing two features instead of one. This behavior is accomplished by incorporating an excess of photobase generator with slower kinetics than the acid generator into the resist.



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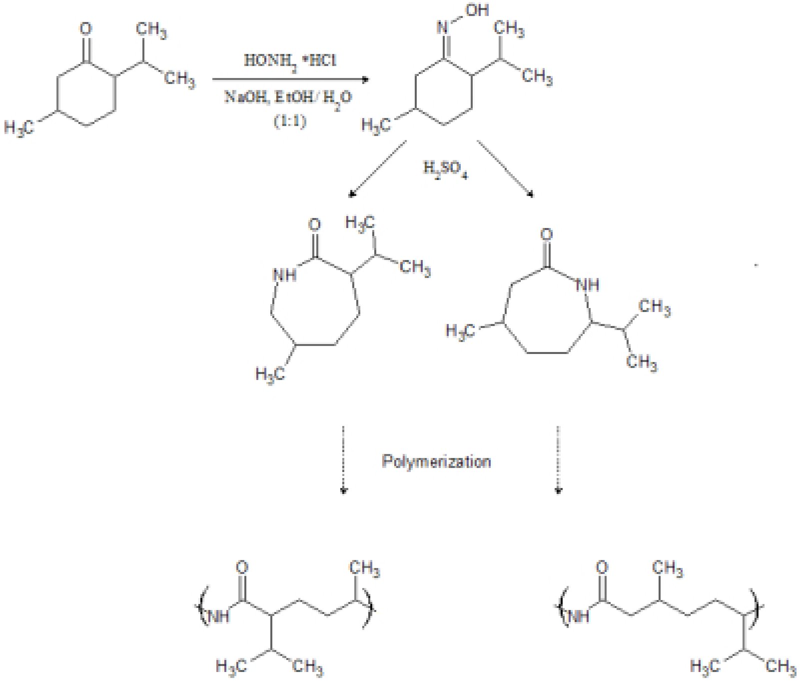
432 - Menthone based polymers

Patrick S Corrigan, *pcorrigan@monm.edu, Eric M Todd. Department of Chemistry, Monmouth College, Monmouth, Il 61462, United States*

Biorenewable polymers offer a green initiative to the largely petroleum based polymers that are in current use. This research has produced an oxime from L-Menthone via a nucleohpillic addition to the carbonyl group. This oxime is then rearranged to form a lactam. This lactam is then able to be polymerized through multiple techniques. The goal of this research is to characterize this lactam polymer and to find a technique to polymerize the lactam into high molecular weight polymers in high yield. Mechanism of synthesis can be seen in the attached figure.



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433 - Practical tactic for improving water solubility of hydrophobic small molecules: With an emphasis toward high sensitivity X-ray contrast media (XRCM)

Sussana A. Elkassih[1], *sxe072000@utdallas.edu, Guorong Sun*[2], *Kellie Seetho*[2], *Ang Li*[2], *Jeffery E. Raymond*[2], *Karen L. Wooley*[2]. *(1) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States, (2) Department of Chemistry & Chemical Engineering, Texas A&M University, College Station, Texas 77840, United States*

We present a facile and practical synthetic approach to significantly improve the water solubility of hydrophobic small molecules by covalently incorporating them into polymeric materials via reversible addition-fragmentation chain transfer (RAFT) copolymerization. The compound 2,3,5-triiodobenzoic acid (TIBA) is a potential X-ray contrast agent for X-ray computed tomography (CT) imaging, but suffers from poor water solubility at both room and physiological temperatures. Using RAFT polymerization, well-defined nonionic and ionic triiodobenzoyl-functionalized statistic copolymers were synthesized. The functional copolymers with oligo(ethylene oxide) acrylate (OEOA) and carboxybetaine acrylate (CBA) comonomer counterparts exhibited up to ~500 mg/mL water solubility at room temperature (> 50-fold water solubility improvement for TIBA), with relatively low solution viscosities and sufficient iodine concentration (> 100 mg iodine/mL). The combined characteristics of these copolymers indicate their great potential application as injectable X-ray contrast medias for targeted CT imaging.

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434 - Injectable hydrogels as reservoirs in biomedical applications

***Sarah Baldivia**, smb0020@tigermail.auburn.edu, Tucker McFarlane, Gisela Buschle-Diller. Department of Polymer & Fiber Engineering, Auburn University, Auburn, AL 36849, United States*

Tissue damage, from broken bones to worn cartilage, is an occurrence that most people face at some point, with surgery being a frequent consequence. This research aims to develop an intelligent delivery system based on hydrogels that could ultimately serve as an injectable tissue repair device. Hydrogels are polymer networks that, upon specific stimuli, absorb and release large amounts of liquids (500-1000% of their dry weight) without losing their physical shape. The goal is to create a biocompatible system that allows the instant release of monomers, catalysts, or initiators necessary for an *in-situ* polymerization for tissue repair. Additionally, pain-relieving drugs could be released this way. A variety of crosslinked and uncrosslinked biopolymers based on polysaccharides was investigated for their balance of stimuli-response, loading and release capabilities, as well as swelling and mechanical properties. The formation of poly(N-isopropylacrylamide), PNIPAM, served as one of the model polymerization reactions.

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435 - Bio-based carbon nanotube composites from tung oil

Scott K. Bice, *sb06552@georgiasouthern.edu, Brenda Beckler, Rafael L Quirino. Chemistry, Georgia Southern University, Statesboro, Georgia 30460, United States*

Tung oil is uniquely reactive among plant-based oils due to the series of conjugated double bonds in its fatty acid chains. This allows for the cationic- or free radical-based formation of different composites. The cationic composites contain varying concentrations of tung oil, styrene and divinylbenzene (DVB), and the free radical composites contain varying concentrations of tung oil, DVB and n-butylmethacrylate.The ideal heating schedule and monomer ratios are explored, as well as the possibility of rapid curing of the composites by microwaving the monomer mixture in the presence of carbon nanotubes.

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436 - Odorless polymers from nicotinic acid

Tayvia Brownmiller, *TB163335@reddies.hsu.edu, Martin J. Campbell. Department of Chemistry, Henderson State University, Arkadelphia, AR 71999, United States*

Synthesis of new systems of ionic liquid based polymers is reported. Diesters and dialchols were prepared from omega halo esters or alcohols and various nicotinic esters. These molecules are expected to undergo polymerization forming new, potentially useful polyesters. Any remaining monomers will be ionic liquids and, therefore, have very low vapor pressures, rendering the polymer virtually odorless. Such plastics are expected to be of interest to NASA and others where air quality in enclosed chambers is of great importance.

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437 - Detection of aqueous toluene: A fluorescent sensor for use in environmental studies

Danielle E Fagnani[1], *daniellefagnani@gmail.com, Marjorie Austero Kiechel*[2], *Caroline L Schauer*[2], *Mira S Olson*[3]. *(1) Chemistry, Drexel University, Philadelphia, PA 19104, United States, (2) Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, United States, (3) Civil, Architectural, and Environmental Engineering, Drexel University, Philadelphia, PA 19104, United States*

Chemotaxis, the phenomenon in which bacteria can sense and direct their movements towards or away from a specific chemical, is a widely studied process as it may improve the efficiency of *in situ* ground water bioremediation. Toluene is model chemical contaminent used to study the chemotactic response of *Pseudomonas putida*. The use of microfluidic devices have produced chemotactic data based on bacterial movement, however a more complete picture of chemotaxis can be gathered by visualizing bacterial response to a known chemical gradient. The goal of this project is to develop a glass coating able to detect changes in dissolved toluene gradients. Polymeric films embedded with hydrophobic-sensitive fluorophores have shown a response to the pure analyte. Pourous glass flims prepared using a sol-gel process are currently being investigated as a more sensitive sensor material able to detect the low concentrations of toluene necessary for this study.

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438 - Investigation of the gelation ability of N,N-dimethyl *n*-alkyl ammonium *p*-toluene sulfonates

***Marcos Pantoja**, mpantoja18@ucla.edu, Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325, United States*

Molecular gelators (MGs) are compounds that form supramolecular networks at low concentration in solution to alter the viscoelastic properties and form gels. This presentation will discuss a new series of MGs that were synthesized through the neutralization of *p*-toluene sulfonic acid with different length N,N-dimethyl *n*-alkyl ammoniums. This simple synthesis produces a series of molecular crystals with similar melting points, but varying solubility. The gelation of six high boiling point organic solvents (polydimethylsiloxane, squalane, decane, dimethyl phthalate, cyclohexylbenzene ethylene glycol) and water was investigated. It was found that as the alkyl chain length increased the breadth of solvents gelled increased. For example N,N-dimethyl *n*-octadecyl ammonium *p*-toluene sulfonate was able to gel solvents ranging from non-polar dodecane to polar ethylene glycol and even water at 1-3% loading by weight, while N,N-dimethyl *n*-octyl ammonium *p*-toluene sulfonate could only gel dimethyl phthalate and cyclohexylbenzene below 10% loading. Overall supramolecular synthesis approaches are a useful approach for designing new MGs as the thermodynamic properties of compounds can be tuned through the choice of molecular building blocks.

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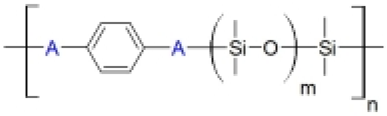
439 - Studies on the refractive index of copoly(arylene-siloxane) constructed with amide, ester, or ether linkage units

Scott Blackburn, *scb49973@huskies.bloomu.edu*, ***Owen O'Sullivan***, *oosull23@gmail.com*, *Diane Hinkens, Mark A Tapsak*. *Department of Chemistry and Biochemistry, Bloomsburg University of Pennsylvania, Bloomsburg, PA 17815, United States*



Where A = amide, ester, or ether units

Copoly(arylene-siloxane) based materials could be useful for optical applications because they are durable, flexible and possess good optical clarity when compared to silica-filled polydimethylsiloxane-based materials. In order to determine the linkage unit (A) influence on the polymer's refractive index, a series of polymers were prepared. The linkages consisted of aliphatic amides, esters or ethers. Values for m range from 6 to 23. It was observed that the refractive index of these polymers was directly proportional to the aryl content. However, the influence on refractive index was not equal across the types of linkage units evaluated. The synthesis, characterization and refractive index data for this series of polymers will be presented.

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440 - Novel composite materials based on chitin from discarded crawfish

Brooke Cambell, *james.mendez@sowela.edu, James Mendez. Sowela Technical Community College, Lake Charles, LA 70616, United States*

Most of the year, it is difficult to drive down the road in southwest Louisiana without seeing a crawfish stand. Everyone seems to be selling those big bags of crustaceans. But what happens when you are done eating? The vast majority of the crawfish; including its tail, head, and claws are discarded as trash. We took this waste and extracted a natural polymer, chitin.

By combining the extracted crawfish chitin with polymers, we were able to make composites. These composites showed similar qualities to other chitin-based materials suggesting crawfish as a viable source for chitin production.

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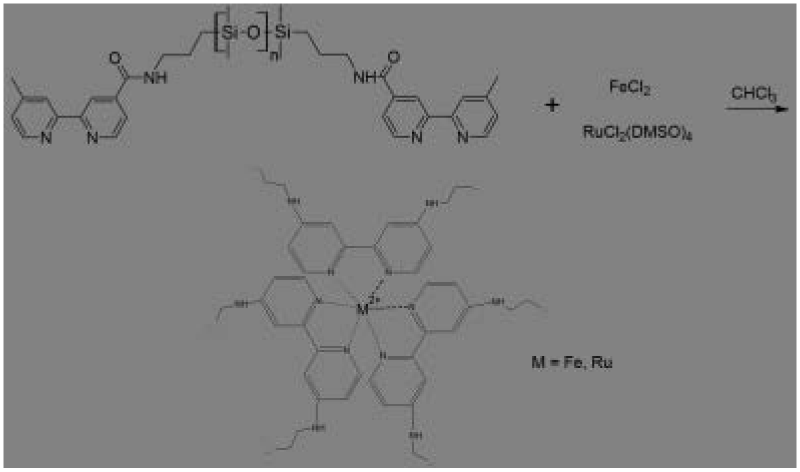
441 - Metal coordination polymer networks of iron(II) and ruthenium(II) tris(bipyridine)

Kristina M Vailonis[2], *kvailonis@students.stonehill.edu, Mallory M McVannel*[1]*, Meredith G Hyatt*[1]*, Marian L Pippin*[1]*, Al D Schwab*[1]*. (1) Department of Chemistry, Appalachian State University, Boone, North Carolina 28608, United States, (2) Department of Chemistry, Stonehill College, Easton, Massachusetts 02357, United States*

Preparation of Metal Coordination Polymer Networks (MCPN) began with attaching a bipyridine ligand, 4'-methyl-2,2'-bipyridine-4-carboxylic acid (MCBPY) to the ends of 2,500 g/mol and 27,000 g/mol bis(3-aminopropyl) terminated poly(dimethylsiloxane) (PDMS). Both molecular weight bpy terminated PDMS products were successfully characterized by Gel Permeation Chromatography (GPC) and ^{1}HNMR. $FeCl_2$ and $RuCl_2(DMSO)_4$ were then added to the bpy terminated PDMS to form MCPN. UV-Vis spectroscopy was used to determine if the complex was formed.



A single absorbance peak at 532nm for Febpy and 450nm for Rubpy indicates that a tris-bipyridine had formed. MCPN films were created to track the rate of the formation of the crosslinking complex.

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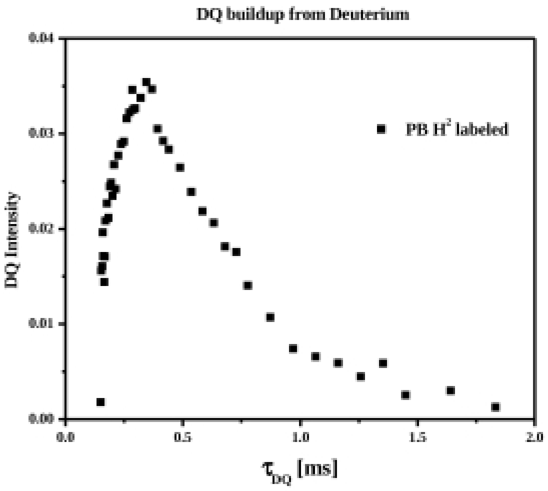
442 - Multiple quantum NMR on deuterium and its application to melted homopolymers

Joshua T Damron, *joshuat.damron@gmail.com, Filipe Furtado, Marie-Luise Trutschel, Kay Saalwaechter. Department of Physics, Martin-Luther Universitat, Halle, sachsen 06120, Germany*

It has been demonstrated that H1 multiple quantum (MQ) NMR experiments can be used very effectively to elucidate molecular dynamics in entangled polymer melts. Such experiments have been used to probe dynamics from Regime II - IV of the tube model, by probing the residual dipolar coupling that exist due to anisotropic motion in constrained molecular environments. This work explores the possibility of using Deuterium as the probe nuclei instead of protons in MQ experiments. Deuterium labeled polybutadiene samples are measured and compared to its proton counterpart.



Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Morial Convention Center
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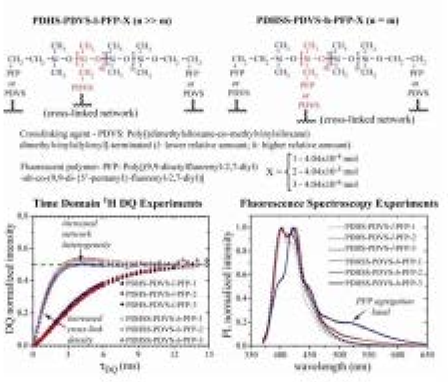
Tuesday, April 9, 2013 05:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

443 - Structure of polyfluorene-labeled polysiloxanes networks as probed by ^{1}H time domain double quantum NMR and fluorescence spectroscopy

Marcio F. Cobo[1], *marciofcobo@gmail.com, F. J. Quites*[2], *R. A. Domingues*[2], *G. F. Ferbonink*[2], *R. Alfonso*[2], *L. A. de O. Nunes*[1], *T. D. Z. Atvars*[2], *Eduardo R. deAzevedo*[1]. *(1) Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, SP 13560-970, Brazil, (2) Chemistry Institute, State University of Campinas (Unicamp), Campinas, SP 13084-971, Brazil*

Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-*co*-(9,9-di-{5'-pentanyl}-fluorenyl 2,7 diyl)](PFP) was attached by hydrosilylation reaction in polysiloxanes with lower(PDHS PDVS *l* PFP X) and higher(PDHSS PDVS *h* PFP X) cross-linking yields, as demonstrated by ^{1}H double-quantum NMR(^{1}H DQ). ^{1}H DQ experiments also show that the increase of PFP content (X) does not affect the PDHS PDVS *l* PFP-X network (similar DQ build ups), but increases the PDHSS-PDVS-*h*-PFP-X network heterogeneity. This explains the optical fluorescence of PDHSS-PDVS-*h*-PFP-X, which indicates the formation of PFP molecular aggregates at higher PFP concentrations, inducing regions with lower cross-link densities in a more confined environment such as PDHSS-PDVS-*h*-PFP.



Tuesday, April 9, 2013 05:30 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)

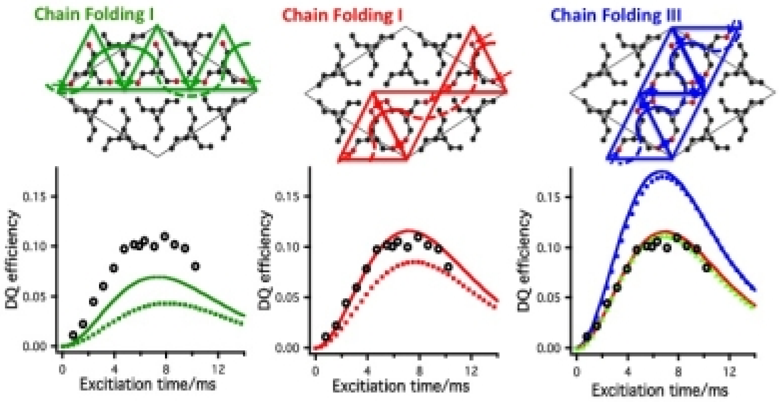
Location: Morial Convention Center

Room: Hall E

444 - Chain-folding structure of a semi-crystalline polymer determined by ^{13}C-^{13}C double quantum NMR

You-lee Hong, *yh31@zips.uakron.edu, Toshikazu Miyoshi. Department of Polymer Science, The University of akron, Akron, Oh 44313, United States*

Understanding of detailed chain-folding structure is still challenging issue in polymer science. Solid-state NMR spectroscopy with selective ^{13}C isotope labeling is applied to investigate local chain trajectory of isotactic-poly(1-butene) in melt grown crystals. ^{13}C-^{13}C double quantum (DQ) build-up curve of isolated ^{13}C labeled chains highly relies on inter-nuclei distance, spin number, and spin topology originating from chain trajectory as well as ^{13}C labeling sites. ^{13}C-^{13}C DQ NMR determines adjacent-reentry site, fraction, and chain-folding number of semi-crystalline polymers.



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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)
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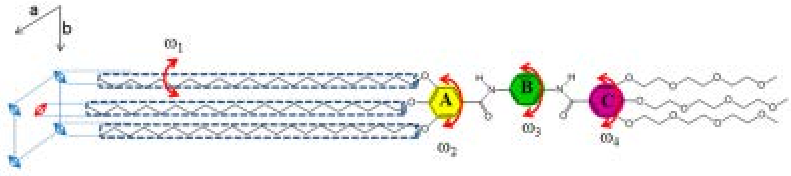
445 - Molecular structure and dynamics study of Janus bisamide supramolecule $C_{22}PhBAEO_3$ by solid-state NMR

Wei Chen[1], *wc25@zips.uakron.edu, Hao-Jan Sun*[2], *Toshikazu Miyoshi*[1], *Stephen Z.D. Cheng*[1]. *(1) Department of Polymer Science, the University of Akron, Akron, Ohio 44325, United States, (2) University of Pennsylvania, Philadelphia, Pennsylvania, United States*

The molecular structure and dynamics of an asymmetric tapered Janus Bisamide -1,4-bis[3,4,5-tris(alkan-1-yloxy) benzamido] benzene bisamide (abbreviated as $C_{22}PhBAEO_3$) in *Crystal II* are investigated by various Solid-State (SS) NMR techniques. Dynamic difference in different functional groups is probed by 2D WIdeline-SEparation (WISE) NMR spectroscopy. Thermal stability, rotator phase transition, and molecular conformation change of alkyl chains are studied by ^{13}C CP/MAS NMR. Geometry of both aliphatic chain and three aromatic rings are determined by Chemical Shift Anisotropy obtained from SUPER.

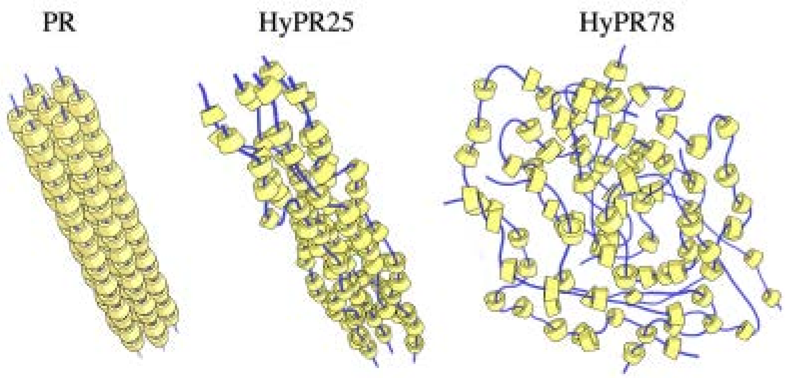


Tuesday, April 9, 2013 05:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

446 - Chemical modification effects on molecular dynamics of complex poly(rotaxane) investigated by solid-state NMR

Chuan Tang[1], *ct40@zips.uakron.edu, Aoi Inomata*[2], *Yasuhiro Sakai*[2], *Hideaki Yokoyama*[2], *Toshikazu Miyoshi*[1], *Kohzo Ito*[2]. *(1) Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States, (2) Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, Kashiwa, Chiba 227-8561, Japan*

The molecular dynamics of polyrotaxane consisting of poly (ethylene glycol) and a-cyclodextrins, hydroxypropylated polyrotaxane with a-cyclodextrins partially modified by hydroxylpropyl groups with different modification ratios are investigated by two-dimensional ^{1}H-^{13}C wide-line separation (WISE) NMR, ^{13}C spin-lattice relaxation time in the rotating frame ($T_{1\mathrm{rc}}$) measurement, and center band-only detection of exchange (CODEX) NMR. The chemical modification on pendant hydroxyl groups significantly suppresses hydrogen bonding interactions between cyclodextrin molecules and lead to unique cyclodextrins molecular dynamics and viscoelastic properties.



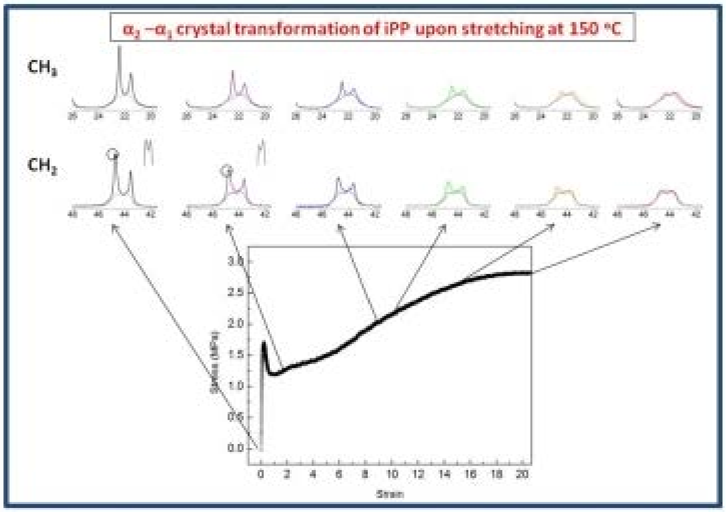
Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Morial Convention Center
Room: Hall D

Tuesday, April 9, 2013 05:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

447 - New insights into molecular deformation of isotactic-polypropylene upon uniaxial stretching by solid-state NMR

***Jia Kang**, jk84@zips.uakron.edu, Toshikazu Miyoshi. Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States*

In order to verify how stress induces crystalline structure change upon drawing, chain packing structures of a form of isotactic polypropylene are investigated via ^{13}C high resolution NMR. It is found that ordered packing fractions monotonically decrease with increasing draw ratio, depending on initial structures and drawing temperatures. Mechanisms of the unique transformation are discussed on the basis of crystallographic constraints. Moreover, molecular dynamics of crystalline region is characterized by 1D exchange NMR. Relationship between molecular dynamics and structures is built.



Tuesday, April 9, 2013 05:30 PM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)

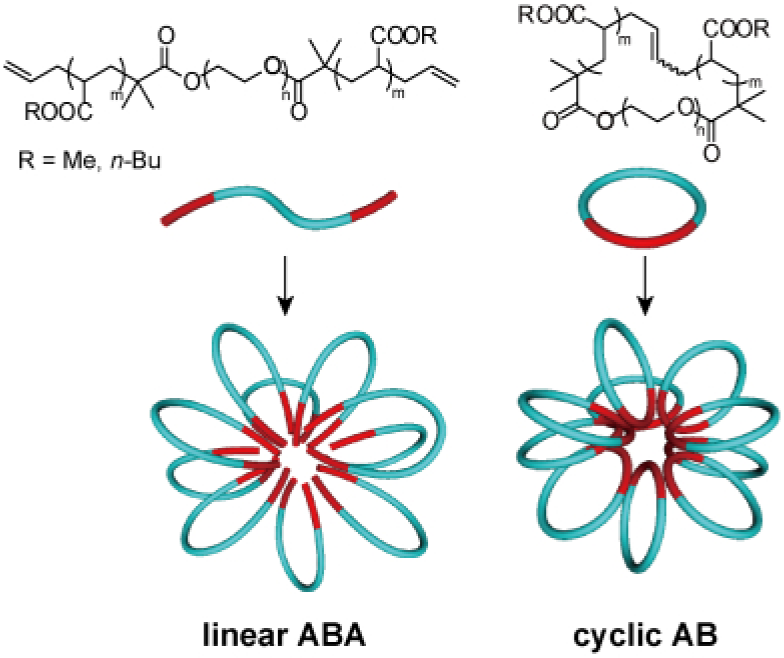
Location: Morial Convention Center

Room: Hall E

448 - NMR relaxometry study on the mechanism for the thermal stability of self-assembled micelles from cyclic AB and linear ABA amphiphilic block copolymers

Haruna Wada, *wada.h.ae@m.titech.ac.jp, Yu Kitazawa, Satoshi Honda, Takuya Yamamoto, Yasuyuki Tezuka, Shigeki Kuroki. Dept. of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan*

Micelles were self-assembled from cyclic and linear amphiphilic block copolymers with a poly(ethylene oxide) hydrophilic segment and poly(methyl acrylate) or poly(*n*-butyl acrylate) hydrophobic segments. Turbidity measurements showed that the micelles formed from the cyclic amphiphiles have higher thermal stability than those formed from the linear counterparts. The mechanism for the enhanced thermal stability was studied by temperature-dependent ^{1}H NMR relaxometry to evaluate the mobility of the respective hydrophilic and hydrophobic segments.

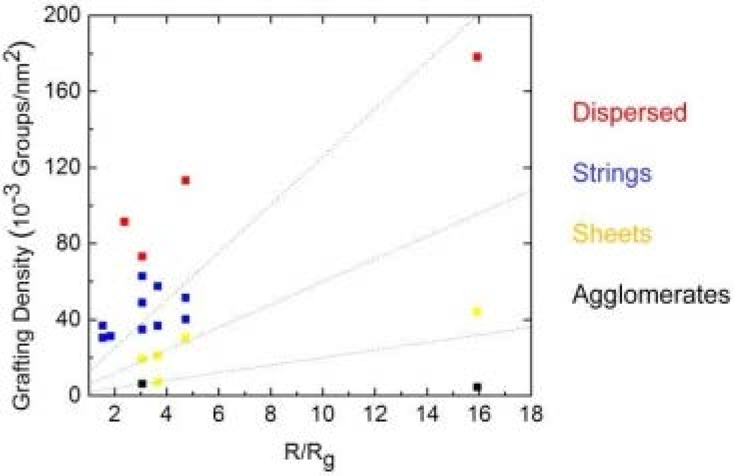


Tuesday, April 9, 2013 05:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (05:30 PM - 07:30 PM)
Location: Morial Convention Center
Room: Hall E

449 - Using click chemistry with polymeric ligands to control nanoparticle organization

Jeffrey T Koberstein, *jk1191@columbia.edu, Department of Chemical Engineering, Columbia University, New York, NY 10027, United States*

Nanoparticles decorated with dense polymer brushes maintain hexagonal packing where the distance between nanoparticles scales with $M_n^{1/2}$, in agreement with spherical brush theory. Non-hexagonal morphologies can be obtained only at low grafting density, as shown in the Figure,



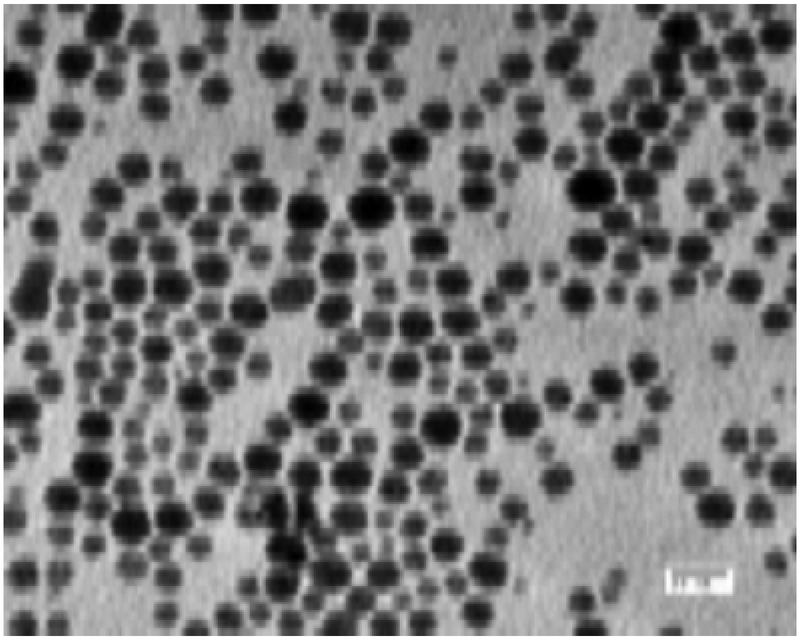
where the dashed lines are predicted phase boundaries. The required low ligand densities are attained by grafting azide functional polymers onto monolayers of alkyne- and alkane-silanes via click chemistry.

Wednesday, April 10, 2013 08:30 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

450 - Organosiloxane supramolecular liquids

John Texter, *jtexter@emich.edu, Kejian Bian, Dan Chojnowski, Joe Byrom. School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI 48197, United States*

We show that auto-condensation of organoalkoxysilanes, followed by suitable anion exchange, produces solvent-free nanoparticle nanofuids we call organosiloxane supramolecular liquids. We find that classical liquid properties are exhibited with some distinct differences. We observe heat capacity anomalies manifested as lambda transitions in excess heat capacity centered around a glass transition (T_g) and around a freezing transition. The T_g-proximal lambda transition is the first experimental realization of an enthalpic phase transition overlying a glass transition. The existence of such a connection or coincidence has undergone decades of theoretical conjecture. The second anomaly spanning the melting/freezing range is the first reported excess enthalpy ever reported for an experimental particulate fluid undergoing a phase transition. The integral enthalpy from these lambda transitions is quantitatively accounted for by the loss of specific surface area of the particles, and the associated surface free energy, upon freezing and upon cooling beneath the glass transition temperature.

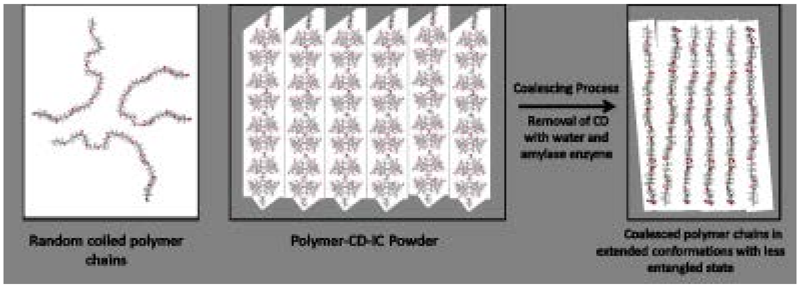


Wednesday, April 10, 2013 09:00 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

451 - Employing coalesced polymer in self-reinforced composites

*Alper Gurarslan, **Jialong Shen**, jshen3@ncsu.edu, Alan E. Tonelli. Fiber and Polymer Science, North Carolina State University, Raleigh, North Carolina 27695, United States*

Coalesced polymers are obtained *via* nano-confinement of guest polymers in cyclodextrin or urea host molecules and their subsequent release. Our research indicates improved mechanical properties, higher non-crystalline densities, higher glass transition temperatures, higher crystallization temperatures, and higher degree of crystallinities for such coalesced samples, and are stable to melt annealing for long periods. These results suggest that we can use coalesced polymers as nucleating agents. Restructuring polymers in this fashion allow us employ coalesced polymer in self-reinforced composites. Self-reinforced composites consist of chemically identical matrix and reinforcement components. Tailored microstructures of reinforced component provides required strength to the composite. Coalesced polymers are suitable candidates for reinforcing their as-received matrixes due to their distinct microstructures and physical properties.



Wednesday, April 10, 2013 09:20 AM

Hybrid Materials (08:30 AM - 11:45 AM)

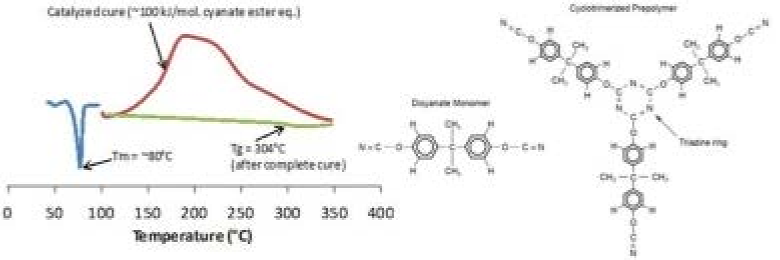
Location: Hilton Riverside

Room: Ste. B, Sec 9

452 - New silicon-containing cyanate esters for high-temperature thermo-oxidation resistance

Andrew J Guenthner[1], *andrew.guenthner@us.af.mil, Josiah T Reams*[3], *Kevin R Lamison*[2], *Christopher M Sahagun*[3], *Vandana Vij*[2], *Suresh Suri*[1], *Timothy S Haddad*[2], *Joseph M Mabry*[1]. *(1) Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, CA 93524, United States, (2) ERC Incorporated, Edwards AFB, CA 93524, United States, (3) National Research Council, Edwards AFB, CA 93524, United States*

Recent synthesis and characterization efforts at AFRL have focused on the creation of thermosetting composite resins with improved char yields at temperatures of 600 degrees Celsius and above. Such performance criteria necessitate the incorporation of significant inorganic content into the thermosetting network. In order to alleviate concerns with phase separation, the incorporation of inorganic content has been undertaken at the molecular level, through the successful multi-step synthesis of new types of silicon-containing cyanate ester resins



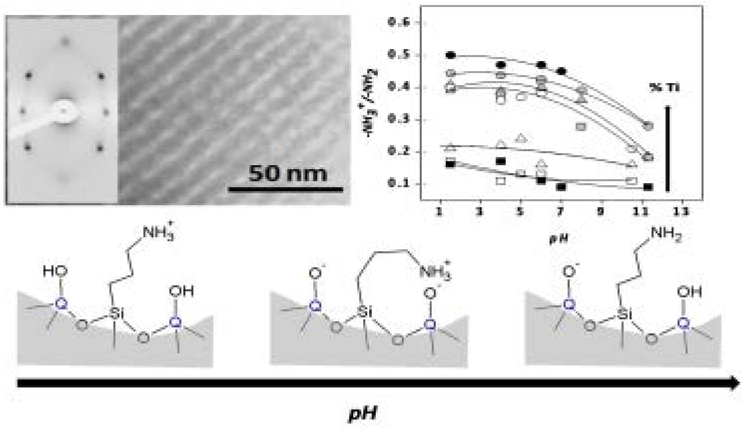
. These new resins feature much higher silicon content than previously synthesized silicon-containing cyanate esters, and have exhibited both the ease of processing and well-defined chemical structure of traditional tri- or terra- functional monomers as well as substantial char yields above 600 degrees Celsius.

Wednesday, April 10, 2013 09:40 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

453 - Spectroscopic surface site speciation in mesoporous hybrid thin films: Probing teamwork between Si-OH, Ti-OH and -RNH_2 groups

Alejandra Calvo[1,2], Leandro Andrini[2], Felix G Requejo[2], Federico J Williams[3,4], ***Galo J. A. A. Soler-Illia**[1,3]*, *gsoler@cnea.gov.ar. (1) Gerencia Química, CNEA, San Martín, Buenos Aires B1650KNA, Argentina, (2) INIFTA, CONICET, La Plata, Buenos Aires 1900, Argentina, (3) Dept Inorg. Anal. and Phys. Chem., Univ Buenos Aires, Buenos Aires, Argentina, (4) INQUIMAE, CONICET, Buenos Aires, Argentina*

Aminopropyl-containing silica-titania mesoporous thin films ($S_{i0.8-x}Ti_x(Si(CH_2)_3NH_2)_{0.2}O_{1.9}$, $0<0.8$) catalysts.

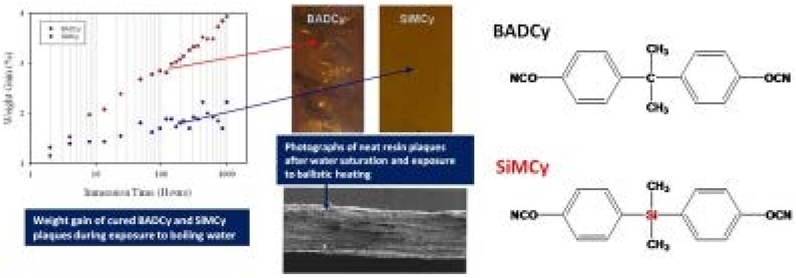


Wednesday, April 10, 2013 10:15 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

454 - Advanced hybrid materials for aerospace propulsion applications

Joseph M Mabry, *joseph.mabry@edwards.af.mil, Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, CA 93524, United States*

Many material improvements are needed for specific aerospace propulsion applications. Because the industrial community in extremely risk-averse, the responsibility to achieve significant advancements in this area falls largely to government laboratories. This presentation will discuss on-going materials research performed at the Air Force Research Laboratory, Rocket Propulsion Division, located at Edwards Air Force Base. Recent research activities focused on inert materials for solid rocket propulsion applications, including the development of alternative high-temperature thermosetting resins, will be described, as well as specialized applications for use in liquid rocket propulsion.



Photographs of neat resin plaques after water saturation and exposure to ballistic heating

Weight gain of cured BADCy and SiMCy plaques during exposure to boiling water

Wednesday, April 10, 2013 10:45 AM

Hybrid Materials (08:30 AM - 11:45 AM)

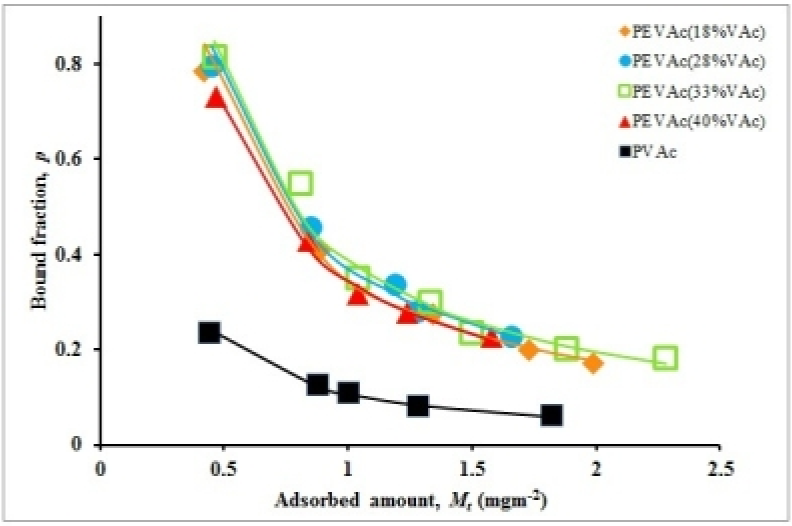
Location: Hilton Riverside

Room: Ste. B, Sec 9

455 - Thermal analysis and FTIR studies of adsorbed poly(ethylene-stat-vinyl acetate) on silica

Madhubhashini M Madduma Arachchilage, *madhubh@okstate.edu, Frank D Blum. Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States*

Adsorbed poly(ethylene-stat-vinyl acetate) (PEVAc) on fumed silica was studied using modulated differential scanning calorimetry (MDSC) and FTIR. Poly(vinyl acetate) was used as the reference. MDSC analysis of the copolymer-silica composites revealed that behavior of the copolymer composites in the glass transition region was complicated because of the crystallinity of the copolymer. Nevertheless, examination of the glass transition region for different adsorbed amounts of the copolymer indicated that there was an increase in the glass transition temperature of the adsorbed copolymers compared to bulk. A series of polymer-silica composites having different adsorbed amounts of polymer (M_t) was used to obtain the amount of tightly bound polymer (M_b) and the ratio of molar absorption coefficient of bound carbonyls to free carbonyls (X). The obtained X values were used to calculate the fraction of bound carbonyls (p). The copolymers had shown very high p values at low adsorbed amounts indicating the change of copolymer conformation to get maximum adsorption to the surface.

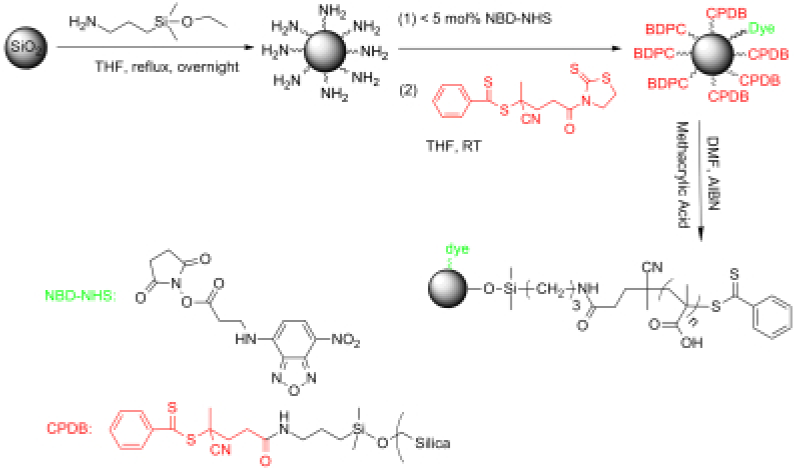


Wednesday, April 10, 2013 11:05 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

456 - Synthesis and characterization of dye-labeled poly(methacrylic acid) grafted silica nanoparticles

***Lei Wang**, wangleiyh@gmail.com, Brian C Benicewicz. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

The synthesis of dye-labeled poly(methacrylic acid) (PMAA) grafted silica nanoparticles was studied. Direct surface-initiated reversible addition fragmentation chain transfer (RAFT) polymerization of methacrylic acid (MAA) was conducted on dye-labeled 4-cyanopentanoic acid dithiobenzoate (CPDB) coated silica nanoparticles with a diameter size as small as 15 nm. A variety of PMAA brushes with different lengths and densities were prepared on nanoparticle surfaces with excellent control and surface grafting densities as high as 0.65 chains/nm^2. The grafted PMAA was methylated by trimethylsilyldiazomethane to conduct normal GPC characterization using tetrahydrufuran as eluent. TEM images showed that the poly(methacrylic acid) grafted silica nanoparticles existed in a individual state and were non-agglomerated. The dye-labeled PMAA grafted nanoparticles provide a platform to bind bio-molecules and to track the movement of the nanoparticles in biological systems.

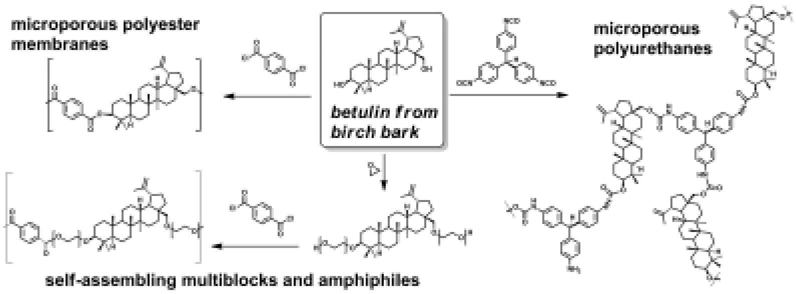


Wednesday, April 10, 2013 11:25 AM
Hybrid Materials (08:30 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

457 - Polymers from birch bark: Microporous membranes and new amphiphiles

__Jens Weber__, jens.weber@mpikg.mpg.de, Jekaterina Jeromenok, Junpeng Zhao, Helmut Schlaad. Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Betulin is a naturally occuring triterpene and can be extracted from birch bark in up to 30% yield. Its diol nature makes it an ideal choice for polycondensation and polyaddition reactions (see Figure 1). We studied its usefulness for the preparation of microporous linear and cross-linked polyesters and polyurethanes. The OH groups can also serve as initiators for anionic polymerization of ethylene oxide (EO), which results in new renewable amphiphiles. The self-assembly of betulin-PEO conjugates of varying PEO length and multiblock copolymers in water was studied and will be discussed.



Wednesday, April 10, 2013 08:35 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

458 - Tailored enzyme catalyzed oxidation of galactose containing natural polysaccharides

*Kirsti Parikka, **Maija Tenkanen**, maija.tenkanen@helsinki.fi. Department of Food and Environmental Sciences, University of Helsinki, Helsinki, Finland*

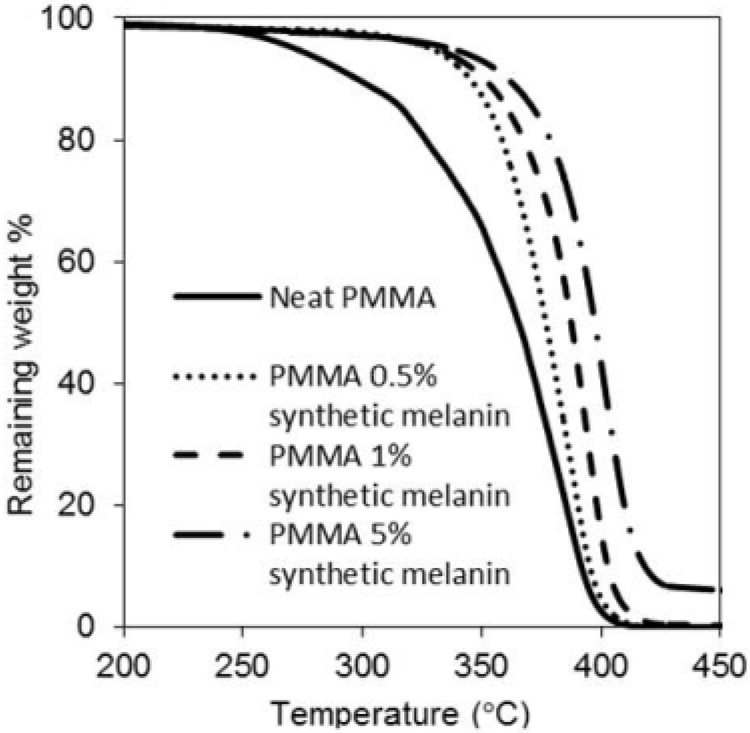
Several natural heteropolysaccharides contain galactose residues. Galactose oxidase (GaO) is a single copper metalloenzyme which catalyzes the oxidation of primary alcohols to the corresponding aldehydes with the high selectivity for C-6 the terminal D-galactopyranosyl residues in oligo-and polysaccharides. GaO uses cheap molecular oxygen as the electron acceptor, which is during the reaction reduced to H_2O_2. We have studied the selective oxidation of different galactose containing polysaccharides, guar galactomannan (GM), spruce galactoglucomannan (GGM), and tamarind seed xyloglucan (XG), with galactose contents varying from 6% to 40%. A novel analysis technique was developed for the quantification of formed aldehydes with GC-MS. The best oxidation degrees of galactosyls were obtained with XG. The highest oxidation degree based on total carbohydrates was achieved with GM. Oxidation of GM and XG, having much higher molar mass than GGM, resulted in significant changes in their rheological behaviour. The dynamic viscosities of ox-GM and ox-XG in 1% w/v solutions were higher than those of the starting materials at all shear rates. Oscillation measurements proved that the oxidized GM and XG formed gels. Further studies revealed the good thermal stability of these novel hydrogels. The oxidized GM formed stable gels already in low concentrations, such as 0.2-0.4% w/v. The reactive aldehyde formed by GaO enabled also the selective chemical modifications of GGM, GM and XG. Further oxidation to carboxylic acid and functionalization were performed successfully as one-pot procedures in aqueous media directly after GaO oxidation. Combination of the selective enzymatic oxidation with chemical reactions was found to be a good method for the production of polysaccharides with new properties.

Wednesday, April 10, 2013 08:55 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

459 - Using natural and synthetic melanins for thermo-oxidative stabilization of polymers

Kadhiravan Shanmuganathan[1], *kadhir@utexas.edu, Joon Hee Cho*[1], *Prashanth Iyer*[1], *Steven Baranowitz*[2], *Christopher J Ellison*[1]. *(1) Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States, (2) Epitek Inc, Medford, New Jersey 08055, United States*

Melanins constitute a fascinating class of biopolymers and are well known for their intriguing chemical structure and physiological functions including photoprotection, radical scavenging and metal-ion chelation. They are ubiquitous in nature and easily accessible in large quantities. However, unlike other biopolymers such as cellulose, or chitin, they haven't been implemented much in technologically relevant materials. To this end, we report here on the potential of natural and synthetic melanins as thermal stabilizers for common polymers. Synthetic melanin-like polymers, synthesized by oxidation of L-3-(3,4-dihydroxyphenyl) alanine (L-Dopa), significantly reduced the radical initiated chain scission behavior of poly(methyl methacrylate) (PMMA) with only 0.5-5 wt% incorporation. As a consequence, the onset decomposition temperature of PMMA was increased by 50-90 °C in both inert and air atmospheres



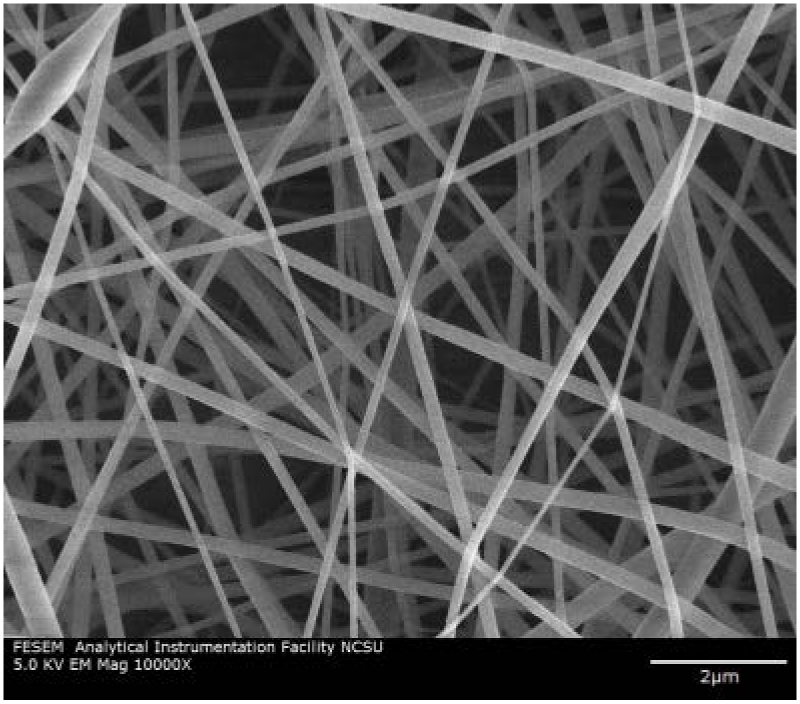
. Natural melanin that was extracted from the ink sac of *Sepia officinalis* also revealed significant thermal stabilization effects on PMMA and polypropylene at similar loadings. The associated delay in the molecular weight decrease of PMMA and other polymers at elevated temperature could be potentially beneficial for high temperature processing or increasing their upper use temperature in demanding applications. Since natural and synthetic melanin additives are macromolecules, they are also less likely to leach from the base polymer in the same way that small molecule additives often do.

Wednesday, April 10, 2013 09:15 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

460 - Cellulose acetate/lignin-based electrospun fibers

Joao V. W. Silveira[1,2], *jvsilveira@feq.unicamp.br, Ana L. G. Millas*[1], *Mariko Ago*[2,3], *Orlando J. Rojas*[2], *Edison Bittencourt*[1]. *(1) Department of Materials Engineering and Bioprocesses, University of Campinas, Campinas, Sao Paulo 13083-852, Brazil, (2) Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina 27695, United States, (3) Department of Nanomaterials and Bioengineering, Tokushima Bunri University, Sanuki City, Kagawa 769-2163, Japan*

In this investigation we produced electrospun nanofibers based on cellulose acetate and organosolv lignin. Scanning electron microscopy revealed regular, defect-free nanofibers with average diameter of ca. 200 nm.



Thermal analysis indicated a reduction in crystallinity with the incorporation of lignin. The tensile modulus was observed to increase upon addition of lignin at 10 wt% levels based on total solids; this effect is likely due to the change in the size distribution of the fibers in the web.

Wednesday, April 10, 2013 09:35 AM

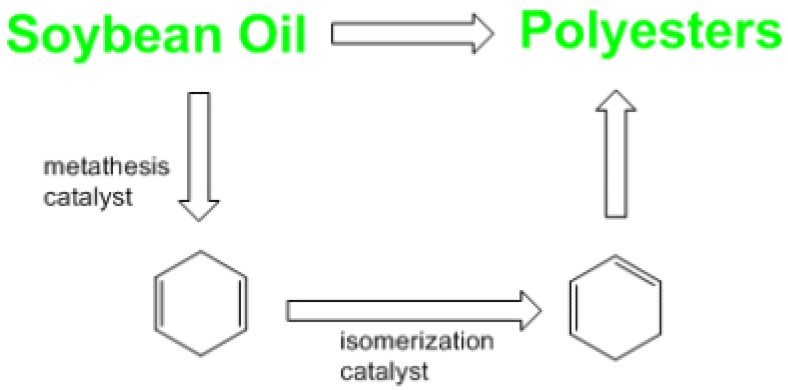
Natural and Renewable Polymers (08:30 AM - 11:50 AM)

Location: Hilton Riverside

Room: Ste. A, Sec 6

461 - Conversion of soybean oil based 1,3-cyclohexadiene to polyesters

Robert T Mathers, *rtm11@psu.edu, Stewart P Lewis, Michael P Cavazza, Aaron Hoover. Department of Chemistry, The Pennsylvania State University, New Kensington, PA 15068, United States*



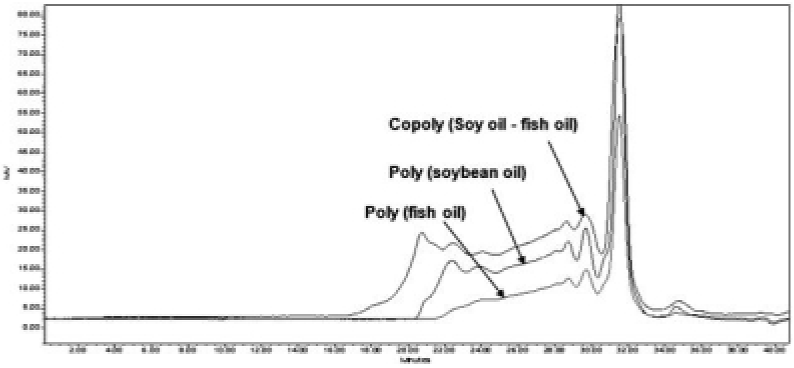
Ruthenium-catalyzed cyclization of alkenes in the polyunsaturated fraction of soybean oil provides renewable-dienes. The synthesis of 1,4-cyclohexadiene (1,4-CHD) proceeds under nitrogen without the need for organic solvents or plant oil purification. Subsequently, the resulting 1,4-CHD was isomerized to 1,3-CHD. The 1,3-CHD was transformed to a renewable polyester and characterized by GPC, TGA, DSC, and FTIR.

Wednesday, April 10, 2013 10:10 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

462 - Cationic copolymerization of biological oils

__Mihail Ionescu__, mionescu@pittstate.edu, Zoran S. Petrovic. Pittsburg State University, Kansas Polymer Research Center, Pittsburg, Kansas 66762, United States

Vegetable oils are triesters of glycerine with fatty acids (triglycerides), especially with unsaturated fatty acids acids containing one double bond (oleic acid), two double bonds (linoleic acid) and three double bonds (linolenic acid). Fish oil and krill oil are highly unsaturated oils having long chains w-3 fatty acids. The unsaturated biological oils with 4-6 double bonds / mol are polyfunctional monomers. We developed a new method of cationic polymerization of vegetable oils by using superacids as catalysts (HBF4, triflic acid, HSbF6 etc.). By using this method we successfully have copolymerized biological oils preparing new copolymers such as: soybean oil-corn oil, safflower oil-linseed oil, sunflower oil-linseed oil, corn oil-camelina oil, soybean oil-fish oil etc. The best oils for synthesis of these unconventional copolymers contain fatty acids with multiple double bonds, especially with three double bonds. The synthesized copolymers, substitutes for heat bodied oils, are suitable for preparation of inks, paints, coatings.



Wednesday, April 10, 2013 10:30 AM

Natural and Renewable Polymers (08:30 AM - 11:50 AM)

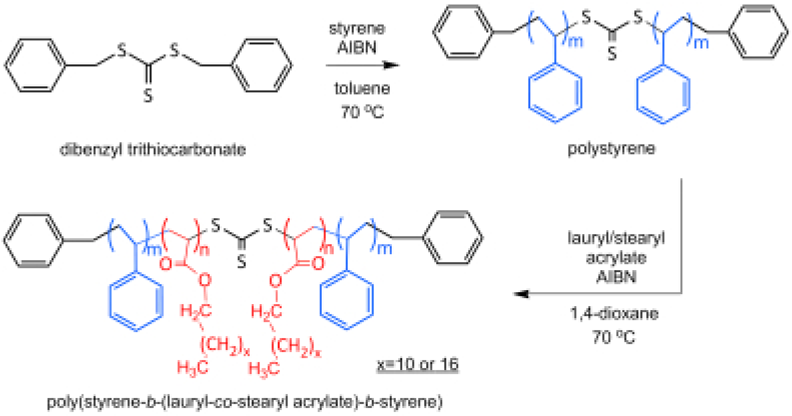
Location: Hilton Riverside

Room: Ste. A, Sec 6

463 - Sustainable thermoplastic elastomers derived from vegetable oils

***Megan L. Robertson**, mlrobertson@uh.edu, Shu Wang. Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States*

The finite availability of fossil fuels and environmental impact of petroleum processing has led to the development of polymers from sustainable sources. In this study, sustainable thermoplastic elastomers were synthesized through the sequential RAFT polymerization of lauryl /stearyl acrylate and styrene, resulting in triblock copolymers with tunable physical properties. The thermal and mechanical properties and order-disorder transition temperature of the triblock copolymers were varied by manipulating the acrylate composition of the middle block and overall molecular weight of the polymer.



Synthesis of poly(styrene-*b*-(lauryl-*co*-stearyl acrylate)-*b*-styrene) triblock copolymer

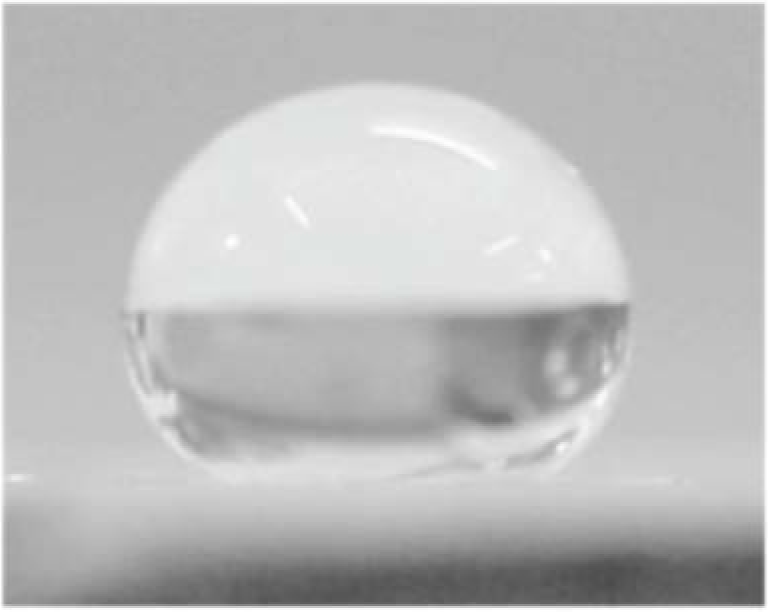
Wednesday, April 10, 2013 10:50 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

464 - Conversion of biowaste silica to value added Si based materials including polymers and high purity silicon

Richard M Laine[1]*, Talsdad@umich.edu, David J Krug*[1]*, Julien C. Marchal*[2]*, Vera Popova*[2]*. (1) Macromolecular Science and Eng. and Department of MSE, University of Michigan, Ann Arbor, MI 48109-2136, United States, (2) Mayaterials Inc, Ann Arbor, MI 48108, United States*

Agricultural byproducts used as alternate energy sources generate considerable waste. Harvested rice is milled producing rice hulls that are often burned to generate electricity also producing rice hull ash (RHA). In the U.S. some 100k tons of RHA are produced annually. RHA consists of 70-90 wt % low impurity, high surface area (20 m^2/g) amorphous, porous silica mixed with low impurity, amorphous carbon.

The rice plant does not extract heavy metals from the ground and as such the resulting RHA is relatively pure. Furthermore, it is very easily purified using simple acid extraction to remove small amounts of phosphates and alumina. We have developed several methods of extracting this silica to produce a wide variety of products including high purity precipitated silica and several silane products. Furthermore, the resulting silica depleted RHA or SDRHA has C:SiO_2ratios of value for electric arc furnace processing of silicon metal. We describe route to 5-6 nines purity silicon with costs that are 30 % of traditional chlorosilane processing costs.



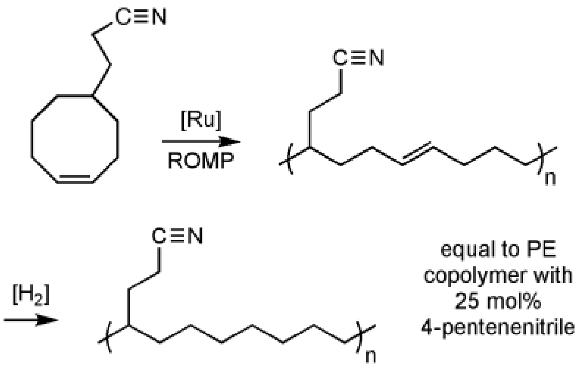
Superhydrophobic polymer coating on low density silica

Wednesday, April 10, 2013 11:20 AM
Natural and Renewable Polymers (08:30 AM - 11:50 AM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

465 - Poly(ethylene-*co*-4-pentenenitrile) elastomers: Synthesis via ROMP/hydrogenation and property comparison to commercial nitrile rubbers

Lisa S Baugh[1], *lisa.s.baugh@exxonmobil.com, Enock Berluche*[1], *Karla S. Colle*[2]. *(1) Corporate Strategic Research, ExxonMobil Research & Engineering Company, Annandale, NJ 08801, United States, (2) Baytown Technology & Engineering Complex, ExxonMobil Chemical Company, Baytown, TX 77520, United States*

A model poly(ethylene-*co*-4-pentenenitrile) copolymer **I** containing 25 mol% pentenenitrile was prepared by ROMP of (*Z*)-3-(cyclooct-4-enyl)propanenitrile with second-generation Grubbs' metathesis catalyst and $(Ph_3P)_3RhCl$ hydrogenation. Elastomeric **I** (M_w 50,920; M_n 26,560) and alkenamer precursor **II** were compared to commercial unsaturated (NBR) and saturated (Zetpol® HNBR) oil-resistant nitrile-butadiene rubbers. Both **I** and **II** showed lower T_gs and greater thermal stabilities than (H)NBRs, with T_g midpoints of -54 to -48 °C (vs. -46 to -27 °C) and decomposition onsets in air of ³ 423 °C (vs. £ 417 °C). Polymer **I** exhibited 50 °C oil swell of 49.8 wt%. This swell value is inferior to Zetpol® HNBRs (4.2 - 14.1 wt%) but comparable to ~20 wt% nitrile NBR and chloroprene rubber (42.6-45.4 wt%), and much lower than EPDM elastomers (> 172 wt%). A solubility parameter of 9.5 $(cal/cc)^{1/2}$ was calculated for **I** , much higher than values for poly(butadiene) and chloroprene rubber and reaching the lowest value calculated for HNBRs (9.5-10.4 $(cal/cc)^{1/2}$).

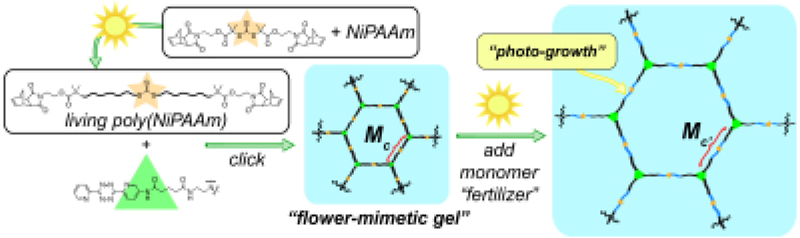


Wednesday, April 10, 2013 08:30 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

466 - Using sunlight to grow telechelic polymers and end-linked polymer networks: Synthesis of “flower-mimetic” gels

***Huaxing Zhou**, huaxing@mit.edu, Jeremiah A Johnson. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The first photo-initiated synthesis of click-telechelic polymers and growth of polymer gels is described. Specifically, UV and sunlight initiated growth of from a bis-norbornene trithiocarbonate moiety were studied in detail. Conditions were identified that enable facile access to living, norbornene-telechelic poly(NiPAAm) macromers. We demonstrate that these macromers (R-A2) can be end-linked with a tri-tetrazine derivative (R-B3) via inverse electron demand Diels-Alder cycloaddition. Addition of a new batch of monomer, followed by exposure to sunlight, leads to “photo-growth” of the network pores.



Wednesday, April 10, 2013 08:50 AM

General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)

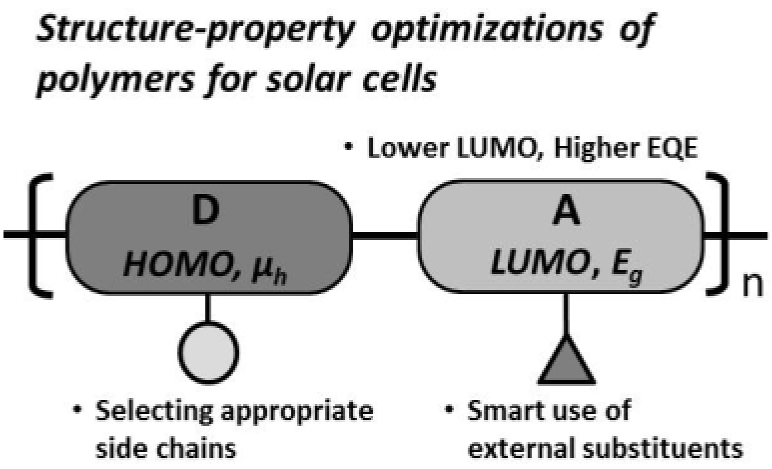
Location: Hilton Riverside

Room: Ste. D, Sec 19

467 - Structure-property optimizations of donor polymers for higher efficiency organic photovoltaics

***Rycel Uy**, uyr@email.unc.edu, Wei You. Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States*

Many advances in organic photovoltaic efficiency are not yet fully understood and new insight into structure-property relationships is required to push this technology into broad commercial use. This research examines the impact of the following structural modifications to: (a) the thienothiazole (TTz) moiety and its effect on lowering the highest occupied molecular orbital (HOMO) level; and (b) the high-performing fluorinated triazole polymer (PBnDT-FTAZ) and its effect on photovoltaic parameters such as short circuit current (Jsc) and open circuit voltage (Voc).

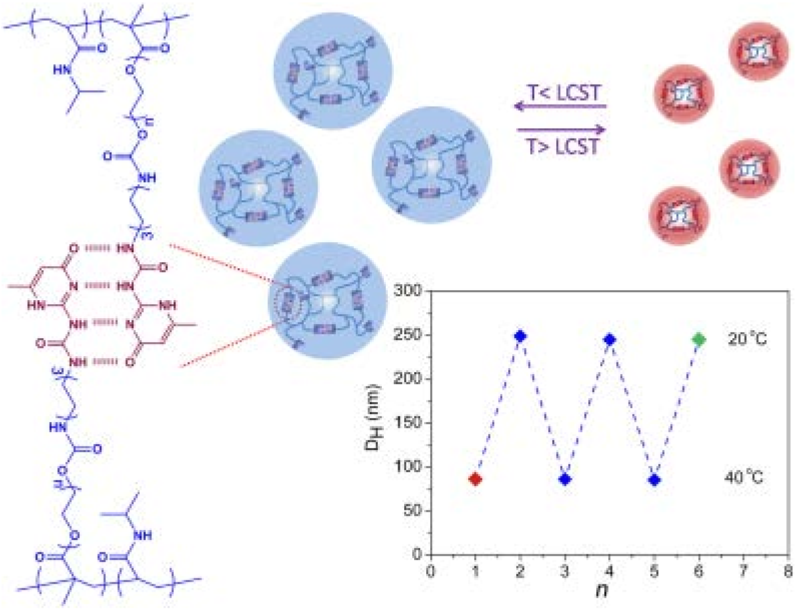


Wednesday, April 10, 2013 09:10 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

468 - Waterborne polymer nanogels non-covalently crosslinked by multiple hydrogen bond arrays

*Yunhua Chen, Nicholas Ballard, **Stefan A.F. Bon**, s.bon@warwick.ac.uk. Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom*

Synthetic colloidal hydrogel particles of sub-micron dimensions, often referred to as microgels and/or nanogels, generally consist of water-soluble polymers held together through chemical crosslinking by covalent bonds in order to preserve the distinct colloidal particle identity. Here we demonstrate the synthesis of non-covalently crosslinked nanogel particles in which the crosslinking through covalent bonds is replaced by physical crosslinking induced by strong self-complementary quadruple hydrogen bond interactions.



The multiple hydrogen bond (MHB) arrays were introduced in the form of a 2-ureido-4[1*H*]pyrimidinone (UPy) functionalized polyethylene glycol methacrylate (PEGMA) comonomer, which was employed in the synthesis of colloidal nanogels made from *N*-isopropylacrylamide (NIPAm) or a mixture of 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene glycol) methacrylate (MEO_2MA-*co*-OEGMA) following conventional free radical polymerization routes. The temperature-dependent swelling properties of the non-covalently crosslinked nanogels with differences in UPy loadings were studied, clearly demonstrating that MHB arrays can work as crosslinking moieties warranting the colloidal particle identity of the prepared hydrogels.

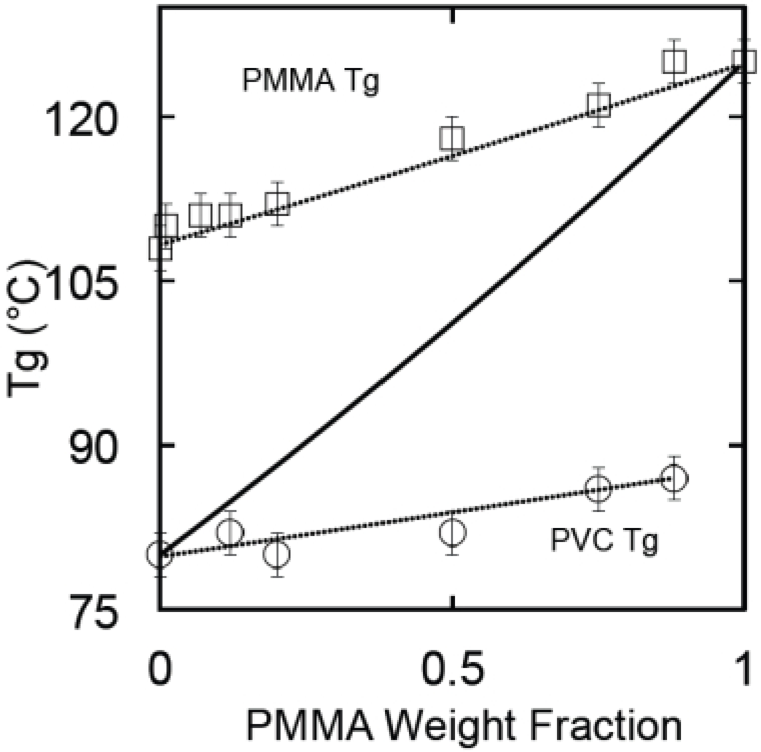
for more info see: www.bonlab.info

Wednesday, April 10, 2013 09:30 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

469 - Fluorescence as a novel technique for determining component glass transition temperatures in miscible polymer blends

Christopher M Evans[1], *cmevans@u.northwestern.edu, John M Torkelson*[1,2]. *(1) Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States, (2) Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, United States*

Fluorescence spectroscopy is employed as a new characterization method for measuring component glass transition temperatures (T_gs) in miscible blends. Pyrene-labeled poly(methyl methacrylate) (MPy-labeled PMMA) was blended with poly(ethylene oxide) (PEO) or poly(vinyl chloride) (PVC) and PMMA component T_gs were characterized over a 0.1 - 100 wt % composition range. Component T_gs determined for PMMA blended with PEO exhibit excellent agreement with previous differential scanning calorimetry (DSC) measurements (Lodge et al. J Polym Sci Part B: Polym Phys 2006;44:756-763) where the DSC T_g values were determined from peaks in the derivative heat flow curves. Blends of PMMA with PVC are also characterized via MPy-labeled PMMA fluorescence, and we demonstrate for the first time that both blend component T_gs can be determined from the temperature dependence of the fluorescence of a pyrenyl dye attached to a single blend component. This special sensitivity of the pyrenyl dye label to both component T_gs is hypothesized to derive from the solvatochromic nature of the dye. Because of the close proximity of the T_gs of neat PMMA and neat PVC, DSC is unable to clearly resolve the two component T_gs in these blends. Fluorescence can also determine T_g values for near-infinitely dilute (< 0.1 wt%) components which have not been previously experimentally characterized by other techniques. Thus, fluorescence provides a new characterization method for blend component T_g measurements unattainable by conventional tools such as DSC.

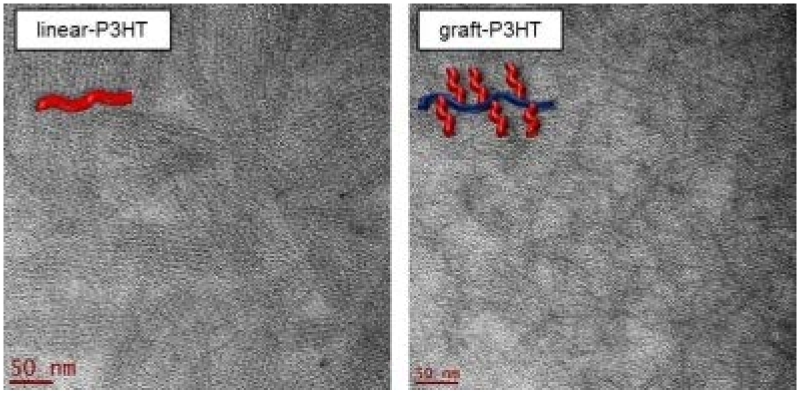


Wednesday, April 10, 2013 09:50 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

470 - Conjugated bottle-brush polymers incorporating poly(3-hexylthiophene) as brush side-chains

Suk-kyun Ahn[1], *sukkyun.ahn@gmail.com, Deanna L Pickel*[1]*, W Michael Kochemba*[2]*, Jihua Chen*[1]*, S Michael Kilbey*[1,2]*. (1) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States, (2) Department of Chemistry, Universty of Tennessee, Knoxville, TN 37996, United States*

Herein we report a facile synthetic strategy to prepare well-defined bottlebrush polymers incorporating poly(3-hexylthiphene) (P3HT) as a conjugated polymeric side-chain through the macromonomer approach. Norbornenyl functionalized P3HT macromonomer was synthesized by Kumada catalyst transfer polycondensation (KCTP) followed by post-polymerization modifications including Suzuki and *N,N'*-dicyclohexylcarbodiimide (DCC)-promoted coupling reactions. The macromonomer was then further polymerized by ring-opening metathesis polymerization (ROMP), producing the conjugated bottle-brush polymer. The unique topology of conjugated bottlebrush polymers resulted in significant changes in their morphologies, thermal and electronic properties as compared to conventional linear P3HTs.



Our synthetic approach will provide an opportunity to synthesize a new and important class of conjugated (co)polymers, by which morphology, and electronic properties of the resulting polymers can be tailored in useful and interesting ways.

Wednesday, April 10, 2013 10:10 AM

General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)

Location: Hilton Riverside

Room: Ste. D, Sec 19

471 - Functionalized polymer additives for novel lubricating regimes

***Athina Anastasaki Anastasaki**, A.Anastasaki@warwick.ac.uk, Christopher Waldron, Paul Wilson, David M Haddleton. Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom*

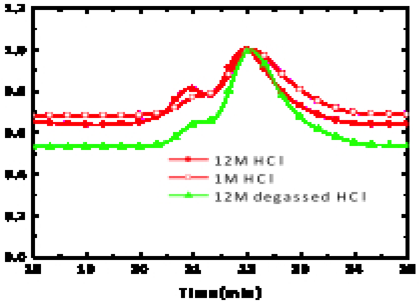
Homo and block copolymers have been synthesised *via*Single Electron Transfer Living Radical Polymerization (SET-LRP) and Catalytic Chain Transfer Polymerization (CCTP). Base-mediated Michael Addition and thio-bromo 'click' reactions have also been performed for further functionization, taking advantage of the excellent end-group fidelity that both SET-LRP and CCTP can provide.

Wednesday, April 10, 2013 10:30 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

472 - Origins of coupled product formation in modified Kumada catalyst transfer polymerization of 3-hexylthiophene

Youjun He, *hey2@ornl.gov, Kunlun Hong. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6494, United States*

P3HT is one of the most widely used conjugated polymers in organic electronic devices. The power conversion efficiency of OPVs based on P3HT as donor and fullerene derivative as acceptor has reached 6.7% (1). P3HT has been synthesized by many methods (2). Different methods result in P3HT with different regioregularity, MW, MWD, and ending functionalities. All these parameters have big influence on their device performance. In this contribution, we report the impact of quenching methods on the molecular weight distribution of 3HT polymerization using modified KCTP (3). Part of the results is shown in the Figure 1. We found out that either the concentration of HCl or presence of oxygen is the determining factor in forming coupling product.



Acknowledgement : This research was conducted at the CNMS, which is sponsored at ORNL by Office of BES, U.S. DOE.

References :

1) Sun, Y. P. et al. Adv. Energy Mat. , **2011** , *1*, 1058.

2) Chujo, Y. “Conjugated Polymer Synthesis” Wiley-VCH Weinheim, Germany, **2010** .

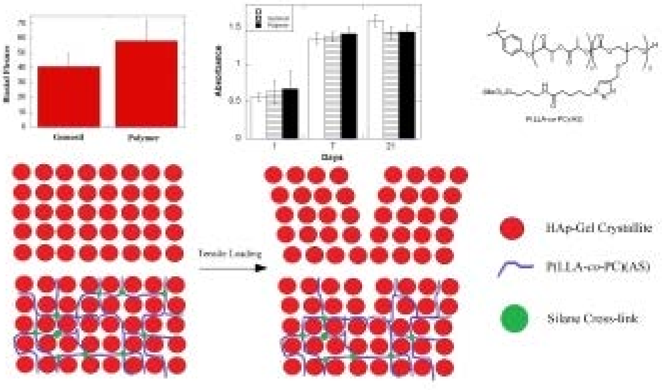
(3) Tamba, S. et al . Chem. Lett., **2011** , *40*, 398.

Wednesday, April 10, 2013 10:50 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

473 - Investigation of siloxane cross-linked hydroxyapatite-gelatin/copolymer composites for potential orthopedic applications

Jason C Dyke[1], *jcdyke33@gmail.com, Wei You*[1], *Ching Ko*[2], *Kelly Knight*[1]. *(1) Department of Chemstry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (2) Department of Orthodontics and Applied Materials Sciences Program, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States*

In order to explore new materials for potential orthopedic applications, we designed a cross-linkable copolymer to help impart improved mechanical strength into bioceramic hydroxyapatite (HAp) composites. Polymers can help improve long range order in the composite, while a grafted cross-linkable group on the polymer chain allows for improved local interaction. These copolymers demonstrated tunable properties, which can help engineer future scaffolds for specific applications. Vitally, composites were shown to help improve mechanical properties of the composite while maintaining biocompatibility.



Wednesday, April 10, 2013 11:10 AM

General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)

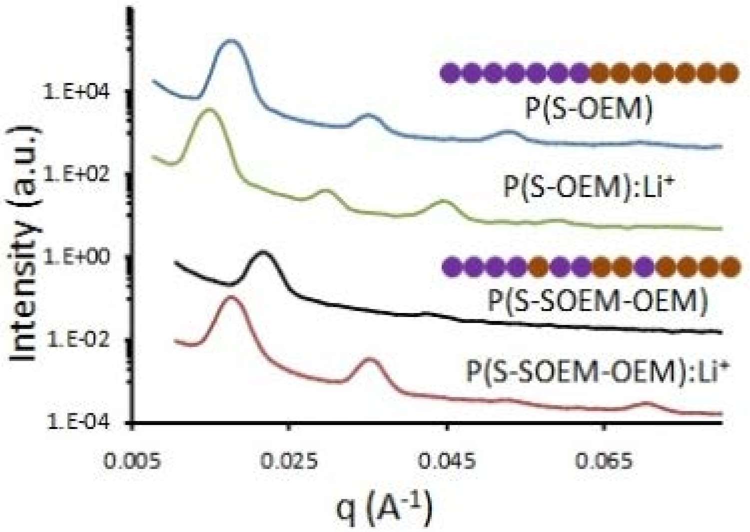
Location: Hilton Riverside

Room: Ste. D, Sec 19

474 - Interfacial modification effects on the self-assembly of lithium-doped block copolymers

***Wei-Fan Kuan**, wfkuan@udel.edu, Thomas H Epps, III. Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States*

Block copolymers are promising materials for nanoscale applications, such as conducting membranes and nanoporous templates, due to their ability to self-assemble into periodically ordered structures. To controllably obtain desirable nanostructures for various applications, it is essential to study the factors that affect the block copolymer self-assembly. The tendency for block copolymers to phase separate into various nanostructures is generally governed by the segregation strength and volume fraction of the copolymer blocks. One area of current project in our group is using tapered block copolymers to investigate the effects of interfacial composition on segregation strength between copolymer blocks. In tapered block copolymers, the composition profile is modified along the polymer backbone by introducing a transition region between two pure blocks that tapers from one component to another. This interfacial manipulation between blocks provides control over the segregation strength in our nanoscale phase-separated materials independent of molecular weight and block constituents. In this work, we are studying the effect of the tapered interface on the domain spacing behavior of salt-doped poly(styrene-*b*-oligo(oxyethylene) methacrylate) (PS-POEM). We synthesized tapered PS-POEM block copolymers with a range of taper lengths and salt doping levels, and we determined the domain spacing of salt-doped block copolymers using scattering and microscopy techniques. We also estimated the influence of salt doping on the thermodynamics of our tapered and non-tapered block copolymers.

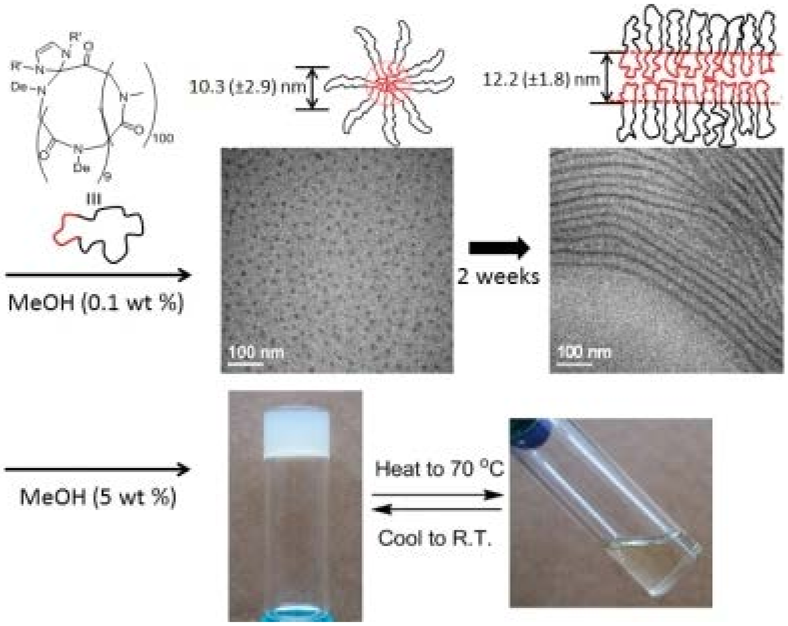


Wednesday, April 10, 2013 11:30 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

475 - Crystallization-driven thermo-reversible gelation of coil-crystalline diblock copolypeptoids

Chang-Uk Lee[1], *clee59@lsu.edu*, *Thomas P. Smart*[2], *Thomas H. Epps III*[2], *Jihua Chen*[3], *Donghui Zhang*[1]. *(1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States, (2) Department of Chemical Engineering, University of Delaware, Newark, DE 19716, United States, (3) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Cyclic and linear diblock copolypeptoid consisting of an amorphous and a crystalline block [i.e. poly(*N*-methyl-glycine)-*b*-poly(*N*-decyl-glycine) (*c*/*l*-PNMG-*b*-PNDG)] form micron-long cylindrical micelles by a crystallization-driven self-assembly in room temperature methanol. The crystallization of the core-forming segments (PNDG) has been verified by selected area electron diffraction (SAED) and ultrasensitive microDSC analysis. At 5 and 10 wt% concentration, the polymer solutions form free-standing gels at room temperature due to the intermolecular entanglement of cylindrical micelles. Rheological measurements reveal that the gels based on cyclic copolymers are stiffer than those based on the linear counterparts. Gel dissolution occurs at 55 °C due to morphological transition from the cylindrical micelles to spherical micelles induced by the melting of the PNDG crystalline core. Variable-temperature NMR analysis reveals that the hydrophobic segment is substantially less solvated in the cyclic polymers than their linear analogs both in gel and sol states. Our findings provide a proof of concept that thermo-responsive gels can be efficiently accessed through crystallization-driven cylindrical micelle formation and inter-micellar entanglement.

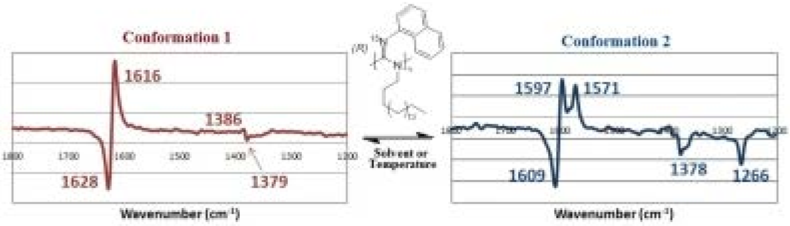


Wednesday, April 10, 2013 11:50 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

476 - Investigating the reversible chiroptical switching phenomenon in polycarbodiimides using ^{15}N NMR and VCD spectrocopy

***James F. Reuther**[1,2], jfr120030@utdallas.edu, Joe D DeSousa[1], Bruce M Novak[1]. (1) Chemistry, University of Texas: Dallas, Richardson, TX 75080, United States, (2) Chemistry, North Carolina State University, Raleigh, NC 27695, United States*

Helical polycarbodiimides have been shown to display a wide variety of interesting and potentially fruitful properties. One of which that has been of particular interest is the reversible solvo- and thermo- driven chiroptical switching phenomenon observed in certain polycarbodiimides containing bulky aromatic pendant groups (i.e., anthryl, naphthyl, etc). Much is still unknown about the specific conformational reorientation that causes the observed chiroptical switching, however. In order to elucidate the cause and possible driving forces behind this phenomenon, poly(*N*-naphthyl-*N*'-octadecylcarbodiimide), the most versatile of all switching polycarbodiimides, was subject to nitrogen-15 enrichment and subsequent ^{15}N NMR analysis. This new data suggests that the chiroptical switching process is consequence of varying populations of two distinct polymer conformations. The populations are able to be specifically modulated simply by altering either the solvent or temperature. Here in, we report the use of vibrational circular dichroism (VCD) spectroscopy coupled with density functional theory (DFT) calculations to determine overall secondary structure of both states.



Wednesday, April 10, 2013 12:10 PM

General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)

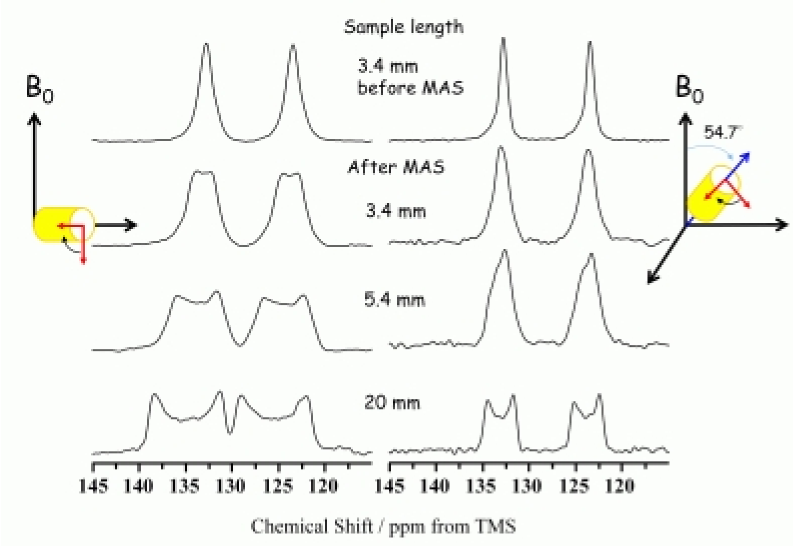
Location: Hilton Riverside

Room: Ste. D, Sec 19

477 - ^{13}C NMR chemical shift and magnetic susceptibility of rubbers elongated and strained by MAS

Atsushi Asano[1], *asanoa@nda.ac.jp, Masashi Kitamura*[1]*, Yoshiaki Hata*[2]*, Hiroshi Yasuoka*[2]*. (1) Department of Applied Chemistry, National Defense Academy, Yokosuka, Kanagawa 2398686, Japan, (2) Department of Applied Physics, National Defense Academy, Yokosuka, Kanagawa 2398686, Japan*

We investigated the effect of deformation of rubbers (natural rubber, NR; polybutadiene, BR; polyisobutylether, PIB) resulting from the high centrifugal pressure of fast MAS on ^{13}C NMR spectra. The static state ^{13}C DD NMR spectra of the rubbers after MAS presented broad and apparently anisotropic peaks. The mass magnetic susceptibility of the rubbers having a double bond (NR and BR) depends on its direction against the static field, while the rubber without a double bond (PIB) did not show such a difference. This indicated that the chemical anisotropy is not predominated the ^{13}C chemical shift for the NR and BR rubbers. We concluded that the anisotropic peaks are caused by the differences in the mass magnetic susceptibility according to the molecular orientation. In this study, we discuss the relationship between the mass magnetic susceptibility and ^{13}C chemical shift obtained from both MAS and static probes.



Wednesday, April 10, 2013 09:00 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

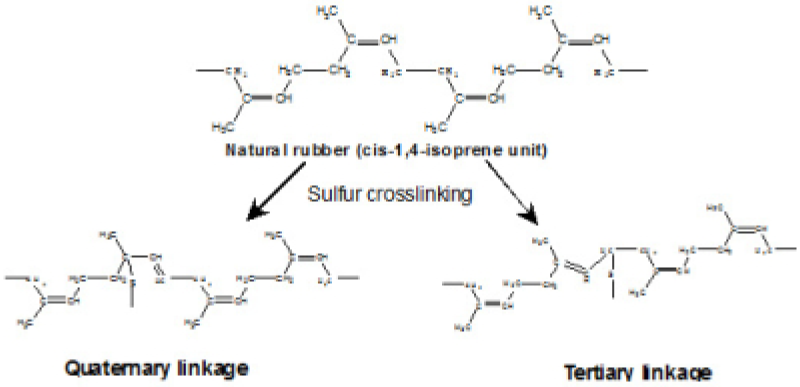
Location: Hilton Riverside

Room: Ste. C, Sec 18

478 - Characterization of vulcanized natural rubber through field gradient-fast magic angle spinning NMR spectroscopy

Seiichi Kawahara, *kawahara@mst.nagaokaut.ac.jp, Oraphin Chaikumpollert. Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan*

Field gradient-fast-magic angle spinning (FG-FMAS) NMR spectroscopy has been developed to analyze crosslinking junctions of vulcanized natural rubber. The dipole-dipole interaction of the rubber was eliminated by fast magic angle spinning. The FG-FMAS NMR spectroscopy enabled to apply various pulse sequences such as DEPT, APT, HETCOR, HMQC, HSQC and HMBC to the vulcanized natural rubber. In the present study, the crosslinking junctions of the vulcanized natural rubbers, prepared by conventional vulcanization (CV), efficient vulcanization (EV) and semi-efficient vulcanization (SemiEV), were analyzed by FG-FMAS NMR spectroscopy. The amount of tertiary carbons linking to sulfur of the CV rubber was the same as those of the EV and SemiEV rubbers, when the rubbers were analyzed by ^{1}H-NMR spectroscopy. ^{13}C-NMR spectroscopy revealed that the amount of quaternary carbons linking to sulfur of the CV rubber was largest among the rubbers. The mechanical properties of the CV rubber were the most excellent; hence, the quaternary carbons linking to sulfur as crosslinking junction was assigned to the molecular singularity.

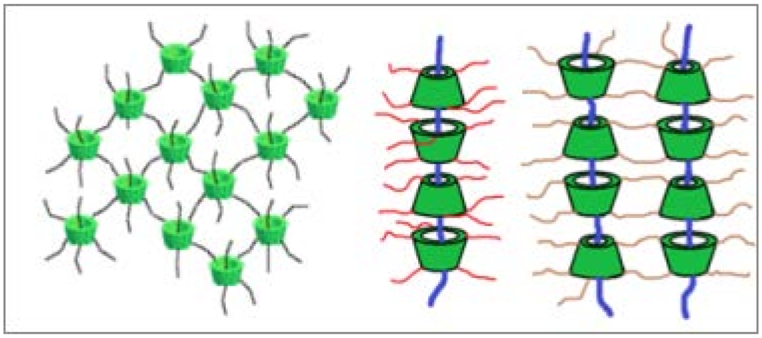


Wednesday, April 10, 2013 09:25 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

479 - Magnetic resonance as a guide for nanoscopic polymer network formation

Gaumani Gyanwali, *gaumani@okstate.edu, Mathis Hodge, Jeffery L White. Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States*

Using simple one-pot methods, we prepared networked cyclodextrins and polymer-cyclodextrin inclusion complexes which were used to create 'bottle brush' type materials and networked complexes. The orthogonally arranged complex networks have unique swelling property and can be made into thin films. These materials have potential applications in polymer science, including free-volume modifiers, scavengers, and stabilizers or compatibilizers. Nuclear magnetic resonance (NMR) spectroscopy was used as a main tool to analyze these interesting materials.



Wednesday, April 10, 2013 09:50 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

Location: Hilton Riverside

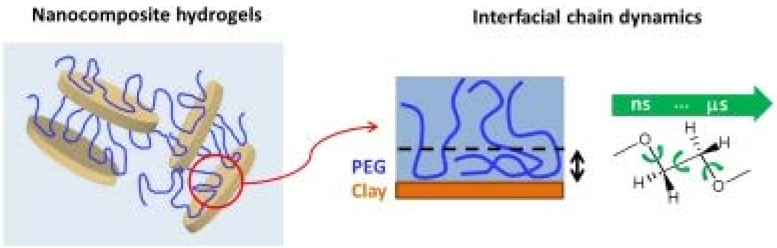
Room: Ste. C, Sec 18

480 - Surface-induced ordering and interfacial dynamics in nanocomposite polymer-based hydrogels: A solid-state NMR investigation

Cédric Lorthioir, *lorthioir@icmpe.cnrs.fr, Véronique Wintgens, Catherine Amiel. Department "Complex Polymer Systems", East Paris Institute of Chemistry and Materials Science (CNRS / University of East Paris), Thiais, France*

Mixing poly(ethylene glycol) (PEG) solutions with aqueous dispersions of clay platelets (Laponite) results in the formation of nanocomposite hydrogels. NMR spectroscopy was used to probe the evolution of the PEG local dynamics during gelation: these NMR measurements led to the description of the chain ordering induced by the clay layer assembling. These experiments also pointed out a significant slowing-down of the PEG chain motions close to the platelets.

The segmental dynamics of these interfacial PEG chains was then investigated through solid-state NMR. While such chain portions are “frozen” on the tens of nanoseconds time scale, PEG segmental motions were detected over several tens of microseconds. Such motions are highly restricted since at room temperature, their frequencies were found to be similar to the ones displayed by **bulk** amorphized PEG chains, considered 10 K below. Complementary ^{2}H NMR experiments enabled to precise the geometry of these reorientational motions.



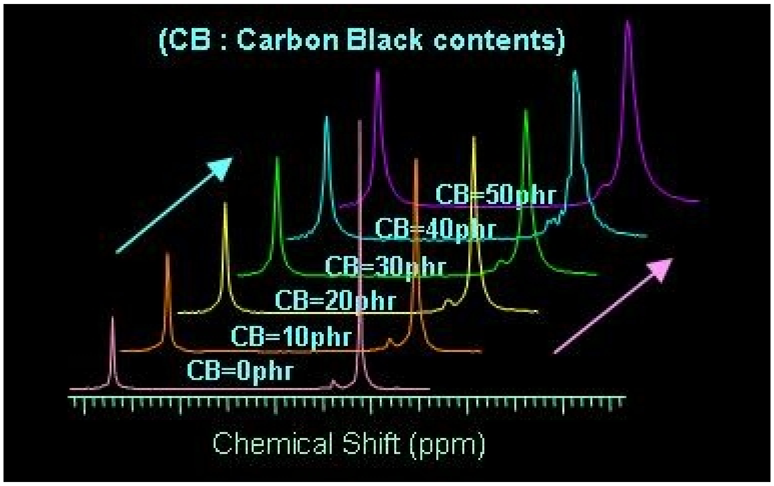
Wednesday, April 10, 2013 10:30 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

481 - Analysis of rubber by high-resolution solid-state ^{13}C NMR

Marina Kotani, *m-kotani.az@srigroup.co.jp, Sumitomo Rubber Industries,LTD., Kobe, Japan*

The characterization of the distribution of carbon black (CB) in rubber blends is important for the improvement of the strength of the rubber materials. It is generally accepted that CB is not uniformly dispersed in rubber blends because of the different compatibilities between the CB and each rubber component. It is considered that the compatibility between the CB and rubber is affected by various environments; i.e., unsaturation, viscosity, polarity, mixing procedure, *etc*.

Solid-state ^{13}C NMR is expected to be a tool to determine the distribution ratio of CB in rubber blends. It is found that the relationships between the line width of polymer's resonance lines and CB contents are estimated from the dipolar decoupling / magic angle spinning (DD/MAS) ^{13}C NMR spectra. These relationships are used as calibration curves. On the basis of these calibration curves, the distribution ratio of CB in the rubber blend is determined.

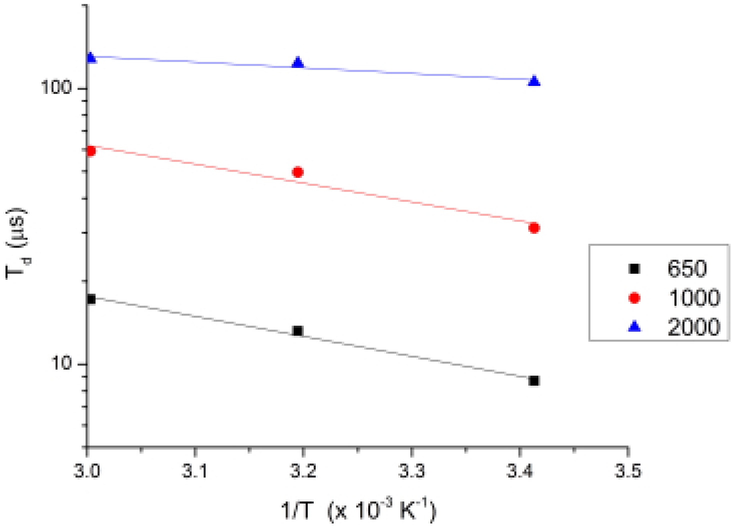


Wednesday, April 10, 2013 10:55 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

482 - Solid-state NMR characterization of a select model poly(urethane urea) elastomer

Weiguo Hu[1], *weiguoh@polysci.umass.edu, Alex J Hsieh*[2]. *(1) Department of Polymer Science & Engineering, University of Massachusetts, Amherst, MA 01003, United States, (2) RDRL-WMM-G, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069, United States*

High performance elastomers have recently gained considerable interest throughout the U.S. Department of Defense, particularly for their potential in ballistic impact protection and blast mitigation capabilities. The major challenges for a rational design of hierarchical elastomers to achieve multi-functionalities reside on the realization of the key material attributes that are critical across various spatial and temporal scales. In this work, we use solid state nuclear magnetic resonance (NMR) techniques to investigate the structure and molecular dynamics in a 4,4'-dicyclohexylmethane diisocyanate-poly(tetramethylene oxide)-diethyltoluenediamine based poly(urethane urea) (PUU) elastomer. A series of samples with varying poly(tetramethylene oxide) (PTMO) molecular weight (650, 1000, and 2000 g/mol) were studied. The molecular dynamics profiles, indicated by the ^{1}H dipolar dephasing time (T_d), suggest that the samples can be described by a single phase model to a good approximation, contrasting to the common notion of hard and soft domains for typical microphase-separated elastomers. Despite identical stoichiometry and soft segment chemical structure, there is a large difference in molecular dynamics across the samples. The T_d of the samples with shorter PTMO segments has higher activation energy, suggesting intimate interaction between the soft and the hard segments. On the other hand, the magic-angle-spinning ^{1}H spin echo and spin diffusion measurements show finely dispersed domains. These morphological and dynamical aspects of the PUU materials are critical for their mechanical performance at high strain rates.

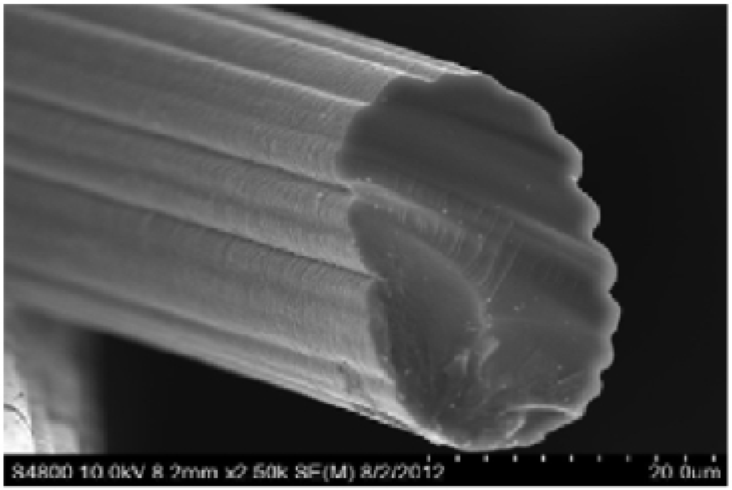


Wednesday, April 10, 2013 11:20 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

483 - Acetylated-lignin as a biopolymer precursor for carbon fibers

*M Zhang, **Amod A Ogale**, ogale@clemson.edu. Department of Chemical and Biomolecular Engineering, and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634-0909, United States*

Bio-based macromolecules provide a sustainable and renewable resource for carbon precursors. Prior literature studies on carbon fibers produced from lignin, an abundant biomass, have employed melt-spinning routes using hardwood lignin as the carbon fiber precursor, due to its lower reactivity (relative to softwood lignin). In the present study, we demonstrate an alternative chemical modification route for a commercial softwood kraft lignin (SKL, Indulin AT). SKL with a low extent of acetylation was solution-spun and successfully thermo-oxidatively stabilized. Both stabilization and carbonization reactions were performed under tension in an attempt to retain molecular orientation within the fibers. Carbon fibers were successfully produced at heat treatment temperatures of 1000 and 2400°C. The fibers were investigated by WAXD and Raman spectroscopy, and show mostly non-graphitic microstructure. The carbon fibers could be produced with diameters as little as about 15 mm due to the solution-spinning route, which also imparted a crenulated surface to carbon fibers. This enhanced surface area has the potential of improving interfacial bonding between such fibers and polymer matrices.



Wednesday, April 10, 2013 08:35 AM

Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)

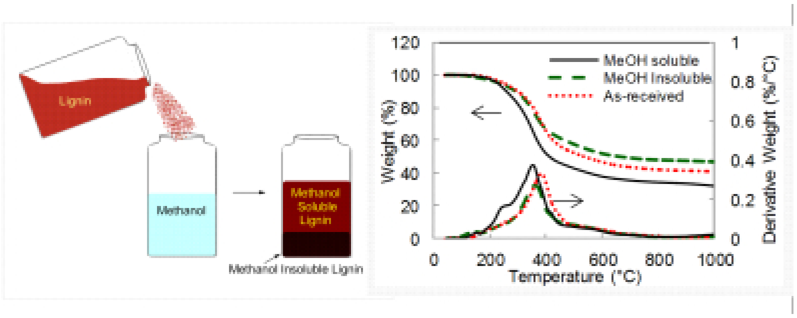
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

484 - Use of lignin as a carbon precursor: Effect of fractionation

Tomonori Saito[1], *saitot@ornl.gov, Joshua H Perkins*[1], *Jamie M Messman*[2], *Amit K Naskar*[1]. *(1) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6053, United States, (2) Center for Nanophase Materials Sciences, Oark Ridge Naitonal Laboratory, Oak Ridge, TN 37831-6494, United States*

Development of technologies to produce high purity lignin is crucial for the novel utilization of lignin such as a carbon precursor. The effect of methanol (MeOH) fractionation to its properties was investigated. Repeating MeOH fractionation of softwood kraft lignin successfully removed low molecular weight fraction. The successfully separated MeOH insoluble high molecular weight lignin possessed T_g of 211 °C and char yield of 47 %, much higher than those of as-received lignin (T_g 153 °C, char yield 41 %,). MeOH soluble fraction of lignin showed increased low molecular weight fraction and lower T_g (117 °C) and char yield (32%). The amount of low molecular weight fraction correlated well with char yield in a linear regression. This study demonstrated novel purification technology of lignin to alter its T_g and char yield.



Wednesday, April 10, 2013 09:05 AM

Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)

Location: Hilton Riverside

Room: Ste. B, Sec 7/10

485 - Self-assembly of lignin molecules in solution

Dilru R Ratnaweera[1], *dratnawe@utk.edu, Dipendu Saha*[2], *Sai V Pingali*[3], *Amit K Naskar*[2], ***Mark Dadmun***[1,4], *Dad@utk.edu. (1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States, (2) Material Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States, (3) Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States, (4) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Recently, there has been a growing interest in utilization of lignins as a precursor for carbon fibers. Proper understanding of association models of lignins during solution processing provides useful structural information that can be utilized to optimize the use of lignins in this value added application. Hence we follow the assembly of lignin molecules from a variety of sources in dimethyl sulfoxide, a good solvent for lignins, using small angle neutron scattering. In order to mimic industrial processing conditions, concentrations of lignins were kept above the overlap concentration. At small length scales, short lignin segments with ~4-10 monolignol units associate to form rigid rod-like/cylindrical building blocks, where the number of repeat units in a cylindrical segment decreases with increasing lignin concentration. These cylindrical building blocks associate to form spherical aggregates with low cross-linking densities and a random coil or network like structures for highly branched systems. The degree of branching of the base lignin molecule, which varies with source, plays a crucial role in determining their association behavior. Overall sizes of aggregates decrease with increasing concentration at low cross-linking densities as illustrates in the accompanying figure, whereas the opposite trend is observed for highly branched lignins.

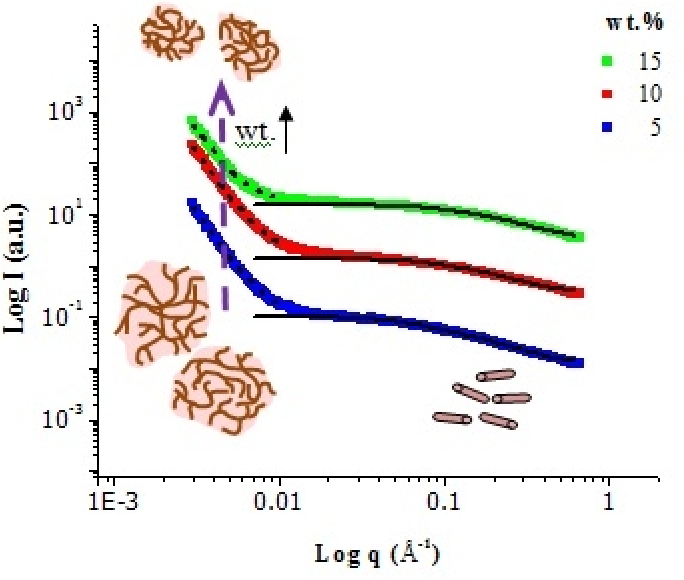


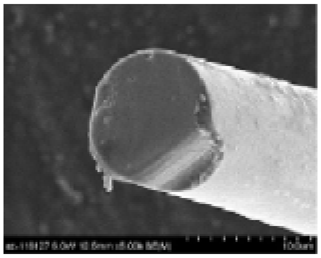
Figure. SANS data of lignins with low cross-linking density. Solid lines are the best fits for cylindrical form factor and dash lines correspond to the best fits of unified model.

Wednesday, April 10, 2013 09:25 AM
Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

486 - Microstructures of lignin-derived carbon fibers

*Dipendu Saha[1], Marcus A Hunt[1], Tomonori Saito[1], Soydan Ozcan[1], E. Andrew Payzant[2], **Amit K Naskar**[1], naskarak@ornl.gov. (1) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States, (2) Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Lignin-derived carbon fibers were obtained by melt-processing of powder lignin followed by thermal treatment. The small angle x-ray scattering data on carbonized filaments yield pore widths within 5 - 20 Å that are close to data from adsorption experiments. However, the fibers exhibit a broad (002) wide angle x-ray diffraction peak indicating poor graphitic order and low mechanical properties. Long-range structural order similar to the commercial carbon fibers is desired for enhanced performance; otherwise, lignin-derived carbon fibers will find non-structural applications such as sorbent and high surface area electrically conductive substrate. For the second applications, controlled nanoscale pore widths are being synthesized in lignin-derived carbon.

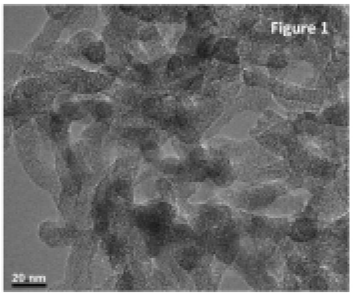


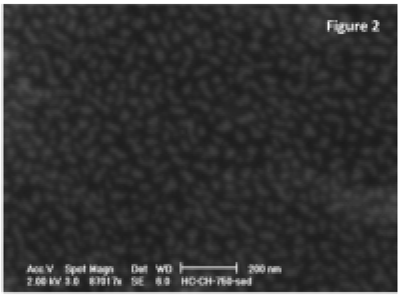
Wednesday, April 10, 2013 09:55 AM
Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

487 - Waterborne dispersions and advanced coatings of hydrothermal carbon

John Texter[1], *jtexter@emich.edu, Rene Crombez*[1], *Li Zhao*[2], *Fernando Perez Caballero*[2], *Robin White*[2], *Magdalena Titirici*[2], *Markus Antonietti*[2]. *(1) School of Engineering Technology, Eastern Michigan University, Ypsilanti, MI 48197, United States, (2) Colloid Chemistry Department, Max Planck Institute for Colloids and Interfaces, Potsdam (Golm), Germany*

Hydrothermal carbon (HTC) produced from carbohydrates and polysaccharides is providing new forms of carbon for advanced materials. On different length scales. Doping with nitrogen containing polymers and monomers provides means for tuning porosity and friability (Figure 1). Nanolatexes 20-30 nm in diameter derived from reactive ionic liquid surfactant acrylates and other co-monomers have been shown to be outstanding aqueous dispersants for nanocarbons including SWCNT, MWCNT, WC, and HTC. FE SEM suggest (Figure 2) that these nanolatexes adsorb randomly and irreversibly. This adsorption process imparts high colloidal stability to waterborne dispersions and immunizes such dispersions to salt-induced destabilization. These dispersions provide conducting inks and show promise as fuel for indirect carbon fuel cells and facile coatings for electrodes supporting electrical double layer capacitors (supercapacitors).





Wednesday, April 10, 2013 10:30 AM

Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)

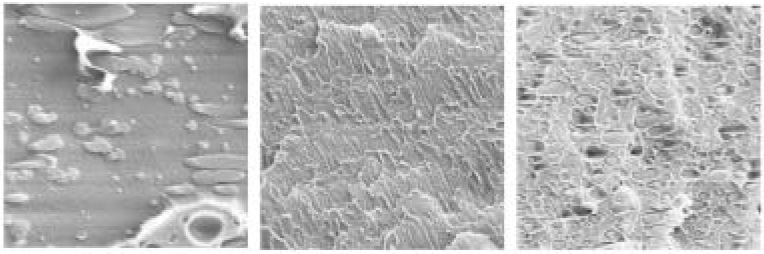
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

488 - Neutron scattering studies of renewable materials for carbon fiber fabrication

*Dilru Ratnaweera[1], Nathan Henry[1], Dipendu Saha[2], Amit Naskar[2], **Mark Dadmun**[1,2], dad@utk.edu. (1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States, (2) Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States*

The use of renewable materials as the precursor to carbon products is intriguing. For instance, lignin is generated in vast quantities as a byproduct from cellulose extraction in the paper industry as well as a byproduct of the emerging cellulosic ethanol industry. It is an amorphous, irregularly branched biopolymer that serves to bind together the cellulose fibers in all plant matter. It is reported that 70 million tons are generated annually from the paper industry, a large percentage of which is simply burned as a fuel for process heat. To improve the economy of biofuel production, new value added applications of lignin are required, such as their use in high quality carbon fibers. Unfortunately, the properties of lignin-derived carbon fiber are often weak and brittle. This talk will focus on our recent neutron scattering studies that focus on understanding the correlation of lignin source on its structure in solution and the porosity of carbon fiber that is formed from renewable and non-renewable sources, with the goal of providing fundamental information that can be used to improve the properties of lignin-derived carbon fibers. We will also discuss the examination of the structure and compatibilization of lignin-synthetic polymer blends and their use as carbon fiber precursors.



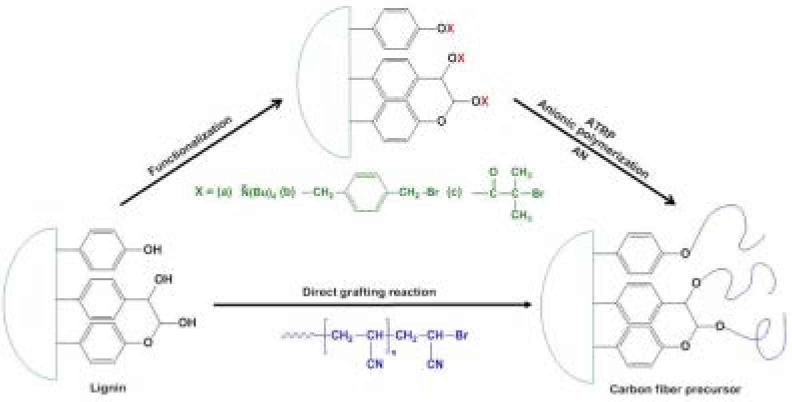
SEM micrographs of the compatibilized lignin polystyrene composite

Wednesday, April 10, 2013 11:00 AM
Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

489 - Lignin based carbon fiber precursors

__Ildoo Chung__[1,2], idchung@pusan.ac.kr, Taeyoon Kim[2], Jimmy Mays[1]. (1) Department of Chemistry, University of Tennessee at Knoxville, Knoxville, TN 37996, United States, (2) Department of Polymer Science and Engineering, Pusan National University, Busan, Republic of Korea

Although lignin is compound generally obtained from wood that will be purified in vast quantities, and utilized in applications such as high quality carbon fibers in the near future, as a carbon fiber precursor, it has failed to supply the desired properties of carbonized fiber primarily due to its low molecular weight. In this work, the molecular weight of lignin was increased through (1) chain extension reaction with inexpensive linear oligomers such as polyacrylonitrile and polybutadiene via anionic or atom transfer radical polymerizations, and (2) direct grafting reaction of polyacrylonitrile prepolymerized by ATRP onto lignin. The covalently-bonded oligomer-lignin will be enough to overcome the problems associated with lignin-oligomer incompatibility and weak filament formation of the blend formulations due to phase separation. The degree of functionalization onto lignin was characterized by ^{1}H NMR, FT-IR spectroscopies, gel permeation chromatography, and thermal analysis (TGA, DSC). The modified lignin as a carbon fiber precursor was evaluated their enhanced mechanical properties after both solution and melt-processed to meet cost-effective automotive industry requirement.



Wednesday, April 10, 2013 11:20 AM
Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

490 - Synthesis of porous carbon from renewable precursor

Dipendu Saha[1], *sahad@ornl.gov, E. Andrew Payzant*[2], *Amar S Kumbhar*[3], *Amit K Naskar*[1]. *(1) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6053, United States, (2) Chemical & Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN, United States, (3) Institute for Advanced Materials, NanoScience and Technology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States*

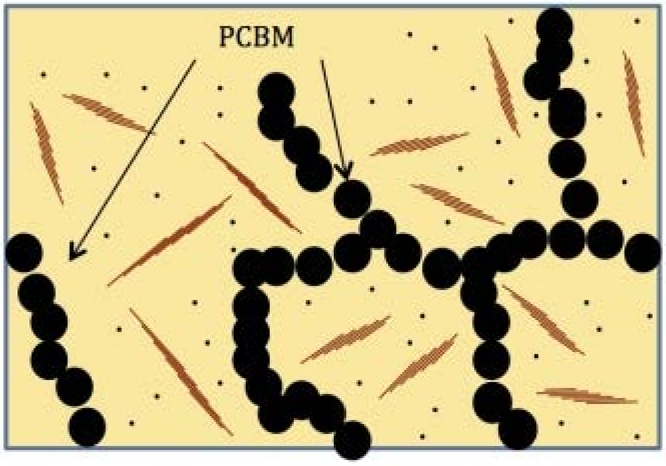
A protocol is being developed for synthesis of porous carbon from lignin and lignocellulose based precursors. Moderate to high char yield, plenty of functional groups and potential availability as a quite inexpressive precursor were the key driving forces for selecting lignocellulosic materials as the precursors of porous carbon. Our result demonstrates that this carbon possesses BET surface area within 400 m^2/g and a large mesopore volume of 0.34 cm^3/g which is twice that of micropore volume supporting the dominance of mesoporosity. Electron microscopy, including scanning and transmission electron microscopy and small-angle X-ray scattering corroborated the success of process-induced porosity in the carbon matrix. In a continuous effort, we seek to demonstrate various functional applications of this carbon. Successful utilization of such porous carbon from renewable sources provide the multiple benefits of sustainability, low-cost, and boosting the economy of industrial processes including biofuel manufacturing and pulp and paper that yield lignin as a co-product.

Wednesday, April 10, 2013 11:40 AM
Polymer Precursor-Derived Carbon (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

491 - Using neutron scattering to characterize the structure of energy harvesting polymer nanocomposites

Wen Yin[1], Huipeng Chen[1], Dilru Ratnaweera[1], Jim Browning[2], Bart Stevens[3], Jaime Grunlan[3], Jeff Peet[4], ***Mark Dadmun**[1,2]*, *dad@utk.edu. (1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States, (2) Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States, (3) Texas A&M, College Station, TX, United States, (4) Konarka, Lowell, MA 01852, United States*

Nanocomposites that are composed of conjugated polymers and carbon nanoparticles are important energy harvesting materials. For instance, the most promising organic photovoltaics consist of mixtures of conjugated polymers and modified fullerenes, particularly [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM). Similarly, recent work has demonstrated that mixtures of conjugated polymers with carbon nanotubes are promising organic thermoelectric materials. Unfortunately, detailed morphological characterization of such materials is difficult primarily due to the limited contrast between the carbon-based conjugated polymer and carbon nanoparticle using optical, x-ray- or electron-based techniques, which may lead to ambiguity in the identification of the resultant structure. Fortunately, neutron scattering provides significant contrast between the two components in these systems, providing a technique that offers access to detailed structural and morphological information. In this talk, we will report our recent progress in using neutron scattering and reflectivity to determine the miscibility, interfacial structure, and morphological characteristics of conjugated polymer-carbon nanoparticle nanocomposites. Careful data analysis provides interfacial surface area, average domain size, and phase composition. We will also discuss how the determination of these crucial morphological characteristics enables the correlation of the performance of the nanocomposite to specific controllable structural properties of the resultant nanocomposite, and provides important fundamental information that can be used to rationally design and optimize these polymer nanocomposites for energy harvesting.



Phase separated structure of P3HT and PCBM in the active layer of organic photovoltaics as determined by neutron scattering.

Wednesday, April 10, 2013 08:35 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

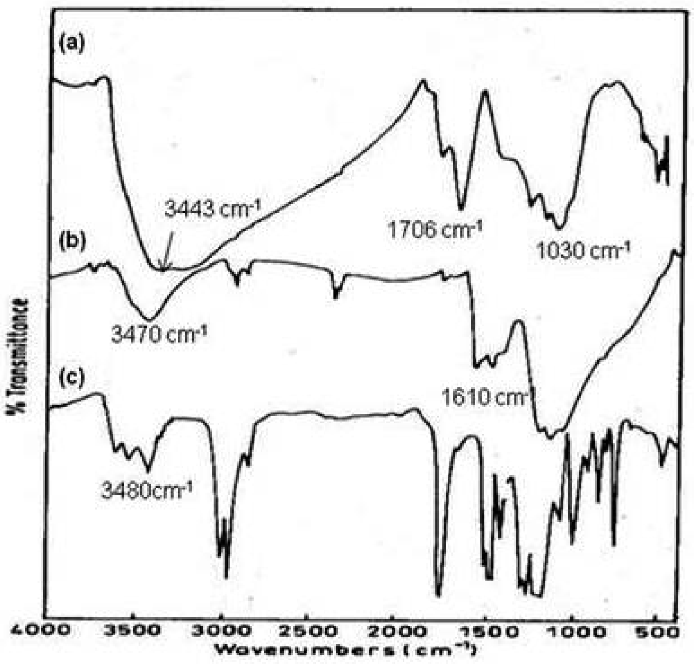
492 - Preparation and characterization of PMMA/reduced graphene oxide (RGO) nanocomposites using in situ bulk polymerization: Effect of processing method

Sandeep Nath Tripathi, *sandyiitd@yahoo.com, Veena Choudhary. Centre for Polymer Science and Engineering, Indian Institute of Technology Delhi, New delhi, Delhi 110016, India*

Abstract:

Graphene being a highly conductive material that consists of two dimensional sheets of sp^2-hybridized carbon atoms in honeycomb symmetry have attracted the attention of material scientists in various fields since its discovery in 2004 by Novoselov et al[1], due to their outstanding mechanical, thermal and electricalproperties.[2] Excellent properties and inexpensive sources (graphite) have spurred intensive interest in developing cost effective high performance polymer nanocomposites. The present study deals with the preparation and characterization of poly(methyl methacrylate) [PMMA]-reduced graphene oxide (RGO) nanocomposites. The effect of incorporation of varying amounts [i.e. ranging from 0.1-2.0 % w/w] of reduced graphene oxide (RGO) on the electrical and morphological properties of PMMA was investigated. The obtained nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR) [Figure1], scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The composite exhibited conductivities in the 10^{-9}-10^{-3} S/cm range, depending on the amounts of RGO and PMMA.

Keywords: RGO (reduced graphene oxide), PMMA, electrical conductivity.



: FTIR spectra of (a) GO (b) RGO (c) PMMA/RGO composite

References:

[1] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science*, **2006** , *306*, 666-669.

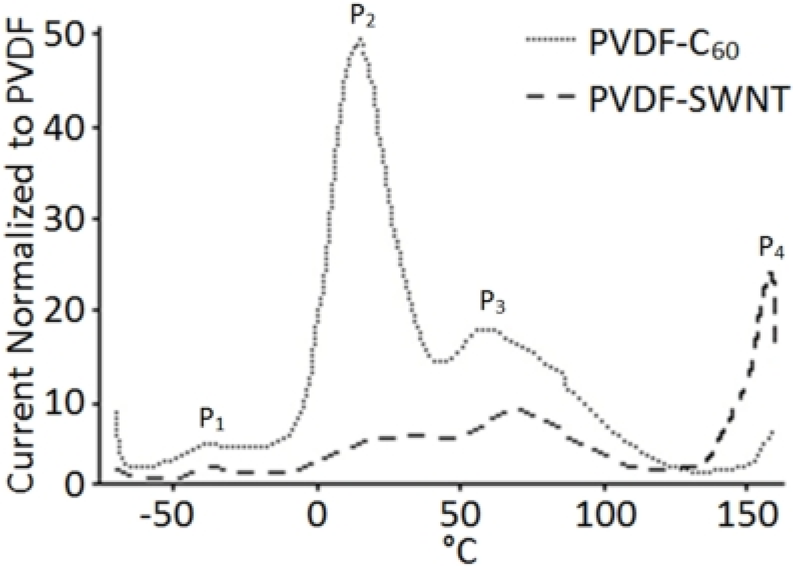
[2] Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A. *Nature*, **2006** , *442*, 282.

Wednesday, April 10, 2013 09:05 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

493 - Improved piezoelectric performance from fluoropolymer carbon nanocomposites

Cary A Baur[1], *cxb115930@utdallas.edu, Elliot McAllister*[2], *Jeffrey R DiMaio*[3], *Dennis W Smith*[1]. *(1) Department of Chemistry and The Alan G. MacDiarmid Nanotech Institute, The University of Texas at Dallas, Richardson, Texas 75080, United States, (2) Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, United States, (3) Tetramer Technologies L.L.C., Pendleton, South Carolina 29670, United States*

The piezoelectric performance of polyvinylidene fluoride (PVDF) is shown to double through the controlled incorporation of carbon nanomaterials. Specifically, PVDF composites containing carbon fullerenes (C60) and single walled nanotubes (SWNT) are fabricated over a range of compositions and optimized for their Young's modulus, dielectric constant, and d31 piezoelectric coefficient. Thermally stimulated current measurements show a large increase in internal charge and polarization in the composites over pure PVDF.



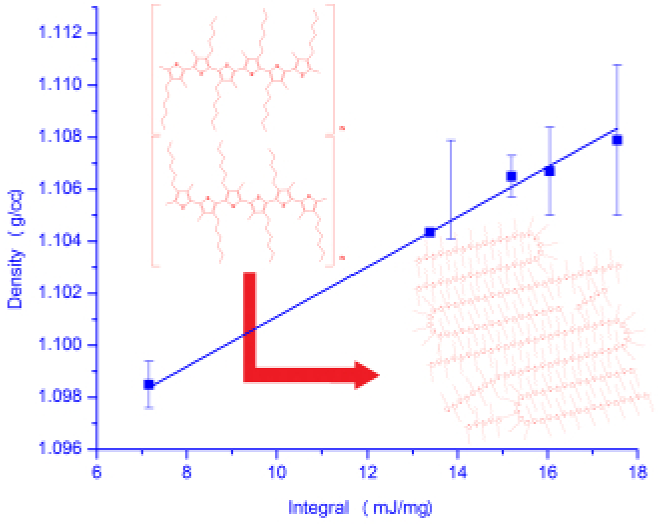
The electromechanical coupling coefficients (k31) at optimal loading levels are found to be 1.84 and 2 times greater than pure PVDF for the PVDF-C60 and PVDF-SWNT composites, respectively. Such property-enhanced nanocomposites could have significant benefit to electromechanical systems employed for structural sensing, energy scavenging, sonar, and biomedical imaging.

Wednesday, April 10, 2013 09:25 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

494 - Density and enthalpy of poly(3-hexylthiophene) crystallization

Cameron S Lee[1], *clee50@utk.edu, Mark D Dadmun*[1,2]. *(1) Department of Chemistry, University of Tennessee, Knoxville, Knoxville, Tennessee 37996, United States, (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States*

Structural and morphological control of poly(3-alkyl thiophenes) (P3ATs), and in particular the well-studied poly(3-hexyl thiophene) (P3HT), is needed to increase their favorable electronic properties. P3ATs tend to be soluble in common solvents, but many aspects of their crystallization are not well understood. Semicrystalline regioregular P3ATs order in three dimensions with conformational ordering along the backbone, p-p stacking of flat polymer chains, and lamellar stacking between chains. The exact dimensions of the crystal packing can change based on a number of variables, including molecular weight or crystallization temperature. Because of this variability, a precise evaluation of the enthalpy of fusion of an ideal crystal $(DH^{0}_{u})$for the well-studied P3HT is still debated in the literature. Using values of densities measured by pycnometery and heat of melting by differential scanning calorimetry, a value for (DH^{0}_{u}) is extrapolated from P3HT crystallized at different temperatures and times. The density of the amorphous portion of the semi-crystalline regio-regular P3HT is also determined from this analysis.



Wednesday, April 10, 2013 09:45 AM

Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)

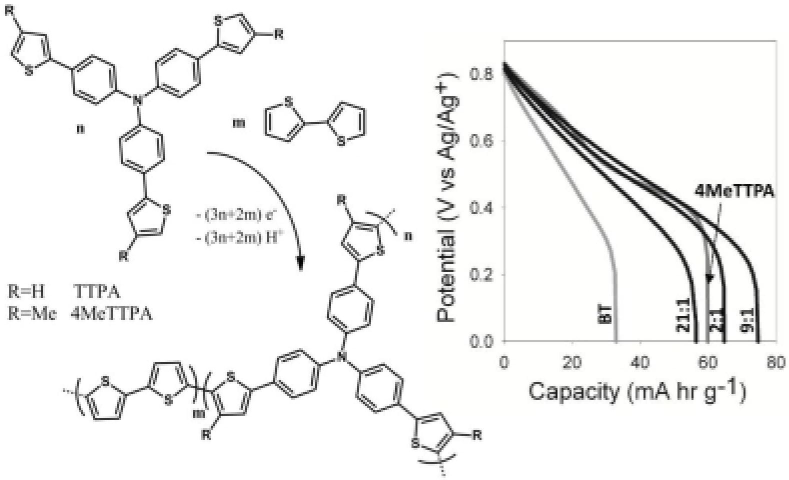
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

495 - Electrochemical synthesis of high-charge capacity triarylamine-thiophene copolymer redox electrodes

Mark E Roberts, *mrober9@clemson.edu, Jeremy T Kearns. Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29631, United States*

Advances in hybrid electric transportation and renewable energy generation require new materials and systems capable of storing and delivering energy at high rates. Inherently conducting polymers (ICPs) have attracted interest for high power and high energy electrodes; however, elaborate organic synthesis requirements has limited the range and composition of materials investigated. In this work, we show that a simple building block approach can be applied to ICP electrode design and synthesis. Efficient, reversible redox couples are incorporated into conventional ICPs to increase the energy and power density of redox electrodes. Copolymers are electrochemically synthesized using thiophene monomers and triarylamine-derivatives to vary the conjugation length of polythiophene between redox-centers. Molecular variations within each monomer are used to tailor the molecular structure and enhance charge storage capacity. Compared to the homopolymer, a factor of 2 increase in charge capacity is achieved for copolymers prepared with only 10 mole % triarylamine groups.

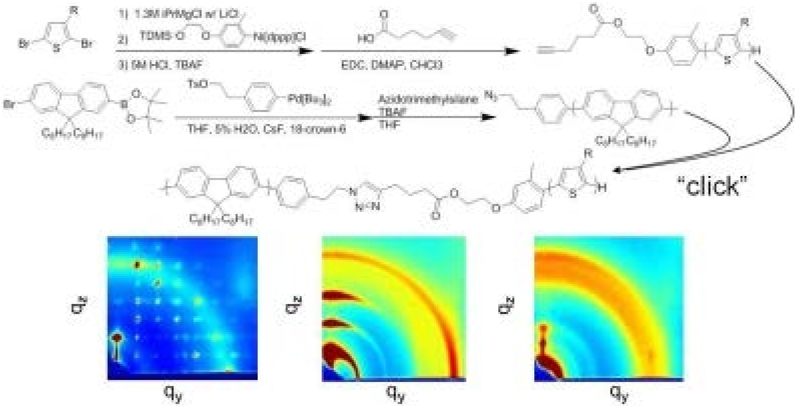


Wednesday, April 10, 2013 10:15 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

496 - All-conjugated block copolymers via functionalized catalysts and click chemistry

Kendall A. Smith[1], *kas9@rice.edu*, ***Rafael Verduzco***[1], *rafaelv@rice.edu*, *Deanna L. Pickel*[2], *Kevin Yager*[3]. *(1) Department of Chemical and Biomolecular Engineering, Rice, Houston, TX 77005-1827, United States, (2) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6494, United States, (3) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973-5000, United States*

A significant challenge in obtaining well defined all-conjugated block copolymers using a macroreagent approach is ensuring good functionality of the starting materials. We utilize functionalized catalysts to synthesize well functionalized polymers, as determined by ^{1}H NMR, MALLS, and MALDI. A series of poly(9-9dioctylfluorene) and poly(3-alkylthiophene) polymers with azide and alkyne groups are synthesized and joined using copper catalyzed azide alkyne click chemistry. Crystal structure of the resulting materials is investigated using GIWAXS and microphase segregation investigated via AFM.

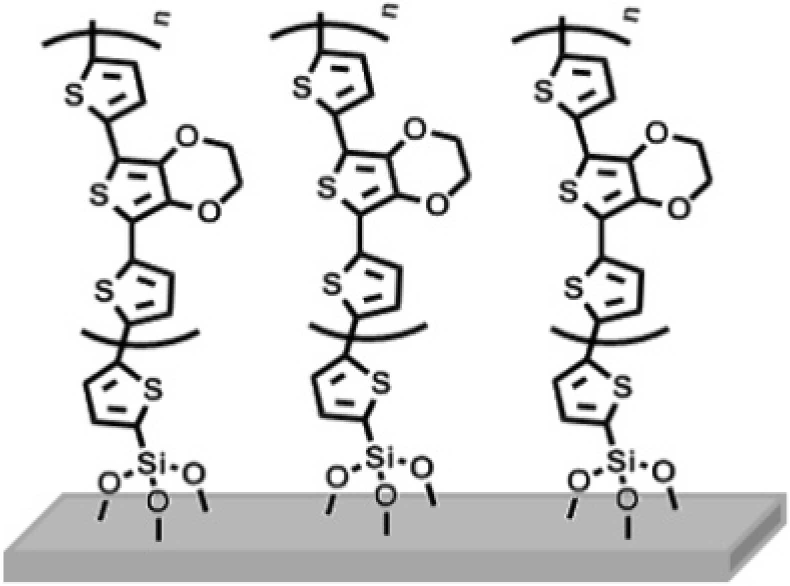


Wednesday, April 10, 2013 10:35 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

497 - Thin films of donor-acceptor type conjugated copolymers via surface-confined polymerization

__Sang Gil Youm__, syoum1@lsu.edu, Christopher R Nelson,, Evgueni E Nesterov. Department of Chemistry, Louisiana State University, Baton Rouge, LA 70808, United States

Donor-acceptor type conjugated polymers are promising materials for enhancing efficiency of organic photovoltaic devices by broadening the spectrum. Since simultaneous report by McCullough and Yokozawa on living character of Ni-catalyzed Kumada cross-coupling polymerization, this area became of broad interest. In addition to solution polymerization, intense efforts have been devoted to heterogeneous surface-confined polymerization to prepare thin films. Despite major progress in this field, to the best of our knowledge, no one has succeeded to prepare thin films of donor-acceptor type copolymers by surface-confined polymerization. In this presentation, we will outline our progress towards development of the reactive catalytic system which enables preparation of this class of conjugated polymers.

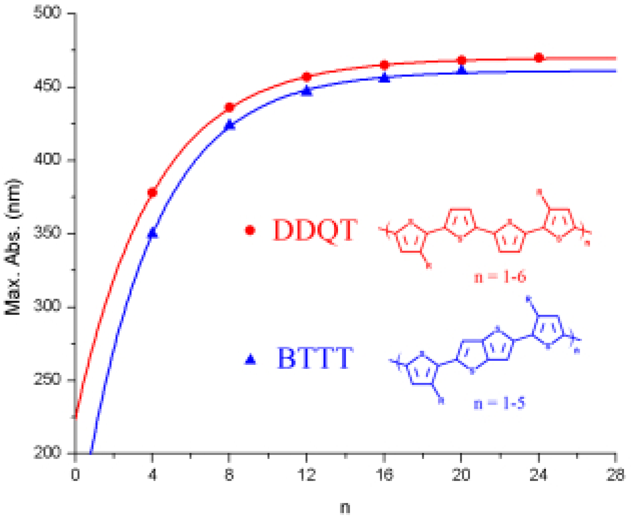


Wednesday, April 10, 2013 10:55 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

498 - Optimal oligothiophenes for modeling charge transport in polymers

Nicholas S. Colella, *nicholas.s.colella@gmail.com, Lei Zhang, James J. Watkins, Alejandro L Briseno. Department of Polymer Science & Engineering, University of Massachusetts - Amherst, Amherst, MA 01002, United States*

For oligomers to be used as representative models for their polymer analogues they must display comparable properties. On a molecular scale, optoelectronic properties in semiconducting systems are directly related to the degree of conjugation. Understanding the evolution of chain packing and conjugation length with regard to chain length is imperative to creating accurate models. Our approach has been to synthesize well-defined series of oligomers of representative polythiophenes, including 3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene (DDQT) and 2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene (BTTT), and characterize their morphological and transport properties.

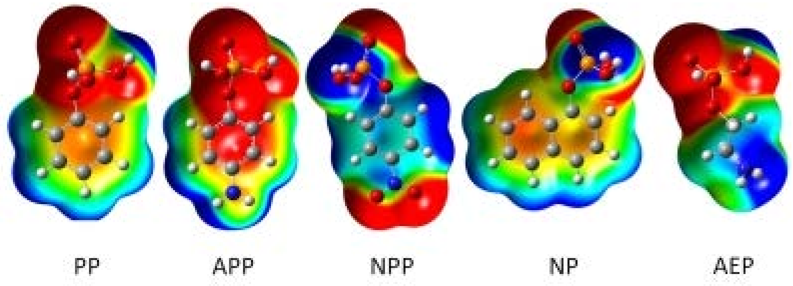


Wednesday, April 10, 2013 11:15 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

499 - Hammett correlation for design of polymer-particle dielectric interfaces

Sasidhar Siddabattuni[1], ***Thomas P Schuman***[1], *tschuman@mst.edu, Fatih Dogan*[2]. *(1) Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States, (2) Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409, United States*

Polymer-ceramic nanocomposites are promising dielectrics for electronic and power devices, which in theory combine the high dielectric constant of ceramic particles with high dielectric breakdown strength (DBS) of polymer. Self-assembled monolayers (SAM) of electron-rich or -poor organophosphate coupling groups were applied to ferroelectric nanoparticles to investigate the role of functionalized interfaces on composite behavior, in particular the leakage current and DBS. The composite films synthesized from the modified filler particles dispersed into an epoxy polymer matrix were analyzed by dielectric spectroscopy, DBS, and leakage current measurements. The analysis results indicated that significant reductions in leakage current and dielectric loss and improvement in DBS resulted only when electropositive, electron-scavenging functional groups were located at the polymer-particle interface. The electronic effect of the organophosphate SAM at the polymer-particle interface was correlated through a Hammett relationship to leakage current and DBS. The Hammett relationship indicated surface group polarity and/or electron delocalization contribution(s) affected dielectric properties. The correlation of only polarity Hammett substituent constants suggested that only polarity, i.e. the electron density of the substituent affected dielectric properties. Correlations were not observed for either combined para- or resonance-effect Hammett substituent constants. A Hammett correlation may provide useful guidance in design of interfaces to improve electrical properties and future generation electrostatic capacitors, piezo or pyroelectric devices, etc.

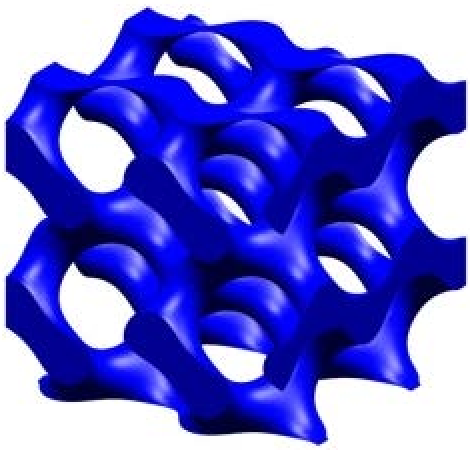


Wednesday, April 10, 2013 11:35 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (08:30 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

500 - Functional hybrid nanomaterials

Ulrich Wiesner, *ubw1@cornell.edu, Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853-1501, United States*

Solutions to global problems including energy conversion and storage, clean water and human health require increasingly complex, multicompoment hybrid materials with unprecedented control at the nanoscale. This talk will give examples for the synthesis and characterization of hybrids based on the assembly of organic macromolecules with inorganic, solid-state type materials. The aim of the described work is to understand the underlying fundamental chemical, thermodynamic and kinetic formation principles enabling generalization of results over a wider class of materials systems.

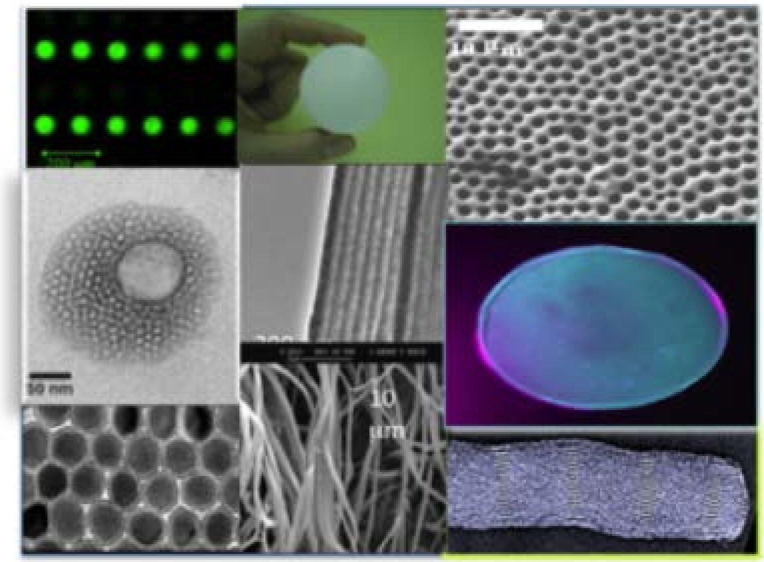


Wednesday, April 10, 2013 01:30 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

501 - Integrative approaches to nanostructured and hierarchically structured materials

Clement Sanchez, *clement.sanchez@college-de-france.fr, Laboratoire de Chimie de la Matière Condensée de Paris, College de France and University of PARIS VI, PARIS, FRANCE 75231, France*

Hierarchical organic-inorganic materials are increasingly taking their position in the free spaces left between inorganic chemistry, polymer chemistry, organic chemistry, and biology. The controlled design of hybrid organic-inorganic interfaces allows the construction of materials presenting complex hierarchical structures; a particularly interesting challenge for the materials chemists. In particular, the integration between the ''chimie douce” driven sol-gel processing'' and ''soft matter'' is a strong success as both can interact without disrupting their own function. These new approaches where chemistry is strongly coupled with processing have been coined “Integrative Chemistry”. They provide the ability to scissor condensed matter at several length scales where final materials and systems will be macroscopically shaped one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D). We will present the main approaches we are developing for multiscale texturation of inorganic and hybrid materials: Nanocasting, cooperative self-assembly (molecular and polymeric surfactants), multiple templating with bigger static (latex, etc) or dynamic templates (breath figures), organogelators templating, ... Moreover the use of all this various templating strategies combined with chimie douce and smart processing methods such as multilayers deposition, aerosols, ink jet printing, electrospinning, foaming, led in the past years to an amazing mushrooming of new hierarchical functional materials with many interesting properties. Some of these materials will be presented.



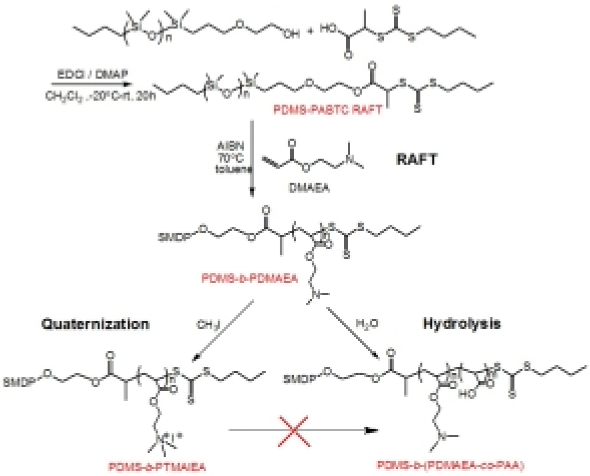
Wednesday, April 10, 2013 02:00 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

502 - Synthesis of poly(dimethylsiloxane)-containing amphiphilic block copolymers via RAFT

Wei Zhao[1], *zhaowei@chem.usyd.edu.au, Pierre Fonsny*[2], *Paul FitzGerald*[1], *Sébastien Perrier*[1]. *(1) Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia, (2) Colgate-Palmolive Pty Ltd, Sydney, NSW 2000, Australia*

In this study, three novel and well-defined amphiphilic (pH-responsive) block copolymers with poly(dimethylsiloxane) (PDMS) as hydrophobic blocks and poly(2-(dimethylamino)ethyl acrylate) (PDMAEA) or its derivatives as hydrophilic blocks were synthesized by the combination of reversible addition-fragmentation chain transfer (RAFT) polymerization, hydrolysis and quaternization reactions as shown in Scheme 1.

Scheme 1 . Polymerization, quaternization and hydrolysis of PDMAEA

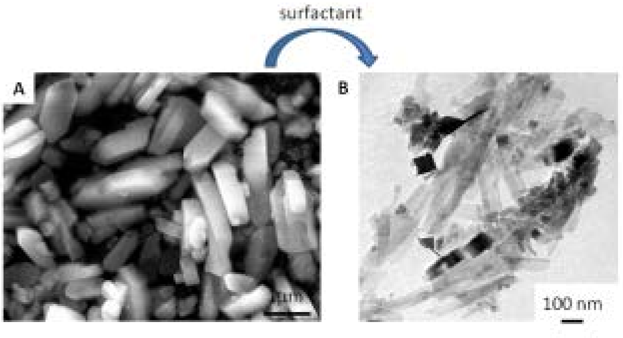


Wednesday, April 10, 2013 02:30 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

503 - Surfactant-templated hydrothermal synthesis of high surface area $LiMnPO_4$

Nicola K Huesing, *nicola.huesing@sbg.ac.at, Qian Liu, Juergen Schoiber. Materials Chemistry, Paris Lodron University Salzburg, Salzburg, Austria*

Olivine $LiMPO_4$ (especially Fe and Mn) is of high interest as cathode in lithium ion batteries because of its high theoretical capacity (170 mAh/g), safety, low cost and the abundance in nature. The intrinsic drawback of $LiMPO_4$ such as its poor electric and ionic conductivity can be overcome by synthesizing nanoscale materials. In the present work, nano crystalline $LiMnPO_4$has been successfully synthesized by a templating approach.



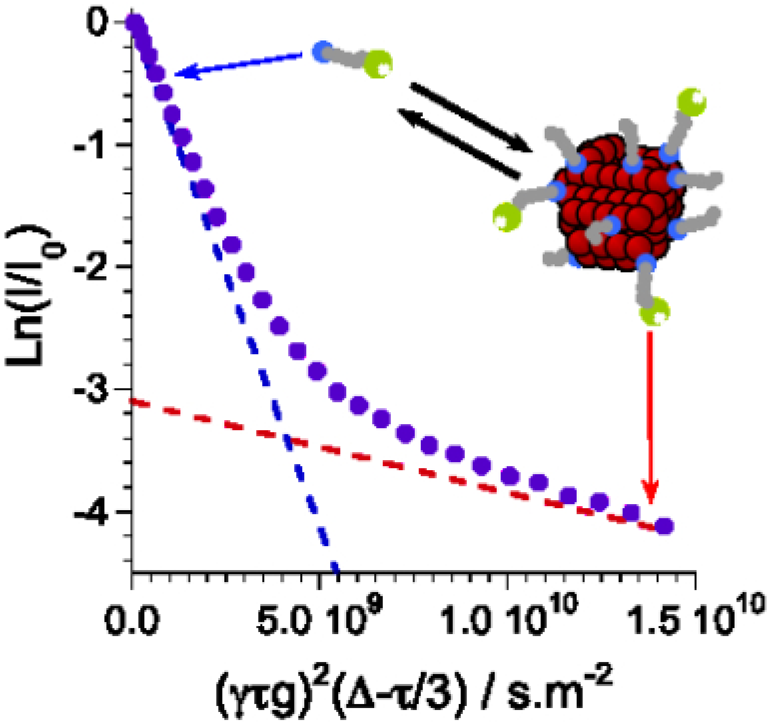
The effect of the surfactant on the resulting $LiMnPO_4$ crystals and a mechanistic model - named as manganese-induced surfactant-templating (MIST) mechanism - will be presented.

Wednesday, April 10, 2013 03:05 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

504 - Probing the functionalization of nano-objects with DOSY NMR

Francois Ribot, *francois.ribot@upmc.fr, CMCP (UMR 7574), UPMC / CNRS / College de France, Paris, France*

Probing in solution or suspension the functionalization of nano-objects such as oxo-clusters or nanoparticles is not a simple task. Pulsed gradient spin echo (PGSE) NMR and diffusion ordered spectroscopy (DOSY), its 2D representation, which allow one to measure the diffusion coefficients of the various components of a mixture can be used to prove if a molecule remains free or interacts with the surface of nano-objects. Various examples will be presented to illustrate this strategy.

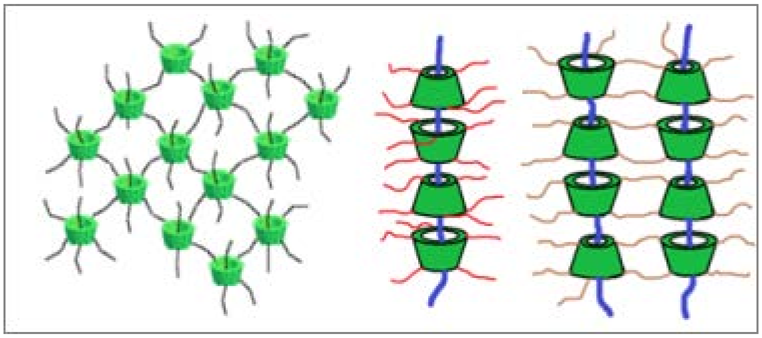


Wednesday, April 10, 2013 03:35 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

505 - Orthogonal polymer networks from cyclodextrins

Gaumani Gyanwali, *gaumani@okstate.edu, Mathis Hodge, Jeffery L White. Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States*

We developed simple, inexpensive, and easy purification methods to functionalize cyclodextrins and to create composite polymer networks and 'bottle brush' structures. Host-guest chemistry was used to prepare cyclodextrin-polymer inclusion complexes which were then functionalized to get the desired products. These hydrophobic networks have unique solution and swelling properties, and can be made into thin films. These materials can potentially be used in polymer chemistry for sequestration of particles and as free-volume modifiers or compatibilizers.

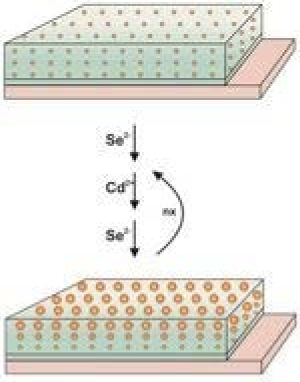


Wednesday, April 10, 2013 04:05 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

506 - Seeded growth approach to fabrication of hybrid materials

Bradley J. Holliday, *bholliday@cm.utexas.edu, Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, TX 78712, United States*

Hybrid materials with nanostructured organic and/or inorganic components have been of great interest in photovolatics, sensors, light-emitting diodes, and molecular electronics due to their unique electronic properties. Strategies to construct these materials with precise control over the composition, distribution, and relative density of the functional components are vigorously being sought to expand the practical utility of this class of materials. We have developed a unique approach to use conducting metallopolymers as active scaffolds within which we can fabricate hybrid nanocomposites.

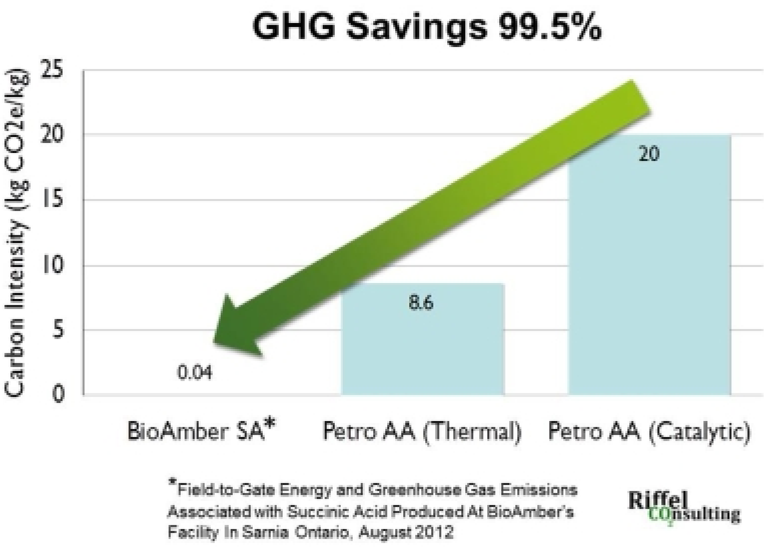


Wednesday, April 10, 2013 04:25 PM
Hybrid Materials (01:30 PM - 04:45 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

507 - Bio succinic acid for renewable polymers: Enabling sustainable new products with performance inspired by nature

***Tara Mullen**, tara.mullen@bio-amber.com, BioAmber, Inc., Plymouth, MN 55447, United States*

Succinic Acid has emerged as one of the most competitive of the new bio-based chemicals. As a platform chemical, bio based succinic acid has a wide range of diverse applications, including food and flavor, solvents, and personal care. Additionally, bio succinic acid has application in renewable polymer systems including polyurethane elastomers, coatings, adhesives and sealants, polyesters and plasticizers. Bio Succinic acid is also a building block for large volume chemical intermediates such as 1, 4-butanediol. A key advantage of bio based succinic acid is the differentiated performance that it enables, in addition to its positive environmental profile compared to petroleum based succinic and adipic acids.



Wednesday, April 10, 2013 01:30 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

508 - Plastics from plants: Using metal catalysts to make sustainable polymers

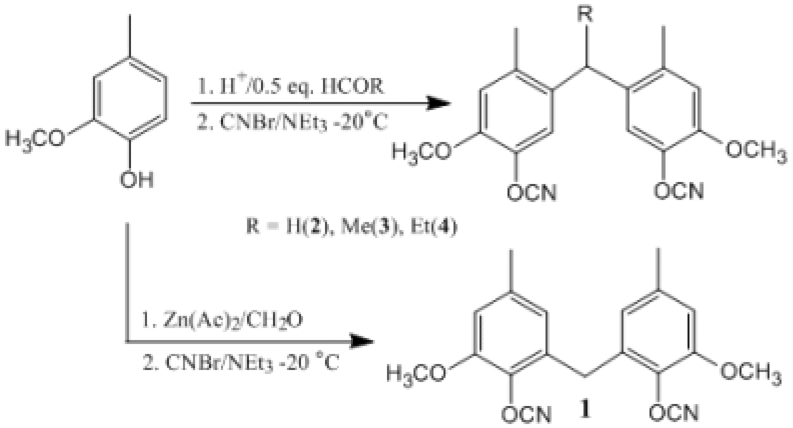
William B Tolman, *wtolman@umn.edu, Marc A Hillmyer. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States*

As replacements for petroleum-based plastics, environmentally-friendly polymeric materials derived from biorenewable feedstocks hold great promise as scientists seek to implement green chemistry practices for sustainable technological development. The widespread implementation of biorenewable polymers will require knowledge of the chemistry involved in converting the molecules (natural or engineered) provided by plants into compounds that can readily be converted to new and useful polymeric materials. We address this goal under the rubric of the University of Minnesota Center for Sustainable Polymers, an NSF Phase 1 Center for Chemical Innovation. Interdisciplinary approaches will be described that involve integrated chemical synthesis and structural definition of new monomers, catalysts, and polymers, mechanistic studies of polymerization catalysis, and characterization of the properties of new and useful multiblock polymeric materials.

Wednesday, April 10, 2013 02:00 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

509 - Renewable high temperature cyanate ester resins synthesized from lignin derived phenols

Benjamin G. Harvey[1], *benjamin.g.harvey@navy.mil, Heather A Meylemans*[1], *Josiah T Reams*[2], *Andrew J Guenthner*[2], *Lee R Cambrea*[1], *Thomas J. Groshens*[1], *Lawrence C Baldwin*[1], *Michael D. Garrison*[1], *Joseph M. Mabry*[2]. *(1) Research Department, Chemistry Division, China Lake Naval Air Warfare Center, China Lake, CA 93555, United States, (2) Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, CA 93524, United States*



Renewable cyanate ester resins have been prepared from bisphenols generated by condensation of 2-methoxy-4-methylphenol (creosol) with formaldehyde, acetaldehyde, and propionaldehyde. These materials have glass transition temperatures of ~250 °C, thermal stabilities up to 400 °C, water uptake in the range of 2.05-3.21%, and wet T_g's from 174-193 °C. The structural differences between resins significantly impact cure behavior, T_g, and thermal stability. The properties of the resins, coupled with the potential to recycle the thermosets, make creosol-based resins compelling precursors to high performance composites.

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Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

510 - Partially renewable poly(butylene terephthalate)-based copolyesters prepared by solid state polycondensation with unique morphologies and properties

***Erik Gubbels**[1], e.gubbels@tue.nl, Lidia Jasinska-Walc[1,3], Bart A.J. Noordover[1], Daniel Hermida Merino[1,2], Johannes G.P. Goossens[1], Cor E. Koning[1]. (1) Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands, (2) European Synchrotron Radiation Facility, Grenoble, France, (3) Department of Polymer Technology, Gdansk University of Technology, Gdansk, Poland*

Poly(butylene terephthalate) (PBT) is a useful polyester but has properties that could be enhanced, such as its T_g or its impact resistance. This can be done by introducing comonomers during melt copolymerization (M-PC) or by solid state polycondensation (SS-PC). Using SS-PC it is possible to obtain PBT-based copolyesters without losing the crystalline features. These copolyesters would have unique morphologies which are not attainable with M-PC.

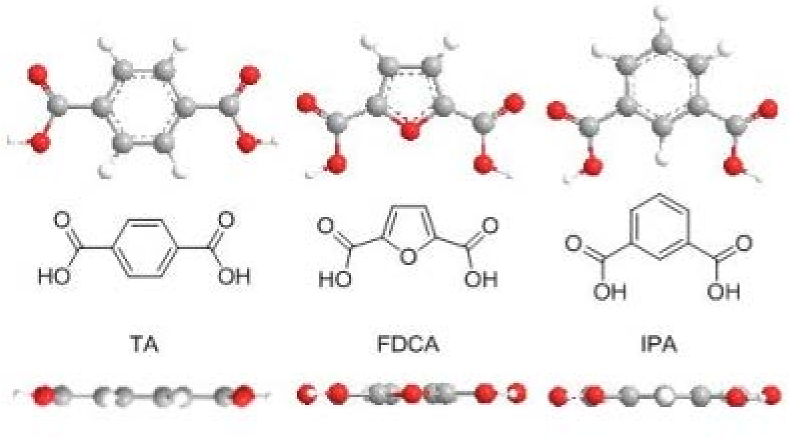
A fatty acid dimer diol (FADD) was incorporated into the PBT backbone using SS-PC and M-PC, and the copolyesters were fully characterized. It was shown using ^{13}C-NMR that the copolyesters prepared by SS-PC have a much more blocky molecular architecture compared to the copolyesters prepared by M-PC. This is a result of the larger extent of phase separation between the PBT matrix and the FADD that was retained during SS-PC process compared to the M-PC reaction. These results are reflected in the significant difference in the thermal properties. The materials prepared using SS-PC showed a higher T_m, T_c and crystallization rate compared to the M-PC prepared materials. The materials prepared with SS-PC can be brought into the melt in the presence of good transesterification catalysts for 300 minutes without the loss of these properties. Hence, the materials should be stable during melt processing. Thus by using phase separation and SS-PC it is possible to prepare PBT-based copolyesters with unique properties and with the crystalline features of PBT.

Wednesday, April 10, 2013 02:50 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

511 - Biobased polyesters comprising rigid, carbohydrate based, building blocks

Jacco van Haveren, *jacco.vanhaveren@wur.nl, Department of Biobased Products, Wageningen University & Research Centre, Wageningen, Gelderland 6700 AA, The Netherlands*

Developing biobased polymers with high thermal stability and mechanical strength is one of the main challenges in order to realise a more biobased chemical and polymer industry. Isohexide and furan based monomers are building blocks that potentially can replace petrochemical based monomers like terephthalic acid or isophthalic acid.



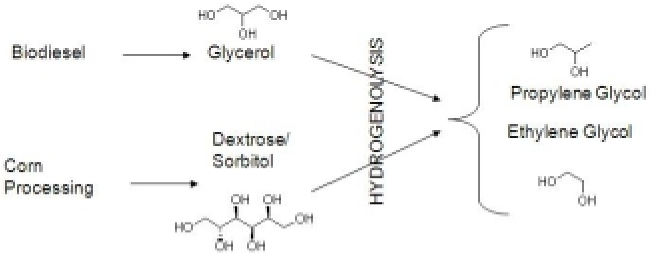
Combined with other renewable building blocks, they result in thermally stable biobased polymers. Synthetic routes towards isohexide derivatives as well as furan derivatives will be described, including a novel method for the production of isoidide and furandicarboxylic acids. Step growth polycondensation chemistry results in both moderate molecular weight and high molecular weight polymers. The potential application of these polymers in powder coatings systems or bottles will be presented.

Wednesday, April 10, 2013 03:25 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

512 - Potential opportunities for renewable building blocks

***Todd A. Werpy**, todd.werpy@adm.com, Archer Daniels Midland, Decatur, IL 62521, United States*

The U.S. chemical industry has undergone significant change in the past two decades. Many companies have moved production off shore to be closer to the raw material supply. New opportunities exist for producing chemical from domestic renewable resources. Archer Daniels Midland has made a strong commitment to the development of new technologies and chemicals for commercial production from agricultural resources. ADM's strength is derived from its integrated sourcing, transporting, processing, transforming and distribution networks. This presentation will discuss the opportunities, challenges and commercial efforts being undertaken by ADM to expand its portfolio in the chemical market segment. The role of chemicals from renewable materials in the revitalizing the U.S. chemical industry will also be discussed.

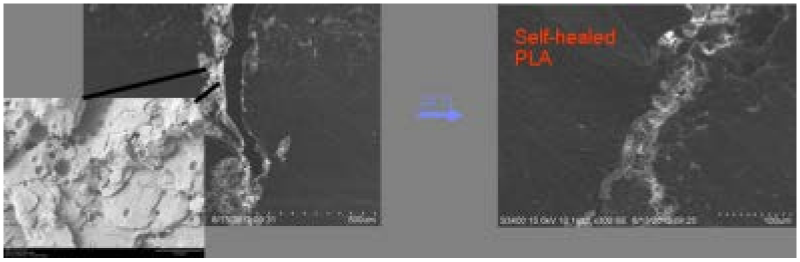


Wednesday, April 10, 2013 03:55 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

513 - Development of renewable polymers for durable applications

Dylan J Boday[1], *dboday@us.ibm.com*, *Joseph P Kuczynski*[2], *Jason T Wertz*[3], *Timothy C Mauldin*[1]. *(1) IBM, Tucson, AZ, United States, (2) IBM, Rochester, MN, United States, (3) IBM, Poughkeepsie, NY, United States*

The use of synthetic polymers from petroleum sources are widespread and can be found in nearly every item we use in our daily lives. There is a growing shift to prepare polymeric materials from renewable sources as petroleum is a finite resource. However, the use of these renewable polymers in applications from disposable materials to durable goods have significant challenges to overcome in order to find wide spread use. Here, we will present an overview of our renewable polymers research efforts for durable good applications. Specific development efforts will consist of renewable fillers, self-healing renewable systems and flame retardant polymers containing renewable content.

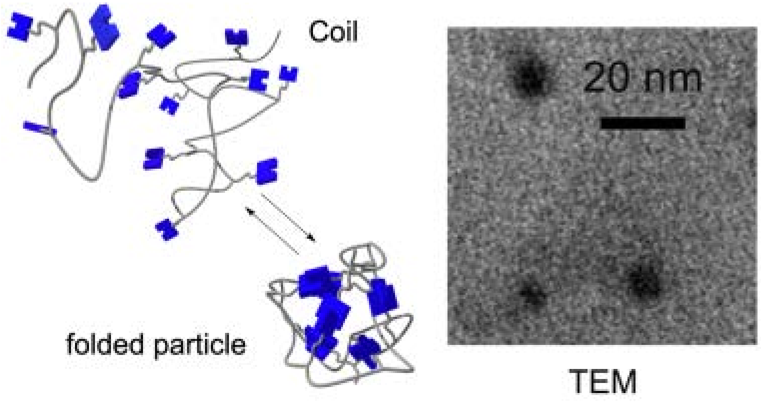


Wednesday, April 10, 2013 04:25 PM
Natural and Renewable Polymers (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

514 - Strategies for folding and unfolding polymer chains via dynamic intra-chain cross-links: Synthesis and characterization

Erik B Berda, *erik.berda@unh.edu, Bryan T Tuten, Danming Chao, Christopher K Lyon. Department of Chemistry and Materials Science Program, University of New Hampshire, Durham, NH 03824, United States*

Recent efforts by our lab to fold single polymer chains into nano-structured particles will be discussed. Specifically, we will highlight the use of SEC with multiple modes of detection as a reliable method to measure the change in solution conformation of polymer chains when folded via intra-chain interactions. The ability to unfold and refold these structures by utilizing dynamic covalent interactions will also be discussed.



Wednesday, April 10, 2013 01:30 PM

General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)

Location: Hilton Riverside

Room: Ste. D, Sec 19

515 - Kinetic study of epoxy resin cure with amines: Quantitative analysis methodology

Sang Ha Son, *son1@purdue.edu, James M Caruthers. School of Chemical Engineering, Purdue University, West Lafayette, IN 47906, United States*

A quantitative FTIR peak deconvolution method has been developed and was used to study the epoxy amine curing reaction. Density Functional Theory calculation of frequency data was utilized for the peak assignment. Various peaks in different wavenumber regions representing the same chemical species were analyzed to obtain the concentration profiles and compared with each other as a consistency check for the deconvolution method. The concentration profiles from FTIR method were validated by HPLC.

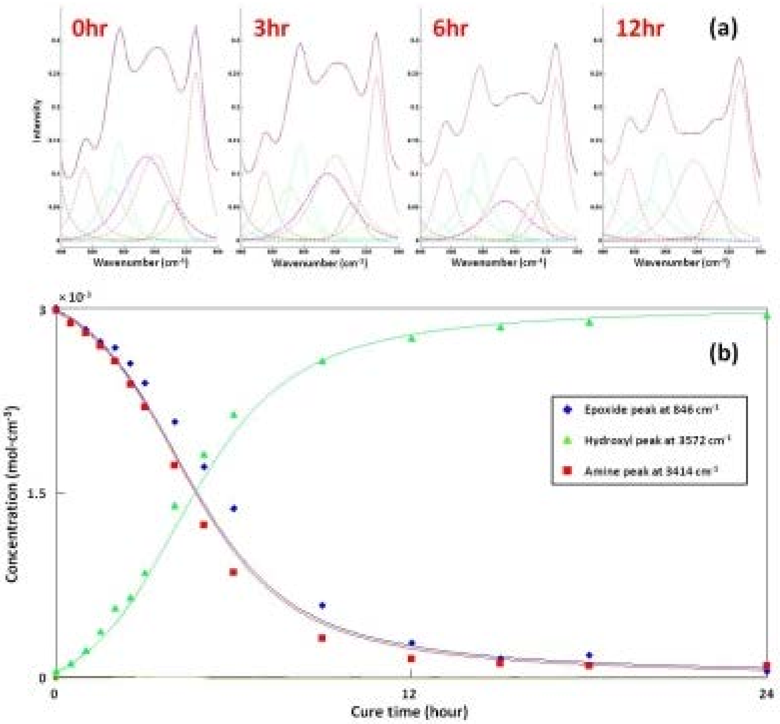


Figure 1. (a) Epoxide peak deconvolution and (b) Concentration profiles

Wednesday, April 10, 2013 01:50 PM

General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)

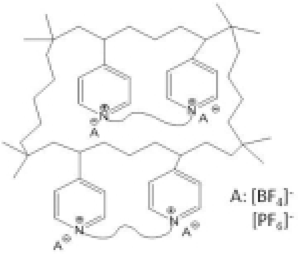
Location: Hilton Riverside

Room: Ste. D, Sec 19

516 - Ionic liquid colloids (ILC) based on polymeric microgel: Synthesis and characterizations

***Nurettin Sahiner**[1,2], sahiner71@gmail.com, Tugce Turhan[2,3], L Andrew Lyon[4]. (1) Department of Chemistry, Canakkale Onsekiz Mart University, Canakkale, Turkey, (2) Nanoscience and Technology Research and Application Center (NTRAC), Canakkale Onsekiz Mart University, Canakkale, Turkey, (3) Department of Chemical Engineering, Istanbul Technical University, Maslak, Istanbul 34469, Turkey, (4) Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, United States*

Ionic liquid particle based on p(4-Vinyl pyridine) (p(4-VP) and p(N-vinylimidazole) (P(VI)) were prepared after chemical modification of the corresponding colloidal particles. P(4-VP) and p(VI) particles were prepared by microemulsion polymerization method using SDS as surfactants. The prepared particle were reacted with dibromide containing alkanes such 1,4- dibromobutane, 1,6-dibromo hexane, and 1,8-dibromo octane to quaternize p(4-VP) and p(VI) particles to generate dicationic linkage. The particles characterization such as size, structure and thermal behaviors were investigated using DLS, SEM, FT-IR and TGA analysis before and after the chemical modifications. The ionic liquid colloidal particles were formed by exchange of anions by ionic liquid forming anions such as tetrafluoroborate and hexafluorophosphate acetonitrile and in water at room temperature. The quaternized particles were further investigated for potential environmental applications and in catalysis.



P(4-VP) ionic liquid colloids.

Wednesday, April 10, 2013 02:10 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

517 - Improvement of polymer dielectric materials

***Mark D Hindenlang**, mark.hindenlang.ctr@mail.mil, Daniel B Knorr, Joseph L Lenhart. Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States*

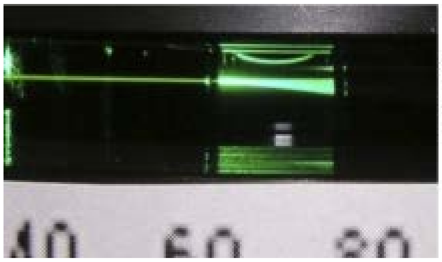
Polymer dielectric materials find utility in a myriad of applications such as in capacitors, structural capacitors, electromechanical transducers, insulation layers, device packaging, and in the semiconductor industry as passivation and interlayer dielectrics. For applications involving capacitors, energy storage density depends on both the dielectric constant and on the dielectric strength, with most research efforts toward the improvement in energy density focusing on dielectric constant manipulation. This presentation will highlight work in this area conducted at the US Army Research Laboratory, which has focused on investigating energy storage performance in terms of both the dielectric constant and dielectric strength of polymeric materials in the presence of various small molecule dopants. Specifically, dielectric strength, dielectric loss, and synchrotron-based techniques XPS (X-ray photoelectron spectroscopy) and NEXAFS (near-edge X-ray absorption fine structure) were used to characterize systems. Change in performance is discussed in light of various models of breakdown behavior and molecular modeling.

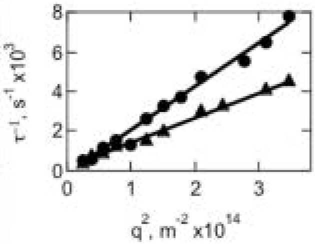
Wednesday, April 10, 2013 02:30 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

518 - Mimicking thermal lensing in dynamic light scattering

Kathryn N Moon, *kathryn.moon@huskymail.uconn.edu*, *Thomas A P Seery. Institute of Materials Science, Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United States*

Thermal lensing caused by solution heating during dynamic light scattering observations of light absorbing solutions alters the experimental geometry. In order to separate thermal lensing from other heating related effects lenses were used to defocus the laser in studies of non-absorbing solutions of carboxylated polystyrene microspheres. Solutions of microspheres in deionized water were prepared by dilution and filtration of microsphere standards from 110 nm to 850 nm in diameter. Polystyrene (2 x 10^6 Da) in toluene was also studied. The lens was placed in front of the refractive index matching bath to defocus the beam before it reached the sample. The change in geometry introduced by the addition of a lens in the optical train was apparent from a change in slope of inverse relaxation time plotted against the square of the scattering vector. Results can be interpreted as a change in apparent diffusion coefficient.





Wednesday, April 10, 2013 02:50 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
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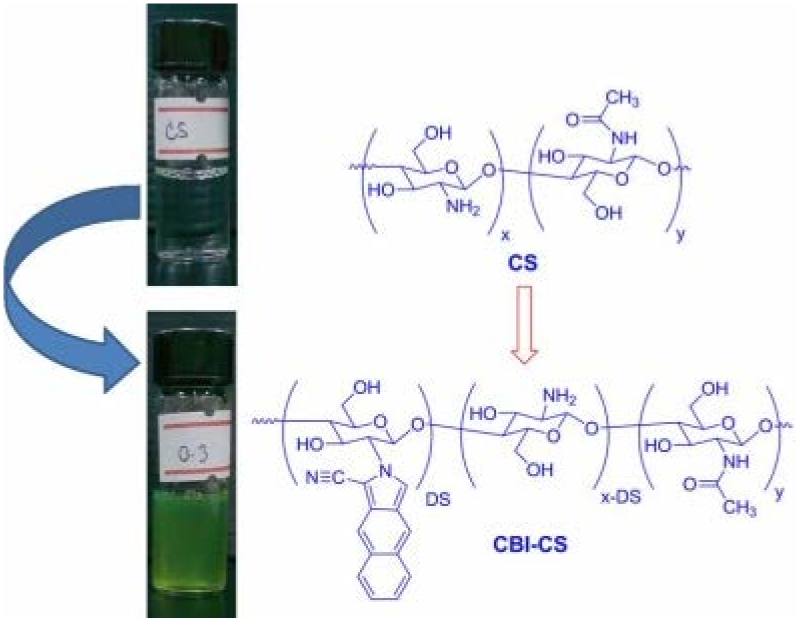
519 - Bioimaging application of novel fluorescent chitosan: Synthesis and characterization

Warayuth Sajomsang, *warayuth@nanotec.or.th, Pattarapond Gonil, Preyawit Na Ubon, Uracha Raktanonchai. National Nanotechnology Center, Klong Luang, Pathumthani 12120, Thailand*

Novel fluorescent chitosan (CS) with different the degrees of N-substitution (DSs) were carried out by reacting chitosan with naphthalene-2,3-dicarboxaldehyde (NDA) in the presence of cyanide ion under mild acidic condition. The reaction of NDA and a primary amino groups of chitosan results in the formation N-substituted 1-cyanobenz[f]isoindole derivatives which have significantly improved quantum efficiencies compared to chitosan fluorescein-5-isothiocyanate. The quantum yield of novel fluorescent chitosan was higher than chitosan fluorescein-5-isothiocyanate 25-flold in 1% (v/v) acetic acid. Since the quantum yield depended on DS and molecular weight of chitosan, therefore, quantum yield was decreased when DS was higher than 10% due to reduction of polymer solubility in 1% (v/v) acetic acid while low molecular weight of chitosan showed higher quantum yield than high molecular weight of chitosan. It is possible that application of novel fluorescent chitosan can be used as a bioimaging agent.



Wednesday, April 10, 2013 03:10 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
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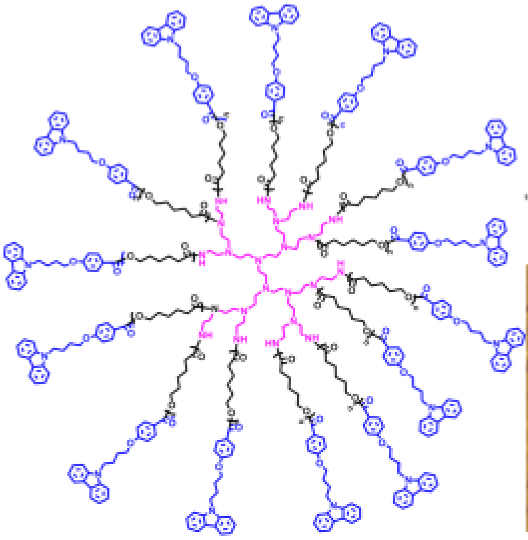
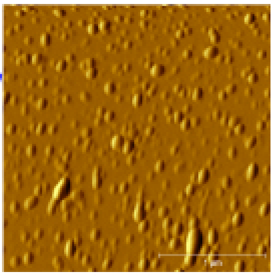
520 - Synthesis and electropolymerization of a star copolymer with peripheral carbazoles

***Pengfei Cao**, caopengfei686@gmail.com, Rigoberto Advincula. Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States*

An electropolymerizable star-like copolymer was afforded by utilizing a hyperbranched cored ring-opening polymerization of e-caprolactone (CL) with extended carbazole peripheral groups. Different arm lengths were obtained based on different degrees of polymerization (DP_n) from the polyethyleneimine (PEI) core, in which complete peripheral functionalization with carbazole groups was observed. This was confirmed by ^1H NMR, FT-IR, SEC, Fluorescence spectroscopy, and UV-Vis spectra quantitative characterization. Atomic force microscopy (AFM) imaging showed two distinct particle aggregation characteristics, before and after functionalization with carbazole groups. Cyclic voltammetry (CV) was also employed to investigate electrochemical cross-linking properties of the star-like copolymers. The obtained polymeric films were further studied by UV-vis spectroscopy and AFM. Results indicated that conformational freedom of the electroactive peripheral functional groups can be controlled by the DP_n or size of the PEI core. Moreover, an interesting “loop effect” together with solid state polymerization is observed.





Wednesday, April 10, 2013 03:30 PM

General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)

Location: Hilton Riverside

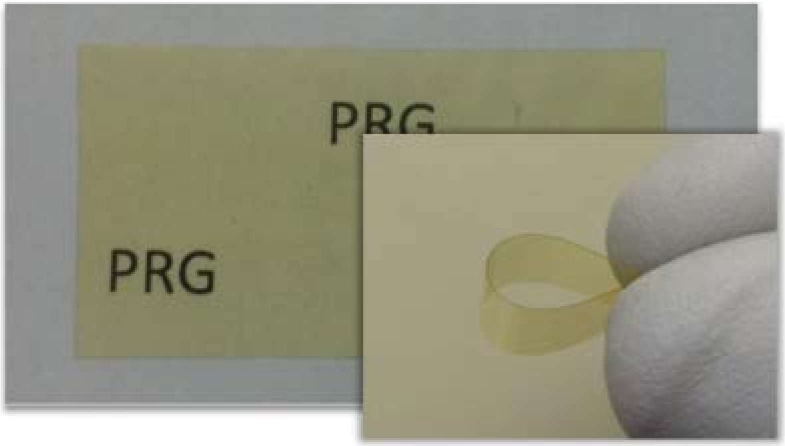
Room: Ste. D, Sec 19

521 - Tailorability of bisphenol-based polybenzoxazines

Austin D Baranek, *austinbaranek@yahoo.com, Laken L Kendrick, Jananee Narayanan, Ginger E Tyson, Steven Wand, Derek L Patton. Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States*

Polybenzoxazines (pBZ) have been investigated as attractive alternatives to traditional phenolic resins for a variety of high performance applications. However, it is observed that the majority of bisphenol-based pBZ consist of short cores resulting in highly cross-linked, but extremely brittle materials. Additives and blends (i.e. rubber toughening) have been used to improve the mechanical strength; however, for material simplicity, it would be advantageous to incorporate the flexibility directly into the pBZ network via monomer design.

This project investigates unexplored molecular design opportunities that are available by incorporating long aliphatic cores into the bisphenol, from which BZ can be easily synthesized and purified. In this study, a series of aliphatic-bridged bisphenol-based pBZ are studied to demonstrate the viability of tailoring the mechanical properties of diphenol-based pBZ networks through monomer design. Additional tailorability is also explored through the copolymerizations of the synthesized monomers (flexible and low T_g) with commercially available BZ monomers (brittle and high T_g) showing predictable properties further expand the tailorability of bisphenol-based pBZ systems.



Wednesday, April 10, 2013 03:50 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
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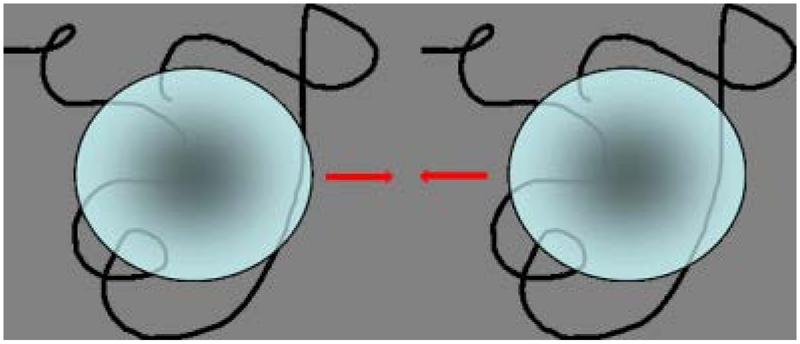
522 - Mutual macromolecular crowding in polymer solutions

Mary K Cowman, *mcowman@poly.edu, Chemical & Biomolecular Engineering, Polytechnic Institute of New York University, Brooklyn, NY 11201, United States*

Ogston and Laurent provided a theory for steric exclusion of spherical particles by a suspension of randomly oriented fibers or polymers. The spheres are excluded from cylindrical shells surrounding the linear polymers. Crowding depends on concentration of the polymer segments, but not polymer molecular mass. Matsuoka and Cowman developed a semi-empirical expression to explain molecular mass-dependent physicochemical properties of polymer solutions. The Matsuoka-Cowman equation has now been derived from steric exclusion due to mutual crowding of polymer hydrodynamic volumes.

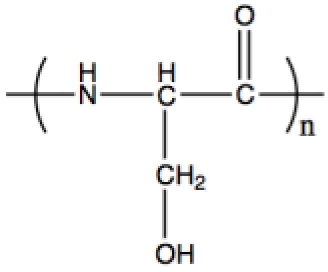


Wednesday, April 10, 2013 04:10 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

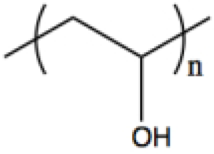
523 - Synthesis and application of poly(4-vinylimidazole) block copolymers

Chetan C Hire[1], *chetan.hire@uconn.edu*, *Ashley Santiago*[2], *Andrew J Oyer*[1], *Douglas H Adamson*[1]. *(1) Institute of Material Science, University of Connecticut, Storrs, Connecticut 06269, United States, (2) Department of Chemistry, California State Polytechnic University, Pomona, California 91768, United States*

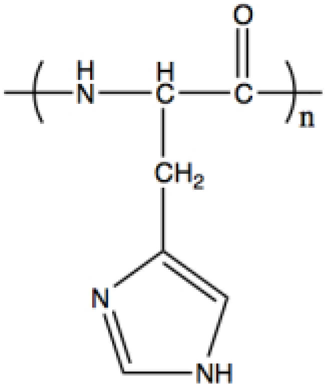
We present the first example of poly(4-vinylimidazole) block copolymers using a RAFT polymerization method. Lack of a controlled polymerization method for 4-vinylimidazole (4VIm) has prevented the successful synthesis of its block copolymers until Long *et.al.* recently synthesized poly(4VIm) homopolymer by a controlled radical method. Here we describe the synthesis of poly(vinyl alcohol-*b*-4VIm) and explore its role in biosilicification as well as its application as a poly(ionic liquid).



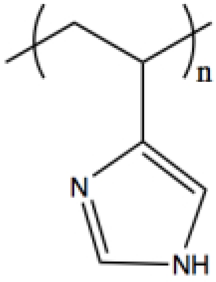
Poly(serine)



Poly(vinyl alcohol)



Poly(histidine)



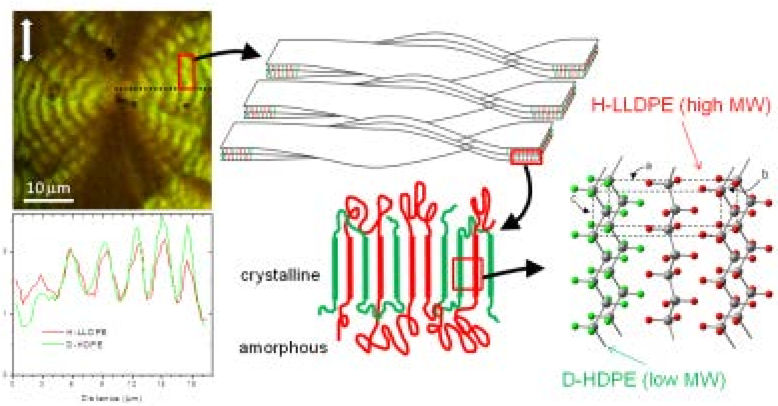
Poly(4-vinylimidazole)

Wednesday, April 10, 2013 04:30 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

524 - Molecular structure of bimodal polyethylene blends imaged with broadband coherent anti-Stokes Raman scattering (CARS) microscopy

Young Jong Lee[1], *yjlee@nist.gov, Chad R. Snyder*[1], *Aaron M. Forster*[2], *Marcus T. Cicerone*[1], *Wen-li Wu*[1]. *(1) Materials Measurement Laboratory, NIST, Gaithersburg, MD 20899, United States, (2) Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States*

Polyethylene (PE) has been widely used in a myriad of consumer products and critical infrastructure products such as underground gas and water pipes. These products are often made of blends of multiple types of PE with different molecular architectures. Although the long-term performance of these products is largely dictated by their local molecular structure, it has been studied mostly by indirect and bulk-averaging methods such as calorimetry and neutron scattering due to lack of chemical contrast for conventional imaging techniques. I demonstrate that broadband coherent anti-Stokes Raman scattering (CARS) microscopy can acquire images of the chemical composition and molecular orientation of a miscible semi-crystalline PE blend with two different molecular architectures. I will discuss the detailed crystal structure observed at different length scales and new insights it provides into polymer crystal morphology.



Wednesday, April 10, 2013 04:50 PM
General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
Room: Ste. D, Sec 19

525 - Sintering dynamics in composites and cross-linked polyesters

suresh ahuja, *patriot_1001@hotmail.com, Xerox Corporation, United States*

Dynamics of sintering and coalescence of particles has application in a variety of industrial processes varying from rotational molding to digital printing. For instance digital printing requires toner particles microns and nanometer aggregates to fuse under pressure and temperature with adequate viscosity and elasticity. Molecular dynamics and Finite Element Method have been used to model sintering of particles. Analysis of Molecular Dynamics shows that diffusion processes dominate the coalescence of particles especially nano-particles. For unequal size particles, coalescence processes became faster when the ratio of two particle sizes (smaller/larger) approaches to zero. The Koch-Friedlander (KF) analysis predicts the coalescence time of two unequal sized particles when benchmarked against the MD simulation, and the characteristic coalescence times is independent of the volume ratio of the coalescing partners. In Finite Element Method (FEM) modeling, cohesive interaction takes place between particles with initial configuration consisting of several hundred particles. Average aggregate projected area scale with equivalent number of constituent primary particles during sintering: from fractal-like agglomerates to aggregates and eventually compact particles. The driving force for sintering is a minimization of the free energy resulting in a reduction of surface area. The energy gained by surface reduction is dissipated by viscous flow, which sets the time scale for sintering. Composites and cross-linked polyesters made by extrusion were characterized for dynamic viscosity and relaxation spectra comparing with an Upper Convected Maxwell Model for sintering.

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General Topics: New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hilton Riverside
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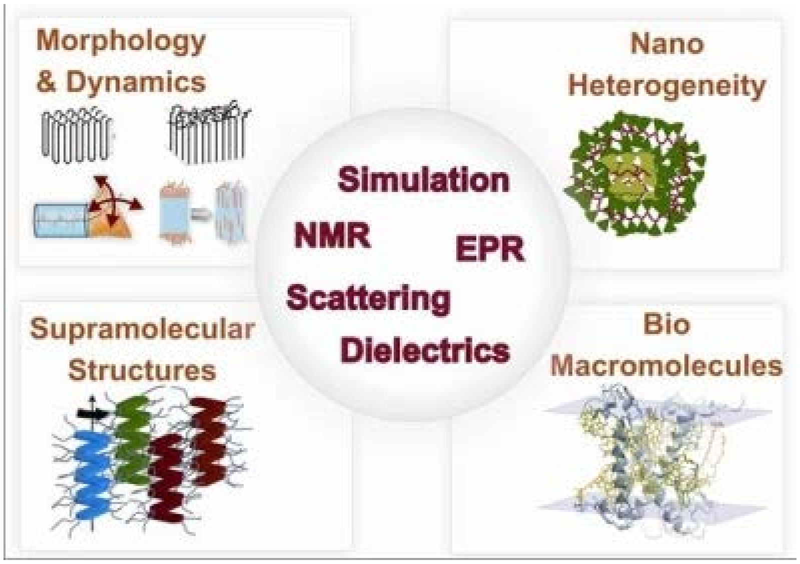
526 - Advanced NMR methods for studying functional materials and for signal enhancement

***Hans W. Spiess**, spiess@mpip-mainz.mpg.de, Max-Planck-Institute for Polymer Research, Mainz, Germany 55021, Germany*

For full structural and dynamic elucidation of functional organic materials a multi technique approach is needed, where the spectroscopic data are combined with other methods such as X-ray scattering, microscopy, dielectric spectroscopy and last, but not least, quantum chemical calculations. Recent examples will be presented and the findings will be related to the function of such materials, such as photo-conductivity. Moreover, recent results on signal enhancement by Para Hydrogen Induced Polarization (PHIP) will be presented.

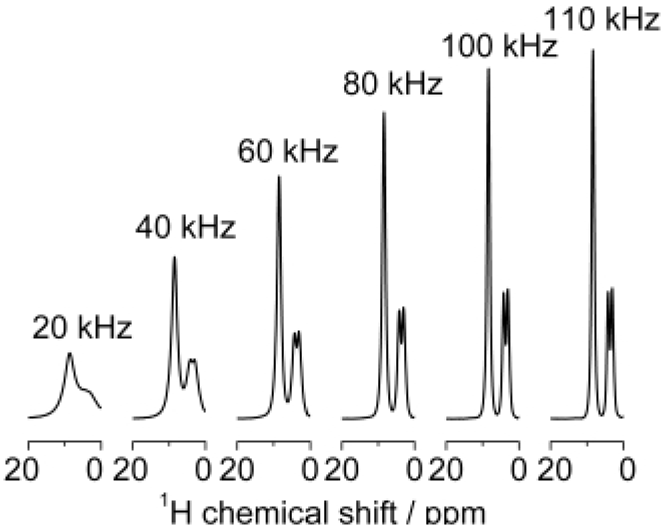


Wednesday, April 10, 2013 01:30 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

527 - Very fast MAS over 110 kHz and several useful methods in solid-state NMR

Yusuke Nishiyama, *yunishiy@jeol.co.jp, JEOL RESONANCE Inc., Musashino, Akishima, Tokyo 196-8558, Japan*

We recently developed a very fast MAS system above 110 kHz with the 0.75 mm MAS system. Very fast MAS increases ^{1}H T_2 relaxation times and thus greatly enhances sensitivity and resolution in ^{1}H NMR experiments.



We also show several practical methods which can be applied to conventional solid-state NMR experiments; quick automatic shimming at magic angle (MAGIC SHIMMING) and sensitivity enhancement of organic thin films by paramagnetic ion doping.

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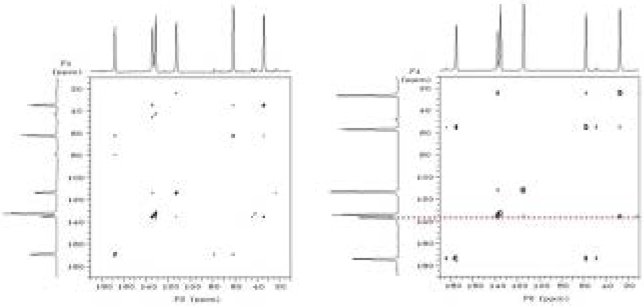
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

528 - Fast acquisition methods for solid state NMR

Jun Ashida, *jun.ashida@agilent.com, Agilent Technologies Japan Ltd., Tokyo, Japan*

NMR is very useful tool for the analysis of the characters of materials, though the sensitivity is very low compared with other analytical techniques. Recently many new hardware and software tecniques to overcome this advantage has been developped. In this presentation, some of fast acquisition techniques in solid state NMR which the author has been contributed are summarised.



[U-^{13}C,^{15}N] histidine ^{13}C-^{13}C DARR Conventional (left) and Hadamard (right) spectra
The experiment time is 18 hours(conventional) and only 9min (Hadamard), respectively.

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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
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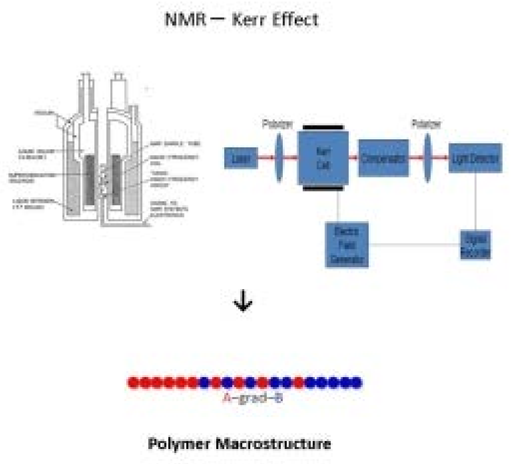
529 - Coupling NMR and the Kerr effect to determine polymer macrostructures

Alan E. Tonelli, *alan_tonelli@ncsu.edu, Fiber & Polymer Science Program, North Carolina State University, Raleigh, NC 27695-8301, United States*

NMR, usually high field, high resolution ^{13}C-NMR observed in solution, has repeatedly been demonstrated to be the premier experimental means for elucidating the constituent microstructural elements present in polymers. Like virtually all spectroscopic probes, however, NMR is generally only sensitive to relatively local, short-range microstructures, such as stereosequences at or below the pentad or hexad levels, or comonomer sequences at the diad or triad levels, which at best do not extend along the polymer backbone beyond 1 or 2 nm in length . To characterize the complete macrostructures of polymers not only requires identif-ication of such constituent short-range microstructures, but it is also necessary to locate their positions along the macromolecular chain backbone. This requires a probe whose consequent observable also depends on a polymer's entire macrostructure. We believe that observation of the birefringence that is produced by application of a strong electric field to dilute solutions of polymers, *i.e.,* their electrical birefringence or Kerr effect, provides a means to characterize the macrostructures of polymers. The contribution made by a polymer solute to the electrical birefringence observed for its dilute solutions both depends on and is highly sensitive to the magnitude and orientation of its overall dipole moment and polarizability tensor. As such, and for the first time, we are able to demonstrate its use to locate along the polymer backbone those short-range microstructural elements that are identifiable by NMR, thus enabling the complete characterization of a polymer chain's macrostructure.

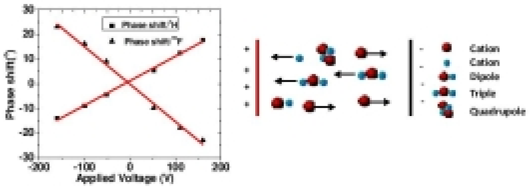


Wednesday, April 10, 2013 02:45 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

530 - Direct measurement of ion mobilities in ionic liquids by electrophoretic NMR

Zhiyang Zhiyang, *zhiyangz@vt.edu, Jianbo Hou, Louis A Madsen. Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24060, United States*

Ionic liquids (ILs) show promise as next-generation electrolytes in organic and polymeric devices due to, e.g., their high ionic conductivity, negligible vapor pressure, and thermal stability. These properties are sensitively controlled by the specific chemical structure of the bulky cations and anions. Transport behaviors of both cations and anions, regulated by a wealth of non-covalent interactions, drive the properties of ILs as electrolytes, which in turn affect the performance of IL-based electrochemical devices. Electrophoretic NMR (ENMR) is a unique technique that can directly measure the driven electrophoretic mobilities of cations and anions separately using spectral separation. ENMR measurement of ILs with high conductivity and slow diffusion presents a challenge, as it is complicated by nonelectrophoretic flow effects such as electro-osmosis and thermal convection. For the first time, we have accurately measured electrophoretic mobilities (see figure) of cations and anions in pure ILs based on our carefully designed sample cell and using a convection-compensated pulse sequence. We use ENMR to measure transference numbers, thus quantifying the contributions of individual charged species to the total ionic conductivity as well as reflecting subtle ion clustering effects. We will also present temperature and concentration dependencies of these conduction-relevant quantities and discuss our further understanding of conduction mechanisms in ILs and related ion-dense organic conductors.



Left: Voltage-dependent phase shift for cations (^{1}H) and anions (^{19}F) of 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate ([C_2mim][TfO]) at 25 °C, with mobilities of 6.6×10^{-10} $m^2s^{-1}V^{-1}$ (cation) and 7.8×10^{-10} $m^2s^{-1}V^{-1}$(anion). Right: E-field-driven motion of various ionic species in ionic liquids (ILs). NMR probes both equilibrium diffusive motions as well as driven motion.

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Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
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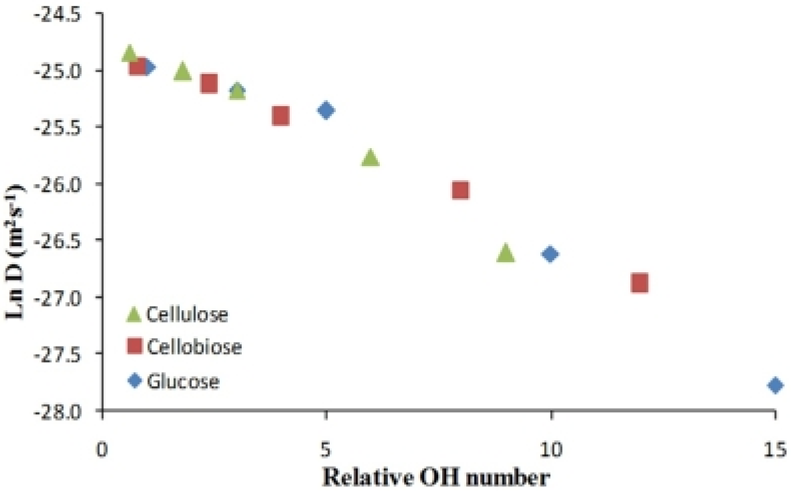
Room: Ste. C, Sec 18

531 - NMR studies of carbohydrate solvation in the room temperature ionic liquid 1-ethyl-3-methyl-imidazolium acetate

***Michael E Ries**[1], m.e.ries@leeds.ac.uk, Tatiana Budtova[2], Asanah Radhi[1], Jason Ovenden[1], Alice Keating[1], Owen Parker[1]. (1) School of Physics and Astronomy, University of Leeds, Leeds, UK LS2 9JT, United Kingdom, (2) Centre de Mise en Forme des Materiaux, MINES ParisTech, Sophia Antipolis, FRANCE BP 207, 06904, France*

We have studied glucose, cellobiose and cellulose dissolution in the ionic liquid (IL) 1-Ethyl-3-Methyl-Imidazolium Acetate. These have been investigated using NMR and rheology. Though the samples have vastly different viscosities, depending on solute used, the microscopic properties are only dependent on the number of solute OH groups per IL molecule. The figure shows the self-diffusion coefficient of the cation as a function of relative number of OH groups, this being proportional to the number of OH groups per IL molecule.

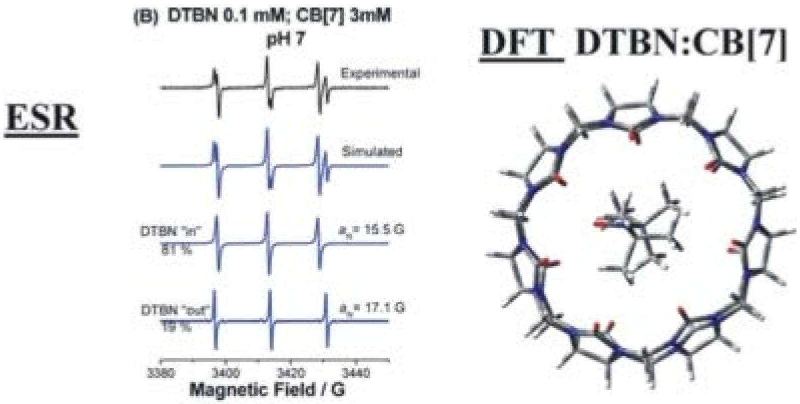


Wednesday, April 10, 2013 03:50 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

532 - Spin trapping in materials: Focus on the hydrogen economy

Shulamith Schlick, *schlicks@udmercy.edu, Mariana Spulber, Marek Danilczuk. Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan 48221, United States*

The fragmentation of perfluorinated membranes used in fuel cells (FC) has been studied by spin trapping ESR using DMPO, PBN, and MNP as spin traps. The method, which is mostly used in biological systems, has been adapted to the study of adducts generated in model compounds (ex situ experiments), and in a FC inserted in the resonator of the ESR spectrometer (in situ). The stability of Nafion, stabilized Nafion, and 3M and Aquivion membranes to attack by the hydroxyl radical, $HO^{\bullet}$, was compared in their aqueous dispersions at 300 K; the $HO^{\bullet}$ radicals were generated by UV-irradiation of hydrogen peroxide, H_2O_2,and radicals were detected by spin trapping with DMPO. The competitive kinetics (CK) approach that has been adapted for ranking the polymer stability led to the determination of their reaction rate constant with hydroxyl radicals. In situ experiments indicated, for the first time, the presence of hydrogen atoms, $H^{\bullet}$, as DMPO/Hadducts. Recently we have demonstrated the important role of $H^{\bullet}$ in the membrane degradation process. Encapsulation of spin adducts in cyclodextrins (CDs) and cucurbiturils (CBs), combined with DFT calculations, has emerged as a method for increasing the lifetimes and enhancing the stability of enclosed radicals and initially generated spin adducts.



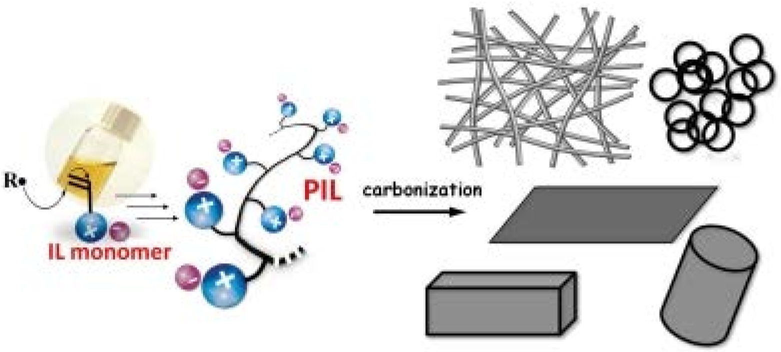
J. Phys. Chem. A **2012**, *116*, 8475–8483

Wednesday, April 10, 2013 04:15 PM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (01:30 PM - 04:40 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

533 - Poly(ionic liquid) for shaped functional carbons

Sebastian Soll, Qiang Zhao, Yongjun Men, Juan Manuel Balach, Markus Antonietti, ***Jiayin Yuan****, jiayin.yuan@mpikg.mpg.de. Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

Carbon has abundant allotropic forms and is a very versatile material with tremendous potential. The incorporation of nitrogen into carbon nanostructures on an atomic level is for some applications highly appreciated and for instance responsible for an enhanced electronic conductivity and catalytic activity. Among a variety of precursor possibilities, imidazolium- and pyridinium-based poly(ionic liquid)s or polymerized ionic liquids (PILs) have emerged very recently as a new and effective precursor for shaped nitrogen-doped carbon-based nanomaterials. The ionic liquid moieties in the PIL matrix worked as the major carbon source and enabled a high carbonization yield due to their intrinsic high thermal stability. Meanwhile the sp^2 nitrogen atoms in the imidazolium and pyridinium cation rings facilitated easy incorporation of nitrogen into the graphitic configurations at elevated temperatures. Due to the polymer nature, PILs could be straightforward processed by a good many of processing techniques into various morphologies, which would be in turn converted into carbons of the same geometry. In this contribution, our attempts to make use of PILs for shaped nitrogen-doped carbons will be demonstrated. Carbons with high nitrogen content and in various forms, such as thin film, fiber, membrane, hollow sphere, tunes, monolith, foam, etc. were prepared via the PIL route. Their versatile applications in catalysis and energy harvesting and storage were discussed.



Wednesday, April 10, 2013 01:35 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

534 - Ionic liquids for controlled synthesis of functional carbon materials

Sheng Dai, *dais@ornl.gov, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States and Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States*

Conventional synthesis of functional materials relies heavily on water and organic solvents. Alternatively, the synthesis of 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 templates and precursors to functional materials, as well as solvent. They offer many advantages, such as negligible vapor pressures, wide liquidus ranges, good thermal stability, tunable solubility of both organic and inorganic molecules, and much synthetic flexibility. The unique solvation environment of these ionic liquids provides new reaction media for controlling formation of polymeric materials and tailoring morphologies of advanced materials. We have described a simple, convenient, and catalyst-free approach for synthesizing high surface area N-doped porous carbons based on open vessel polymerization and thermolysis of a task-specific ionic liquid (TSIL) carrying char-forming nitrile functionality on the cation or anion. The structural morphology (porosity and surface area) of the resulting carbon is strongly dependent on the nature of the cation/anion pairing within the TSIL. Notably, a mesoporous carbon was successfully synthesized by direct carbonization of a TSIL precursor which acted as a self-porogen in the absence of either solvent or template species. This novel strategy can be extended to incorporate other carbon-producing functionality as well as more structurally diverse ions and highlights several exciting opportunities in functional carbon composites. These possibilities and others form the subject of current investigation in our labs. Challenges and opportunities in this research area will be discussed.

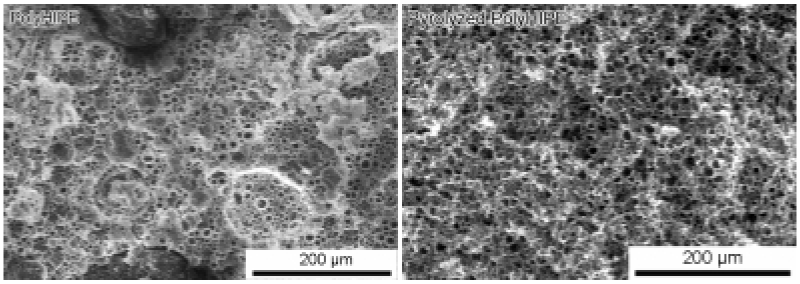
Acknowledgments : This work was conducted at the Oak Ridge National Laboratory and supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

Wednesday, April 10, 2013 02:05 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

535 - Emulsion-templated polymer precursors for highly porous carbon monoliths

***Michael S. Silverstein**, michaels@tx.technion.ac.il, Sima Israel, Noa Cohen. Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel*

PolyHIPEs are porous emulsion-templated polymers that are usually synthesized within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs). Typical polyHIPEs have highly interconnected porous structures, low bulk densities, and the ability to rapidly absorb large quantities of liquid through capillary action. The miscibility of acrylonitrile (AN) with water has made it difficult to synthesize PAN-based polyHIPEs. The successful synthesis of PAN-based polyHIPEs by crosslinking through copolymerization with divinylbenzene (DVB), by stabilization with a polyglycerol polyricinoleate surfactant, and by initiation with both oil- and water-soluble initiators will be described. The PAN-based polyHIPEs had porosities of over 86 % and porous structures that were different from those of typical of polyHIPEs. Pyrolysis of these PAN-based polyHIPEs was used to produce porous carbon monoliths. Pyrolysis did not produce significant changes in the porous structures, which were quite similar to those of the original polyHIPEs. The porosities were around 95 % and the carbon monoliths were largely macroporous and mesoporous, with some microporosity. Alternative routes to emulsion-templated polymer precursors for porous carbon will also be described. These results demonstrate that polyHIPE templates can be used for the *a priori* design of porous carbon monoliths.

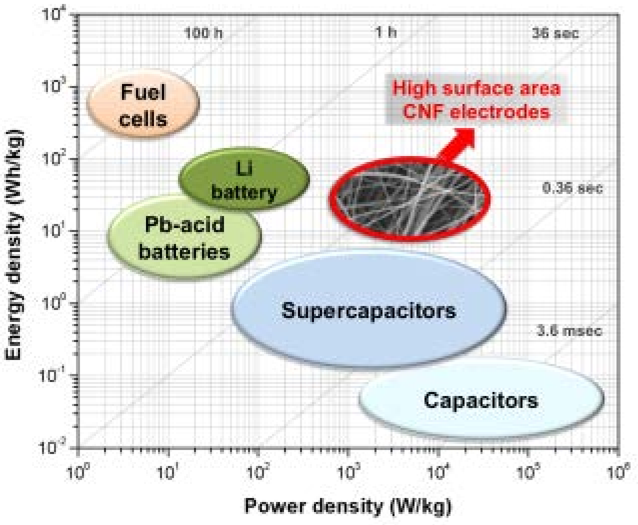


Wednesday, April 10, 2013 02:35 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

536 - Energy storage devices utilizing carbon nanofibers derived from electrospun high free volume polymer precursors

Jeliza Bonso, Kyung Hye Jung, ***John P Ferraris****, ferraris@utdallas.edu. Chemistry, University of Texas at Dallas, Richardson, TEXAS 75080-3021, United States*

Nonwoven mats of carbon nanofibers derived from electrospun polymer precursors were used as freestanding and binder-free electrodes for high energy density supercapacitors. In this study, high free volume precursor polymers including 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-based polyimides and polymers of intrinsic microporosity (PIMs) were employed. The inherent high free volume in the precursor polymer nanofibers could be translated into high surface area (>500 m^2/g) carbon nanofibers upon pyrolysis, circumventing the need for additives such as sacrificial polymers or porogens. Their surface area was further improved by steam activation, rising to ~1200 m^2/g. These mats were directly employed as electrodes in a coin cells using ionic liquid electrolyte. Electrochemical tests including cyclic voltammetry and galvanostatic charge/discharge tests gave energy (power) densities of 60-80 Wh/kg (1-2 kW/kg) at 1 A/g and 40-50 Wh/kg (8-10 kW/kg) even discharge rates as high as 5 A/g.



Wednesday, April 10, 2013 02:55 PM

Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)

Location: Hilton Riverside

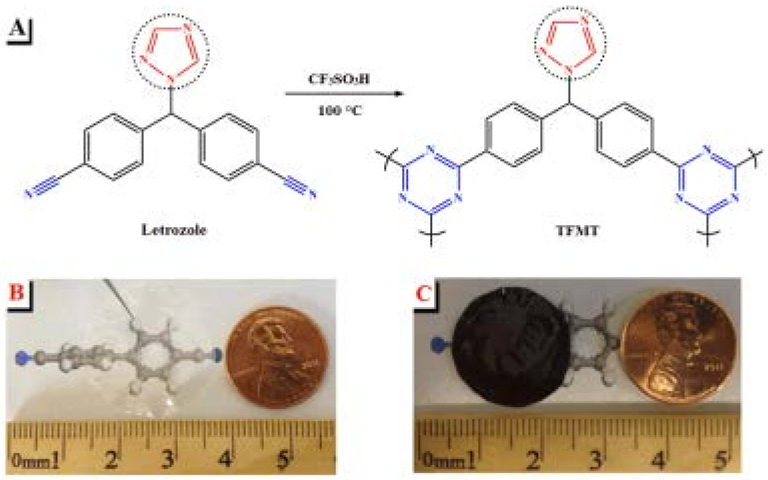
Room: Ste. B, Sec 7/10

537 - Facile synthesis of porous, nitrogen-doped adsorption/diffusion carbonaceous membranes for efficient CO_2 separation

__Xiang Zhu__[1,2], zhuxiang.ecust@gmail.com, Songhai Chai[2], Chengcheng Tian[1,2], Pasquale Fulvio[2], Kee Sung Han[2], Edward W. Hagaman[2], Gabriel M. Veith[4], Shannon M. Mahurin[2], Suree Brown[3], Honglai Liu[1], Sheng Dai[2,3]. (1) State Key Laboratory of Chemical Engineering and Department of Chemistry, East China University of Science and Technology, Shanghai, Shanghai 200237, China, (2) Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States, (3) Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, United States, (4) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

A tremendous attention has been recently paid to the selective capture and separation of carbon dioxide because of the anthropogenic carbon dioxide emissions. Membrane-based gas separation is considered to be one of the most promising candidates due to its lower energy costs, a small footprint, and high reliability. In this study, a porous, nitrogen-doped adsorption/diffusion carbonaceous membrane (TFMT-550) was facilely prepared from triazole-functionalized-triazine-framework , exhibiting a good membrane separation performance of CO_2 over N_2 and surpassing the recent upper bound. An exceptional ideal CO_2/N_2 permselectivity of 47.5 was achieved with a good CO_2 permeability of 718 barrer based on the strong dipole-quadrupole interactions between the large quadrupole moment of CO_2 molecules and the polar sites associated with N groups (e.g., triazine units) within the framework.

Acknowledgment: Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

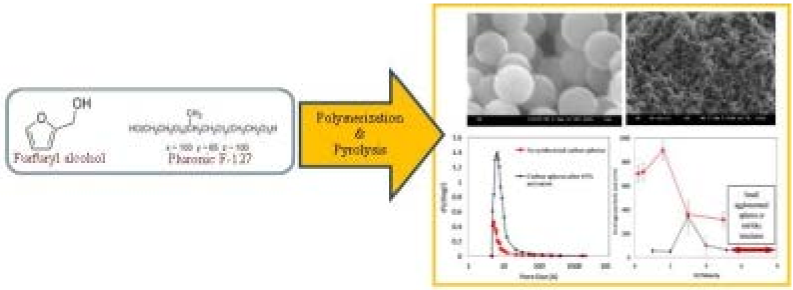


Wednesday, April 10, 2013 03:30 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

538 - Tuning morphology and porosity of poly(furfuryl alcohol)-derived nanoporous carbon

Maryam Peer[1], *mop5104@psu.edu, Ali Qajar*[1], *Ramakrishnan Rajagopalan*[2], *Henry C Foley*[1]. *(1) Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States, (2) Material Research Institute, The Pennsylvania State University, University Park, PA 16802, United States*

Nanoporous carbon materials with controlled morphological and textural properties are of great interest in different applications like catalysis, adsorption and membrane separation. In this study, furfuryl alcohol was used to synthesize poly(furfuryl alcohol) using an emulsion polymerization approach, in the presence of Pluronic F-127 as the structure directing agent. The surfactant assisted polymerization of furfuryl alcohol led to formation of polymeric spheres (and in some cases other morphologies) which were then pyrolized at 800°C to form carbon. The intrinsic pore size of the as-synthesized carbon spheres is 0.5 nm and it can be controlled by adding pore forming agents (poly(ethylene glycol) with different molecular weights) during polymerization. The other approach used to shift the pore size was oxidation of carbon under CO_2 at different temperatures. Size of the carbon spheres was also controlled by adjusting the surfactant to monomer ratio. It was possible to make mono dispersed spheres with sizes ranging from 50 nm to few microns using this approach. The effect of other factors including solvent composition and polymerization initiator concentration was also studied and the pseudo-ternary phase diagram of the system was developed. Platinum nanoparticles embedded in these carbon spheres was successfully used as catalyst support in shape selective liquid phase hydrogenation reactions



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Wednesday, April 10, 2013 03:50 PM

Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)

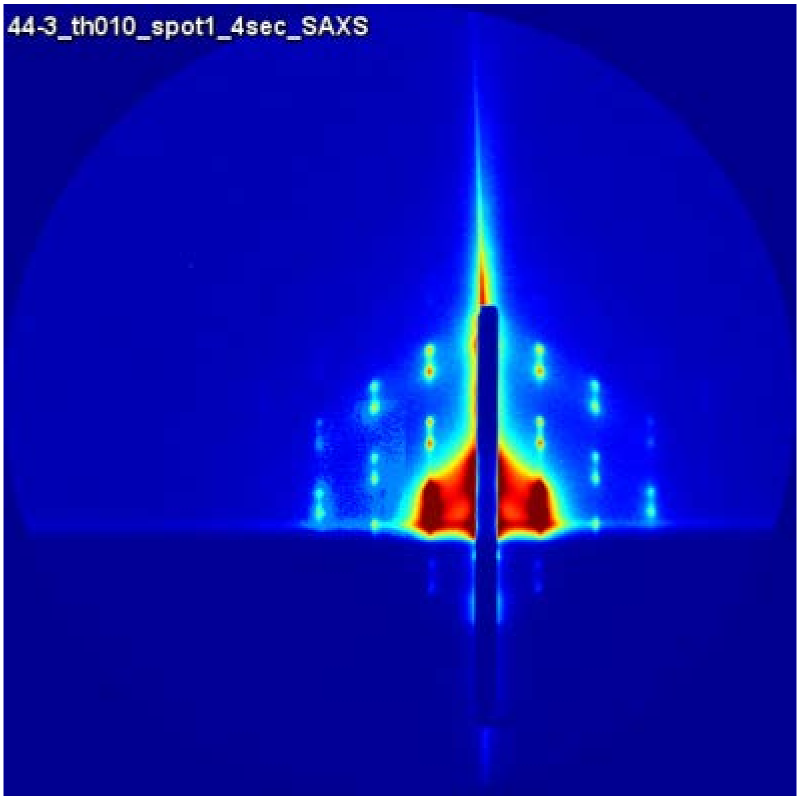
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

539 - Processing effects on the morphology of mesoporous carbon films fabricated by cooperative self-assembly of phenolic resins

Bryan D Vogt, *vogt@uakron.edu, Zhe Qiang, Jiachen Xue, Kevin A Cavicchi, Alamgir Karim. Department of Polymer Engineering, University of Akron, Akron, OH 44325, United States*

Cooperative assembly of phenolic resins with amphilphiles provides a facile route to fabricating ordered mesoporous carbons through pyrolysis of the assembled composite. The high carbon yield of the phenolic resin provides a solid framework, while proper selection of the surfactant or block copolymer yields pores from its thermal decomposition. Thin films can be challenging due to increased stresses during carbonization from confinement by the substrate, sluggish template mobility, and difficulties with achieving a preferred orientation. Here we will discuss two routes to control the structure of these self-assembled films based upon solvent processing and thermal gradients. These methods provide routes to achieve highly ordered and oriented mesoporous carbon films. We use GISAXS (see Fig 1) and AFM to characterize the morphology as a function of processing conditions. Significant moduation in the structure is possible through minor changes in the processing.

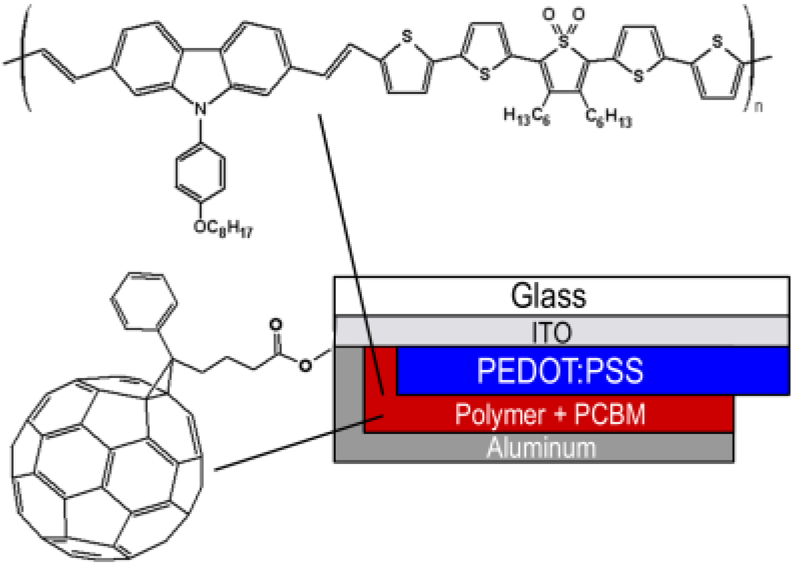


Wednesday, April 10, 2013 04:10 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:35 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

540 - New polymers for plastic solar cells

Mario Leclerc, *mario.leclerc@chm.ulaval.ca, Department of Chemistry, Université Laval, Quebec City, Quebec G1V 0A6, Canada*

Solar cells are one key technology for solving world energy needs. The development of new materials such as semiconducting conjugated polymers as active components in bulk heterojunction (BHJ) photovoltaic devices could help to significantly reduce the fabrication cost of such devices. In the last few years, many chemists proposed new polymeric structures. Among them, we would like to report new polycarbazole and polythienopyrrolopyrrole derivatives that show good solubility and good hole mobility, resulting in power conversion efficiencies up to 7-8%. We will also report about new promising polymeric structures that could lead to efficiencies up to 10% in a single cell configuration. Finally, we will describe novel synthetic methodologies for a simple preparation of known and new well-defined conjugated polymers.

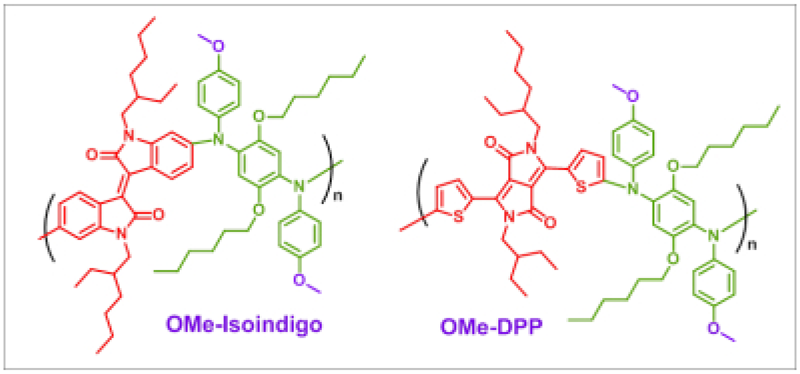


Wednesday, April 10, 2013 01:35 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

541 - Tuning organic molecules and macromolecules for photovoltaic applications

Robert B Grubbs[1,2], *robert.grubbs@stonybrook.edu*, *Tejaswini Kale*[1], *Young S Park*[1]. *(1) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, United States, (2) Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, United States*

The design and synthesis of new molecules and macromolecules for photovoltaic applications continues to be a major experimental endeavor in many laboratories. Two widely targeted goals are (1) the design of materials with narrow band gaps that can harvest a broader range of the solar spectrum and (2) the preparation of more efficient ordered heterojunction structures with mean donor-acceptor domain sizes on the order of the exciton diffusion length. This presentation will cover efforts in the Electronic Materials Group of the Center for Functional Materials toward both of these goals. We have synthesized a range of narrow band-gap donor polymers and small molecules with a range of structures and investigated their performance in OPV devices. As a step toward the stabilization of nanostructured heterojunction devices, we have synthesized photo-crosslinkable azide-functionalized polythiophenes and shown them to be effective in improving the long-term stability of P3HT:PCBM-based bulk heterojunction solar cells.

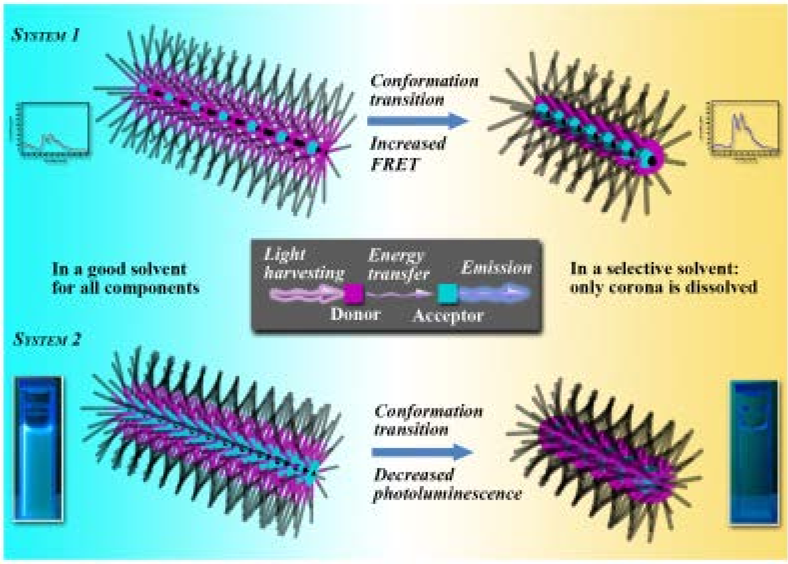


Wednesday, April 10, 2013 02:05 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

542 - Novel light-harvesting and energy transfer molecular architectures

Zhicheng Zheng, *zhicheng.zheng@uni-bayreuth.de, Jun Ling, Axel H. E. Müller. Department of Macromolecular Chemistry II, University of Bayreuth, Bayreuth, Bavaria 95440, Germany*

Nature has been using ingenious molecular architectures to effectively harvest sunlight and efficiently transfer energy. Imitating the natural “energy cascade” architecture, we designed a novel concept providing a highly efficient light absorption and energy transfer process for synthetic light-harvesting systems. To prove the concept, two single-molecular one-dimensional nano-light harvesting architectures on the basis of cylindrical polymer brushes (CPBs) were developed. In system 1, a number of block copolymer side chains carrying light absorbing antennae groups (energy donors, *i.e.* 9,9-diethylfluorene) are tethered to a linear polymer backbone containing emitting groups (energy acceptors, *i.e.* anthracene). In system 2, the light absorbing groups and the emitting groups are built as adjacent blocks in the side chains. Both systems provide very efficient energy absorption and energy transfer from antennae to energy acceptors, confirming our novel concept. Furthermore, the energy transfer efficiency of system 1 can be manipulated as much as 20 times by tuning the distance between energy donors and energy acceptors in physical and/or chemical ways. In the case of system 2, changing the nature of solvent leads to a molecular conformation transition and thus a fluorescence quenching of the emitting groups. This novel “energy cascade” mimicking concept is also readily to be transplanted to other applications in artificial photosynthesis systems, light sensors, solar cells, organic light-emitting diodes and further photoelectronic devices.

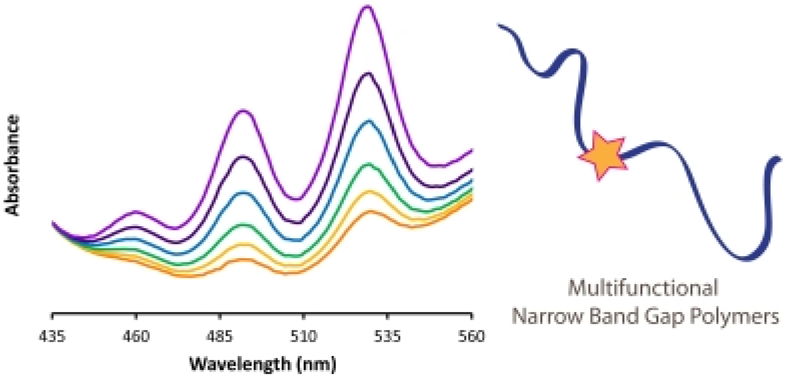


Wednesday, April 10, 2013 02:25 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

543 - Multifunctional conjugated polymers for organic electronics

Maxwell J. Robb[1,2], *mrobb@umail.ucsb.edu, Nancy Eisenmenger*[2,3], *Damien Montarnal*[2], *Sung-Yu Ku*[2], *Michael L. Chabinyc*[2,3], *Craig J. Hawker*[1,2,3]. *(1) Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, United States, (2) Materials Research Laboratory, University of California, Santa Barbara, CA 93106, United States, (3) Materials Department, University of California, Santa Barbara, CA 93106, United States*

The ability to control the properties at the interface of donor and acceptor components in bulk heterojunction organic photovoltaic devices is a paramount goal. We have recently developed a synthetic strategy that enables the preparation of well-defined, p-type low-band-gap polymers containing n-type functional moieties. These multifunctional polymers represent a new class of materials with promising characteristics for enhancing a variety of fundamental properties in organic electronic devices.



Wednesday, April 10, 2013 02:45 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

544 - Dye sensitized polymer composites for energy conversions

Sam-Shajing Sun[1,2], *ssun@nsu.edu, Amanda Harding*[1], *Eumee Song*[1], *Bianca Christian*[2]. *(1) Center for Materials Research, Norfolk State University, Norfolk, Virginia 23504, United States, (2) Chemistry Department, Norfolk State Univeristy, Norfolk, Virginia 23504, United States*

A donor-dye-acceptor triple materials system has been designed and preliminarily investigated for potential light harvesting and photoelectric conversion applications. Figure 1 below exhibits a general frontier orbital scheme of the triple system, where the dye desirably has an energy gap matching a specific or intended light radiation energy and also has a relatively large absorption coefficient to the intended radiation. Specifically, several molecular dyes including Zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (ttb-ZnPc), Methylene Blue (MB), New Methylene Blue N (NMB), and *cis*-Bis(isothiocyanato)(2,2¢-bipyridyl-4,4¢-dicarboxylato)(4,4¢-di-nonyl-2¢-bipyridyl)ruthenium(II) (Z-907), and at least two donor type conjugated polymers Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Poly(3-dodecylthienylenevinylene)s (C12-PTV), and composites of the dye/polymer pairs have been investigated due to their frontier orbital levels (HOMOs, LUMOs) and energy gaps appear suitable or attractive for sunlight harvesting and photoelectric energy conversions. For instance, molecular dyes act as photoelectric acceptors to the mentioned polymers, but also act as photoelectric donors to a number of electron acceptors such as [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) and metallic single wall carbon nanotubes (m-SWCNT). Photo induced charge and/or energy transfers have both been observed in the polymer/dye composites under different conditions. For instance, the concentration of P3HT was found to switch the fluorescence emission trend of ttb-ZnPc in the P3HT/ttb-ZnPc blend solution from decreasing to increasing or vice versa, and we tentatively attribute the phenomena to a possible P3HT aggregation induced frontier orbital relationship change for the P3HT/ttb-ZnPc pair.

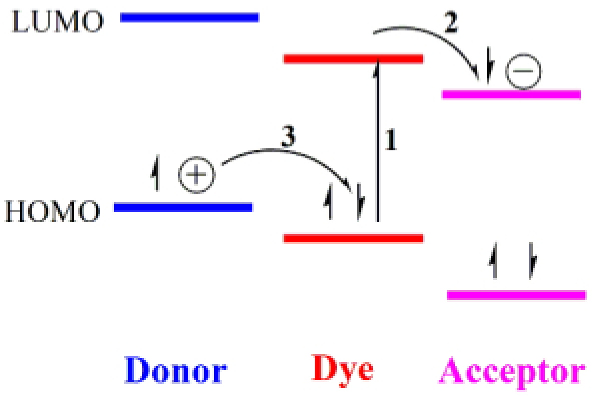


Figure 1. General scheme of a Donor-Dye-Acceptor 'triple' materials system for pohotoelectric conversions.

Wednesday, April 10, 2013 03:20 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

545 - Dithienopyrrole-thiophene derivative copolymers for organic electronic applications

Racquel C Jemison, *rjemison@andrew.cmu.edu, Sarada P Mishra, Courtney L Balliet, Richard D McCullough. Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States*

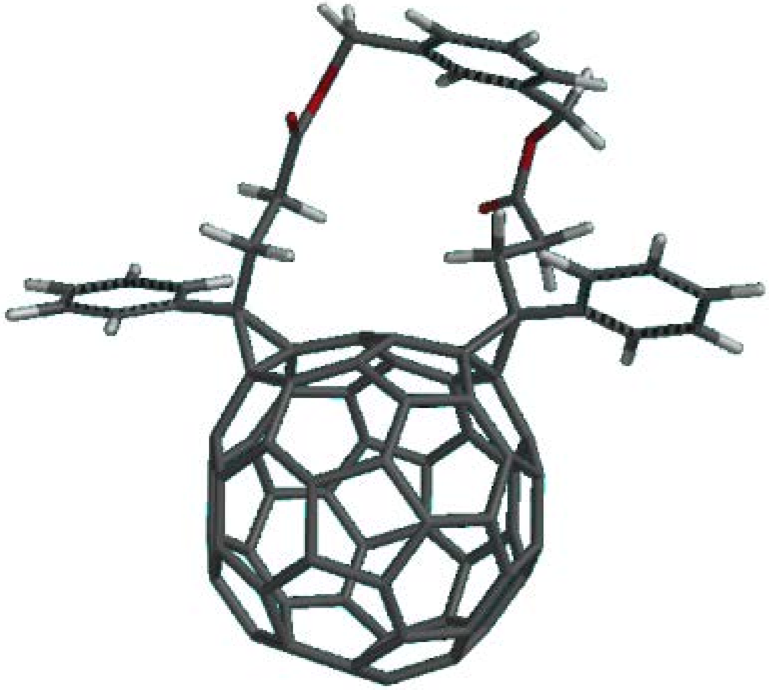
Third generation semiconducting polymers rely on the unique approach of pairing electron donors with electron acceptors in a nano hybrid system. Regioregular poly(3-alkylthiophene)s have emerged as excellent donor material candidates for organic photovoltaics. Introducing fused rings, and alternating electron-rich with electron-poor monomers can improve charge transfer capabilities by effectively reducing the optical band gap, thus increasing the amount of sunlight that can be absorbed into the active material. This study details the copolymerization of fused ring systems of electron rich dithienopyrrole (DTP) with thiophenes bearing various ethynyl side chains as well as thiophene dioxide monomers. Field effect mobility and conductivity was measured. Polymer morphology was examined using atomic force microscopy (AFM) and grazing incidence X-ray scattering (GIXS). The polymers' optical band gaps were calculated using UV-Vis absorption and cyclic voltammetry experiments and both demonstrated a decrease in band gaps to less than that of *rr*-P3AT. Photovoltaic performance was also measured and optimized.

Wednesday, April 10, 2013 03:40 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

546 - Multifunctional fullerenes for application in organic solar cells

John S. Cowart[1,2], *jcowart@chem.ucsb.edu, Christopher Liman*[1,3]*, Craig J. Hawker*[1,2,3]*, Michael Chabinyc*[1,3]*, Fred Wudl*[1,2,3]*. (1) Materials Research Laboratory, University of California at Santa Barbara, Santa Barbara, CA 93106, United States, (2) Department of Chemistry, University of California at Santa Barbara, Santa Barbara, CA 93106, United States, (3) Department of Materials Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106, United States*

Materials design of fullerene acceptors has become an increasingly relevant topic in photovoltaics research. Synthetic modifications of C_{60} fullerene can be utilized to impart functionality and vary frontier orbital energies, enhancing structural and electronic compatibility with p-type materials in organic solar cells. For most photovoltaic applications, the ability to modulate C_{60}'s LUMO is of great interest because a tunable electron affinity would facilitate a higher degree of control over V_{oc}s in heterojunction active layers. Furthermore, minimization of energy loss during photoinduced charge transfer would likely lead to noticeable improvements in charge extraction and power conversion efficiencies.Here we present a systematic study of the influence of tether directed fullerene bisadducts in bulk heterojunction devices. The electrical properties of these polymer/tether directed fullerene bisadduct systems are discussed and correlated to structural observations from 2D x-ray and depth profiling experiments.

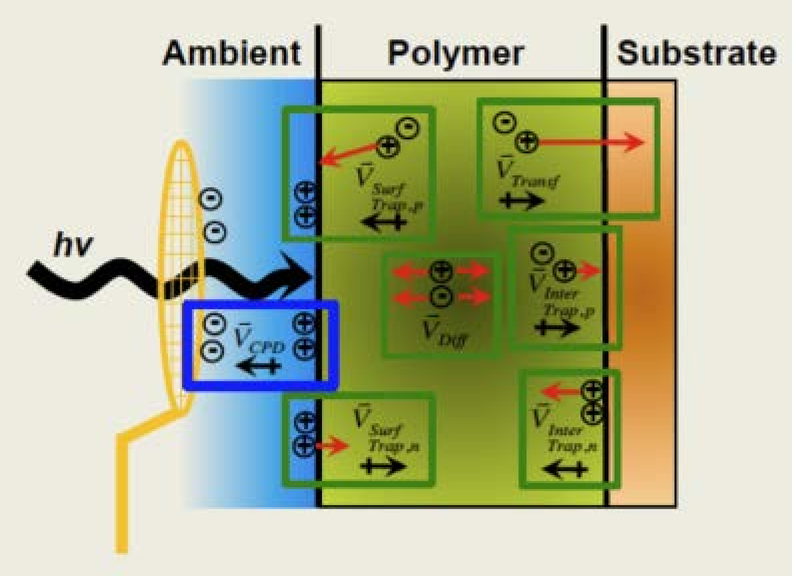


Wednesday, April 10, 2013 04:00 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

547 - Surface photovoltage in PCBM/P3HT bulk heterojunction photovoltaic cells

Frank E Osterloh[1], *fosterloh@ucdavis.edu, Michael A Holmes*[1], *Jing Zhao*[1], *Lilian Chang*[2], *Th Dittrich*[3], *Adam J Moule*[2]. *(1) Chemistry, UC Davis, Davis, CA 95616, United States, (2) Department of Chemical Engineering and Materials Science, UC Davis, Davis, CA 95616, United States, (3) Helmholtz Center Berlin, Berlin, Germany*

Surface photovoltage spectroscopy was used to directly observe photon induced charge separation in thin films of PCBM, P3HT and mixtures of the two on ITO and silver substrates. Strong SPV signals are observed under sub-band gap and band gap excitation of the films. The former correspond to direct excitation of charge transfer (CT) states present in P3HT and in the PCBM/P3HT blend. The energy of the CT state determines the maximum possible voltage output of an organic photovoltaic cell. Variations in annealing temperature, films thickness and illumination intensity are employed to derive a comprehensive model for charge transport in the polymer films and at the interfaces



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Wednesday, April 10, 2013 04:20 PM

Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 04:50 PM)

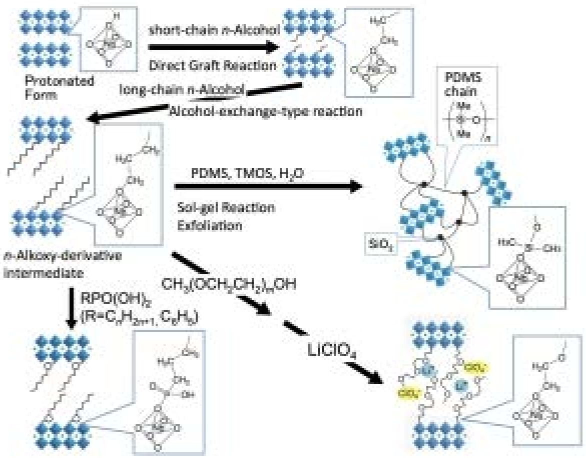
Location: Hilton Riverside

Room: Ste. C, Sec 13/16

548 - Organic-inorganic hybrids based on inorganic nanosheets

Yoshiyuki Sugahara, *ys6546@waseda.jp, Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan and Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-0051, Japan*

It is well known that some inorganic compounds, which consist of stacked nanosheets, undergo graft reactions besides intercalation reactions to yield organic-inorganic hybrids, where organic groups are bound to the nanosheets via covalent bonds. We have developed the graft reactions of Dion-Jacobson-type ion-exchangeable layered peroviskites, and graft reactions have been achieved with several types of organic molecules, including alcohols and organophosphonic acids. These grafted nanosheets can be further utilized for materials preparation.

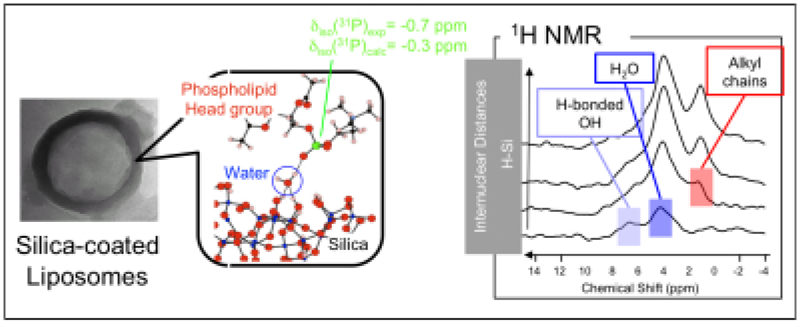


Thursday, April 11, 2013 08:30 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

549 - Exploring inorganic-organic interfaces in hybrid materials with advanced NMR tools

Nicolas Folliet, Niki Baccile, Thierry Azais, Christel Gervais, Guillaume Laurent, Christian Bonhomme, ***Florence Babonneau****,*
florence.babonneau@upmc.fr. Laboratoire de Chimie de la Matière Condensée de Paris, Université Pierre et Marie Curie/CNRS/Collège de France, Paris, France

In this presentation, the strength of advanced solid state NMR techniques to investigate interactions between organic and inorganic components in hybrid materials will be illustrated. Newly developed methods (Magic Angle Coil Spinning and Dynamic Nuclear Polarization) will be introduced. Finally, computer modeling will be presented in connection with solid-state NMR experiments and GIPAW method, a well established tool of calculation for NMR parameters. One example that will be developed to illustrate this combined NMR-modeling strategy concerns silica-coated liposomes



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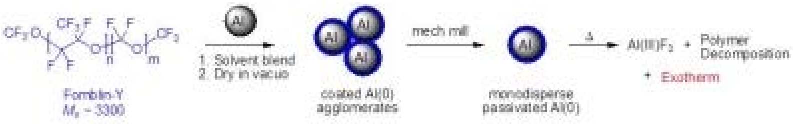
Thursday, April 11, 2013 09:00 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

550 - Metastable metalized perfluoropolyether functionalized composites

Seth T. Danielson[1], Bradley S. Kusel[1], James W. Neat[1], Eryn Avjian[1], Hannah A. Miller[1], David W. Ball[2], Scott T. Iacono[1], ***Sharon C. Kettwich**[1], sharon.kettwich@usafa.edu. (1) Department of Chemistry, United States Air Force Academy, USAF Academy, CO 80840, United States, (2) Department of Chemistry, Cleveland State University, Cleveland, OH, United States*

Fluorinated polymeric matrices are an attractive class of materials due to their applicability for use in various environments including use as high performance materials. Specifically, perfluoropolyethers (PFPEs) are low molecular weight oligomers that have low volatility, minimal shear thinning, and a viscosity that is nearly independent of temperature making them stable in extreme processing conditions. PFPEs are well-known to undergo accelerated thermal degradation in the presence of native metals and Lewis acids.The work presented herin is motivated by the potential of harnessing the energetic behavior as a result of degradation pathways facilitated by exothermic metal-mediated oxidation. Computational modeling/simulation supported by thermal experimental studies showed that micron- and nanometer sized aluminum Fomblin-Y (a PFPE) blended formulations produced a viable energtic material. These formulations serve as an additive in commerical, mechancially polymeric matrices including epoxy resins and poly(urethane)s. This work will discuss the preparation, properties, and characterization of these composite systems.

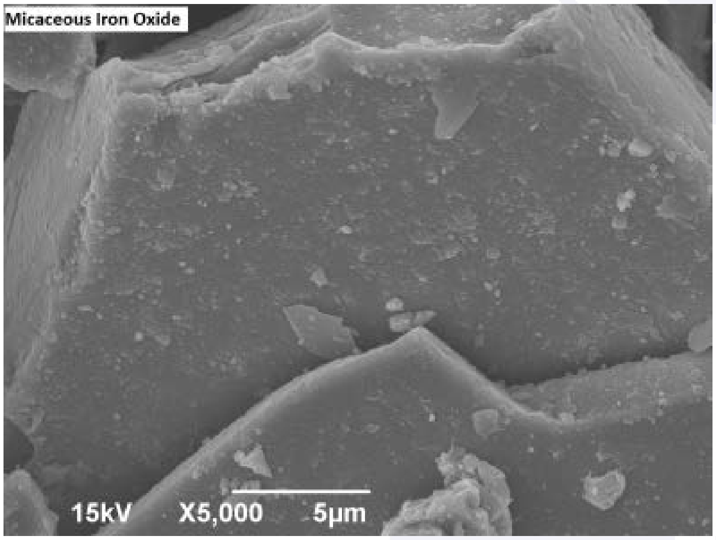


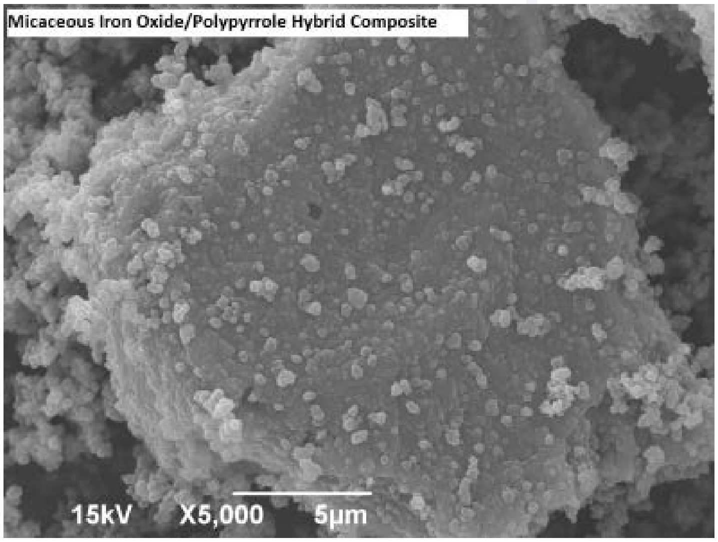
Thursday, April 11, 2013 09:30 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

551 - Synthesis and characterization of micaceous iron oxide/polypyrrole hybrid composites by chemical oxidative polymerization

*Niteen Jadhav, **Victoria J Gelling**, V.J.Gelling@ndsu.edu. Department of Coatings & Polymeric Materials, North Dakota State University, Fargo, ND 58108-6050, United States*

A hybrid composite material consisting of Micaceous Iron Oxide (MIOX) and Polypyrrole (PPy) was synthesized by employing a relatively simple chemical oxidative polymerization method in water. The synthesized hybrid composite material was characterized by Scanning Electron Microscopy (SEM) for morphology, Energy Dispersive Spectroscopy (EDS) for elemental analysis and Conductive-Atomic Force Microscopy (C-AFM) for conductivity studies. Density assessment of the resulting hybrid was also performed to determine the adhesion between MIOX and PPy. Uniform growth of PPy particles was observed on the MIOX surface as evidenced in SEM micrographs. The presence of nitrogen and lesser amount of iron in EDS results indicated the formation of PPy on the surface of MIOX. Additionally, conductive regions found in C-AFM studies confirmed the conducting nature of synthesized MIOX/PPy hybrid composite particles.





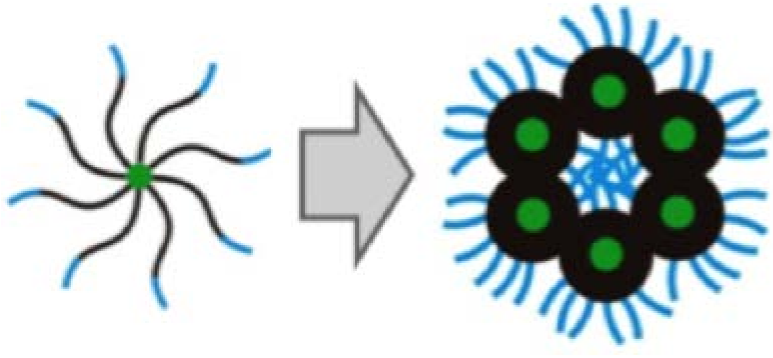
Thursday, April 11, 2013 09:50 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

552 - Controlling the architecture of boron-containing polymers

Frieder Jaekle, *fjaekle@rutgers.edu, Department of Chemistry, Rutgers University - Newark, Newark, NJ 07102, United States*

Organoborane polymers are promising for the development of emission and electron conduction layers in organic light emitting devices (OLEDs), acceptors in photovoltaics, sensors for anions and sugars, battery electrolytes, bioimaging, as components of stimuli-responsive materials, etc.

Recently, we have succeeded in the preparation of oligomers and polymers of well-defined structure and controlled molecular weight, which allows us for the first time to derive clear structure-property relationships. Going one step further, incorporation of the boron functional groups into nanostructured materials is expected to allow scientists to develop next generation materials for sensing, electronic devices, catalysis, biomedical applications, etc. We have succeeded in the decoration of block and star polymers with a diverse range of functional groups, including anionic organoborate, cationic organoboronium, pH sensitive boronic acid, and luminescent organoborane moieties. Details of their preparation, self-assembly behavior, and potential applications will be discussed.

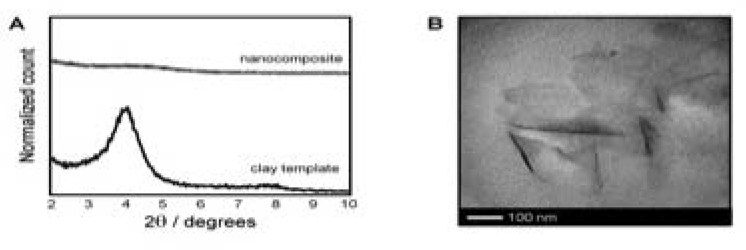


Thursday, April 11, 2013 10:25 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

553 - Montmorillonite poly(norbornene) nanocomposites from ruthenium alkylidene surface-initiated polymerization

Thomas A P Seery[1,2], *thomas.seery@uconn.edu, David Penaloza*[2]. *(1) Institute of Materials Science, Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United States, (2) institute of Materials Science/Department of Chemistry, University of Connecticut, Storrs, CT 06269, United States*

An exfoliated clay-polymer nanocomposite was prepared by surface-initiated ring opening metathesis polymerization (SI-ROMP) of norbornene from a previously surface-modified naturally occurring montmorillonite (MMT) clay template. Utilizing the hydrothermal-silylation reaction between a norbornenyl-bearing chlorosilane agent and silanol groups of the MMT clay template, we were able to successfully tether a metal alkylidene catalyst to the MMT surface in order to mediate the ROMP and grow poly(norbornene) chains directly from the surface. Our approach produced nanocomposites having poly(norbornene) chains that are covalently attached to the inorganic substrate, as opposed to the conventional polymer-clay composites having ionically tethered chains (via the ammonium-based modifiers of the organoclay) or physically adsorbed polymers. Various organophilic clays were used in initial studies and appeared to limit the accessibility of the surface of the clay to silane coupling agents resulting in composite materials that were primarily edge functionalized. Final products produced from Cloisite 15A however were well exfoliated as seen in the XRD and TEM below.



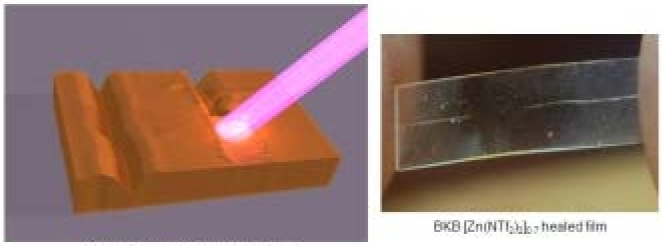
Thursday, April 11, 2013 10:55 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

554 - Optically-triggered healing and adhesive properties of metallosupramolecular materials

Gina L Fiore[1], *gina.fiore@unifr.ch, Souleymane Coulibaly*[1], *Christian Heinzmann*[1], *Stuart J Rowan*[2], *Christoph Weder*[1]. *(1) Polymer Chemistry and Materials, Adolphe Merkle Institute, Marly, Switzerland, (2) Department of Macromolecular Science and Engineering, Case Western Reserve University, Clevelend, OH 44106, United States*

Optically-healable metallosupramolecular materials of poly(ethylene-*co*-butylene) polymer core, end-capped with 2,6-bis(1'-methylbenzimidazoyl) pyridine ligands (BKB) and coordinated to metal salts (Zn(NTf$_2$)$_2$) were developed ([Zn(BKB)](NTf$_2$)$_2$). Damaged films of [Zn(BKB)](NTf$_2$)$_2$ were healed via UV irradiation, which causes reversible disengagement of the supramolecular motifs. Reinforcement of [Zn(BKB)](NTf$_2$)$_2$ with cellulose nanocrystals increased the tensile storage modulus, while the healing ability was little affected. Interestingly, neat materials of [Zn(BKB)](NTf$_2$)$_2$ show stimuli-responsive adhesive properties where light or heat-triggers can be used for bonding and debonding on demand features

Optically-Healable Metallosupramolecular Materials



Schematic of light-activated healing

BKB [Zn(NTf$_2$)$_2$]$_2$ - healed film

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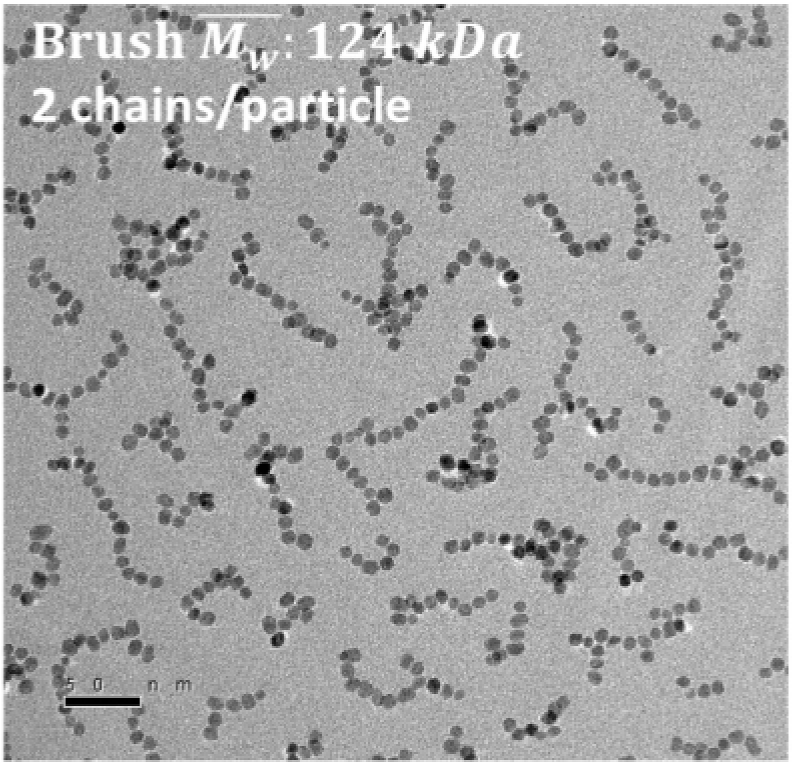
Thursday, April 11, 2013 11:15 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

555 - Sulfonated poly(styrene) chains grafted on magnetic nanoparticles

Yang Jiao, ***Pinar Akcora***, *pakcora@stevens.edu. Department of Chemical Engineering & Materials Science, Stevens Institute of Technology, Hoboken, NJ 07030, United States*

Ion containing polymers find variety of applications such as ion transport for actuators, batteries and fuel cells. In this work, we graft poly(styrene) (PS) chains from surfaces of iron oxide nanoparticles at different grafting densities and report the effect of sulfonic group locations within chains on the aggregation state of polymer-grafted nanoparticles. Structures formed by the random and diblock copolymers of PS-PSS grafted particles will be discussed with small-angle x-ray scattering (SAXS) measurements in solution and melts.

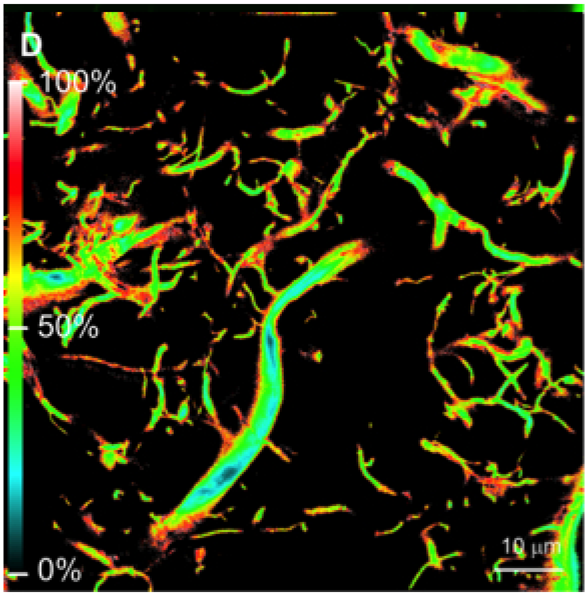


Thursday, April 11, 2013 11:35 AM
Hybrid Materials (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

556 - Cellulose nanomaterials: Nanocomposite imaging using FRET

Jeffrey W. Gilman, *jwgilman@nist.gov, Materials Science and Engineering Division, NIST, Gaithersburg, MD 20899, United States*

Cellulose nanomaterials are found in plants, marine animals, algae, bacteria and even amoeba. Critical features of the structural performance of cellulose in these diverse settings are the large aspect ratio and high strength properties of the cellulose nanocrystals and cellulose nanofibers, which provide reinforcement. Primary drivers for their industrial use include their renewability and proven low toxicity. Use of confocal microscopy and Forster resonance energy transfer (FRET) has enabled multi-scale characterization of cellulose fibers in a polymer matrix.

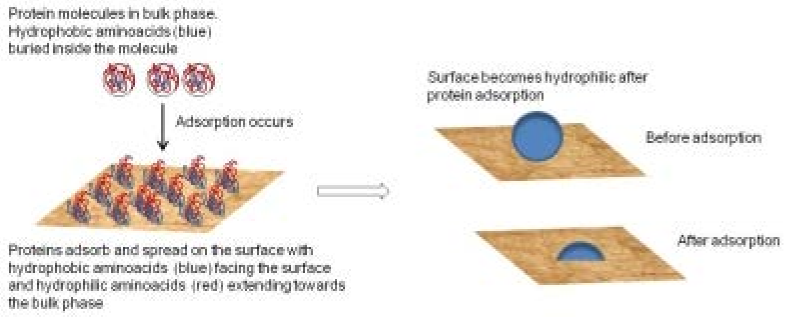


Thursday, April 11, 2013 08:00 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

557 - Surface modification of hydrophobic substrates by soy protein adsorption

Carlos L. Salas[1], *clsalasa@ncsu.edu, Orlando J. Rojas*[1,2], *Jan Genzer*[2], *Martin A. Hubbe*[1], *Lucian Lucia*[1]. *(1) Forest Biomaterials, North Carolina State University, Raleigh, NC 27695-8005, United States, (2) Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-8005, United States*

Controlling wettability of hydrophobic materials is very important in a variety of applications, including textiles, membranes, etc. In this work, the enhancement of wettability of hydrophobic polypropylene nonwovens was studied by physical adsorption of soybean proteins. Adsorption from aqueous solutions (PBS, pH 7.4, 25 °C) on polypropylene and nylon 6 thin films was studied by using Quartz Crystal Microbalance and Surface Plasmon Resonance. A higher adsorbed mass was measured on the polypropylene surfaces compared to nylon 6, which highlights the role of hydrophobic interactions in the adsorption process. Nonwoven substrates were immersed into 1 mg/ml protein solutions at native (25 °C) and denatured condition (95 °C). The change in contact angle from 118° to completely wettable surfaces (0°) indicate a significant improvement in surface wettability. Wicking tests with ultrapure water indicate that after protein adsorption at native or denatured conditions the hydrophobic nonwoven are able to absorb water from 14 to 18 times their weight.

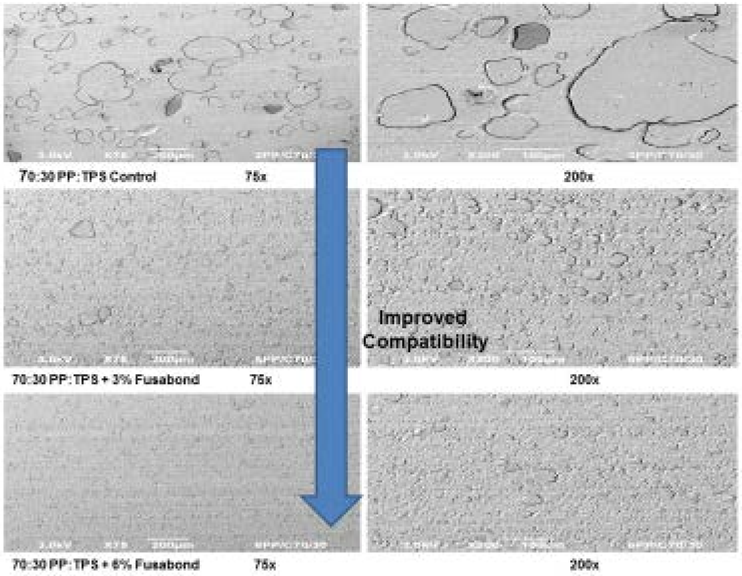


Thursday, April 11, 2013 08:30 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

558 - Thermoplastic carbohydrate polymers for sustainable applications

***James H. Wang**, jhwang@kcc.com, Gregory Wideman. Corporate Research and Engineering, Kimberly-Clark Corporation, Neenah, WI 54956, United States*

Carbohydrate polymers are the most abundant natural polymers on earth. The most common natural carbohydrates include cellulose, hemicellulose, starch, etc. A wide variety of high volume renewable carbohydrates are produced by photosynthesis each year. Carbohydrate polymers should play a vital role to meet the increasing need of sustainable polymers of the society. This paper will focus on one of the carbohydrate polymers -starch for thermoplastic applications. In order to extrude starch, it had to be converted into thermoplastic starch (TPS), but the TPS has poor mechanical properties and limited processability. In the first part, TPS was successfully modified by biodegradable polymers including polylactic acid (PLA) and a biodegradable copolyester for sustainable film applications. Highly ductile biodegradable films with balanced mechanical properties were developed. In the second part, TPS was investigated for sustainable injection molding applications. To overcome the incompatibility between TPS and polypropylene (PP), a compatibilizer was found effective to improve the tensile properties of the resulting injection molded materials. The effect of compatibilizer was further demonstrated by Scanning Electron Microscopy (SEM) showing significantly improved dispersion with the presence of and increasing level of the compatibilizer. The results of this presentation will show that it is possible to utilize thermoplastic starch in sustainable film and molding applications by simultaneously engineering the microstructure of the TPS-containing blends containing and improving the melt processability.

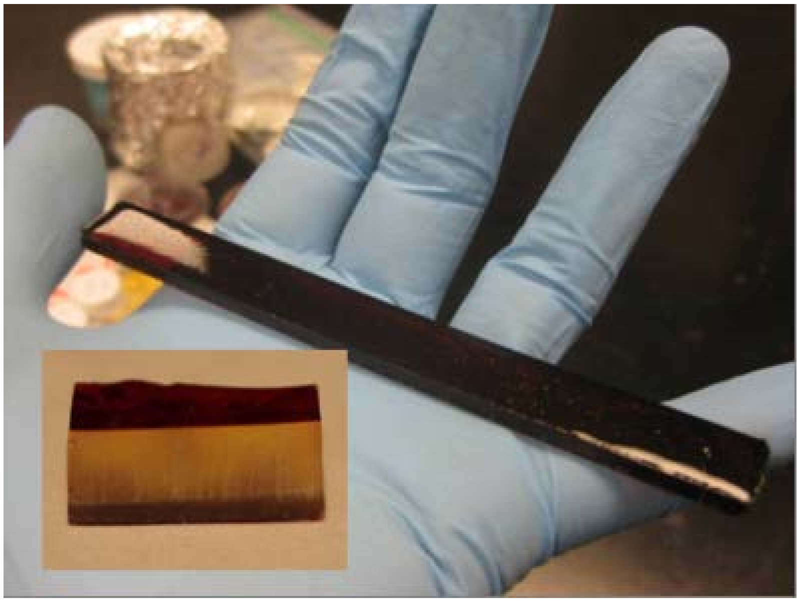


Thursday, April 11, 2013 08:50 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

559 - Minimally toxic bio-derived structural adhesives

*Shivshankar Sivasubramanian[1], Khozema Jafferji[1], Daniel F. Schmidt[1], **Emmanuelle Reynaud**[2], emmanuelle_reynaud@uml.edu. (1) Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, United States, (2) Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, MA 01854, United States*

In the context of alternatives to petroleum-derived thermosets for engineered wood products, this study focuses on bio-derived, non-toxic epoxidized linseed oil cured with low toxicity poly(ethyleneimine). We present the results of our efforts to optimize resin composition and curing procedures (the final material is shown below) and report the performance of the resultant materials, both neat and reinforced with nanoclays. The formation of particle board based on the optimized resin gives properties on par with commercially available systems.

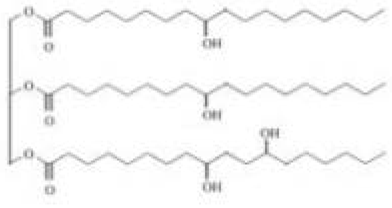


Thursday, April 11, 2013 09:20 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

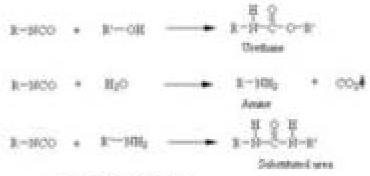
560 - Use of renewable resources in the manufacturing of automotive interior components

Hamdy Khalil, *hamdy_khalil@WoodbridgeGroup.com, Woodbridge Foam Corporation, Woodbridge, ON, Canada*

The selection, validation and commercialization of Automotive Interior Components that are manufactured with various percentages of chemicals or products derived from renewable and sustainable resources will presented.



Soy Oil Based Polyol



Basic reactions

Thursday, April 11, 2013 09:40 AM

Natural and Renewable Polymers (08:00 AM - 12:05 PM)

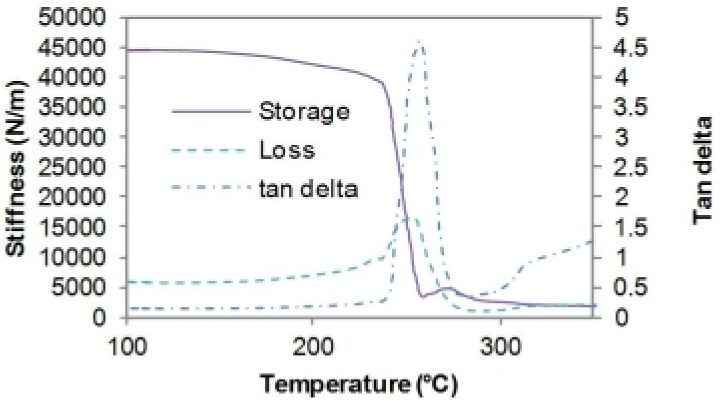
Location: Hilton Riverside

Room: Ste. A, Sec 6

561 - Structure/property relationships of cyanate ester resins from renewable sources

Christopher Sahagun[1], *christopher.sahagun.ctr@edwards.af.mil*, *Heather Meylemans*[2], *Benjamin Harvey*[2], *Kevin Lamison*[3], *Josiah Reams*[3], *Andrew Guenthner*[4], *Lee Cambrea*[2], *Thomas Groshens*[2], *Lawrence Baldwin*[2], *Michael Garrison*[2], *Joseph Mabry*[4]. *(1) Aerospace Systems Directorate, National Research Council / Air Force Research Laboratory, Edwards AFB, California 93524, United States, (2) NAWCWD Research Department, US Navy, China Lake, California 93555, United States, (3) AFRL Aerospace Systems Directorate, ERC, Inc., Edwards AFB, California 93524, United States, (4) Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, California 93524, United States*

This work presents the results of an investigation into the structure/property relationships of a series of cyanate ester resins prepared from renewable precursors derived from lignin. These materials possess thermal and water uptake properties comparable to conventional cyanate ester resins with dry glass transition temperatures above 200°C and wet glass transition temperatures above 175°C with water uptake below 4%. Char yields of the resins were around 30% under nitrogen and around 10% in air. Differential scanning calorimetry showed that resins with more sterically restrictive bridge groups between the reactive moieties cure more slowly, yet also more completely. The favorable physical properties of these resins suggest that they are appropriate for demanding environments with a variety of potential uses in military and commercial applications.



Thursday, April 11, 2013 10:25 AM

Natural and Renewable Polymers (08:00 AM - 12:05 PM)

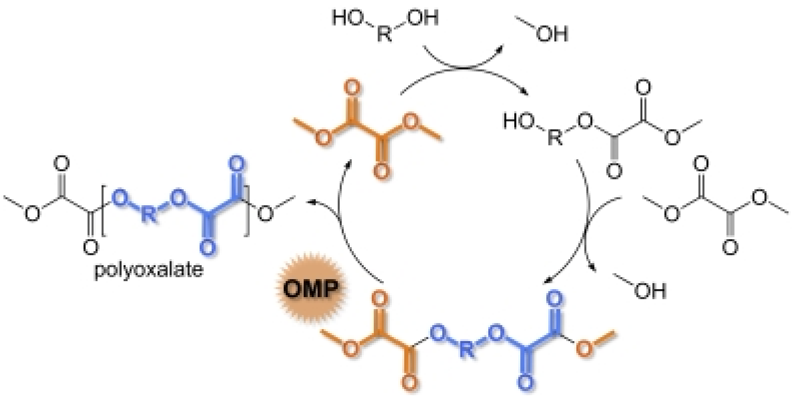
Location: Hilton Riverside

Room: Ste. A, Sec 6

562 - Pinpointing the thermal properties of renewable polycarbonates and polyoxalates

Stephen A. Miller, *miller@chem.ufl.edu, Rob Vanderhenst, John J. Garcia. Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States*

Worldwide efforts have increased greatly to identify polymeric building blocks that are not derived from fossil fuels and to employ these monomers to create polymers that readily degrade in natural environments. We have developed novel methods for synthesizing linear thermoplastic polymers from a variety of biogenic feedstocks, including sugars, triglycerides, lignin, and C1 feedstocks that can be obtained from trees. This presentation will focus on methodology that directly converts renewable diols into polycarbonates and polyoxalates. Diol selection and copolymerization strategies are crucial for tuning the thermal properties. These novel thermoplastics will be discussed in the context of replacing specific petroleum-based plastics.

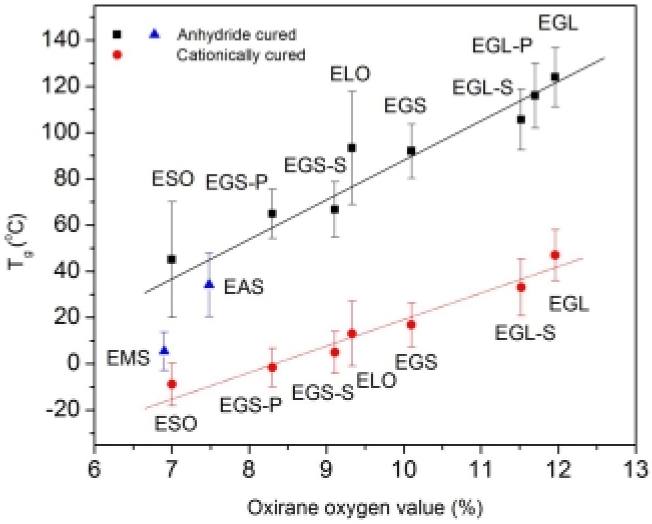


Thursday, April 11, 2013 10:45 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

563 - Structure-property relationships of vegetable oil derived epoxy monomers and thermosetting polymers

Rongpeng Wang, ***Thomas P Schuman***, *tschuman@mst.edu. Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States*

Epoxidized glycidyl esters of fatty acids (EGE) derived from soybean oil/linseed oil have been synthesized to have higher oxirane contents and enhanced reactivities compared to epoxidized soybean oil (ESO), epoxidized linseed oil (ELO) or epoxidized alkyl soyate (EAS). The thermoset polymers were fabricated through direct cationic curing of the epoxy monomers or by copolymerization with anhydride or polyamines. The curing behaviors of each system and glass transition temperatures (T_g) of the respective polymers were monitored by differential scanning calorimetry. The performance of the polymer products was further studied by measurements of thermal stability and mechanical properties. The results indicated that T_g and performance, i.e., reactivity and strength, of the vegetable oil derived epoxies were mostly a function of the respective oxirane contents.



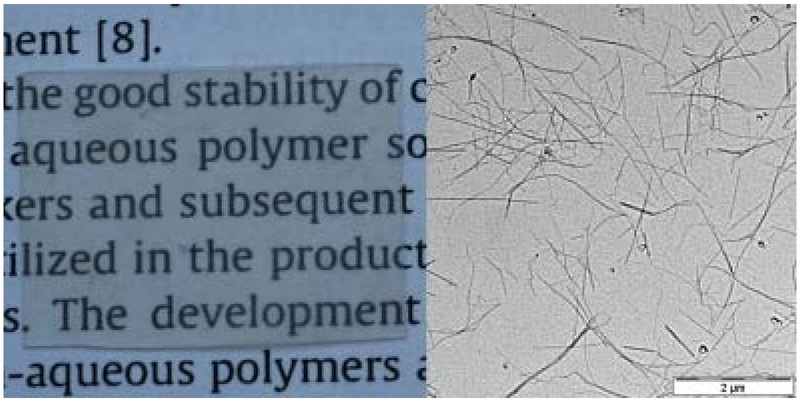
Performance was enhanced by presence of the glycidyl moiety versus only internal oxirane. In addition, the presence of pendant chain chemical structures or presence of saturated components tended to reduce performance. Therefore, EGE products displayed improved T_g and mechanical properties compared to their ESO or ELO counterparts or EAS. An added benefit is that the biorenewable EGEs have inherently low viscosity, are efficient solvents with regard to viscosity reduction and superior as a reactive diluent for commercial epoxy, the diglycidyl ether of bisphenol A (DGEBA). EGE could be advantageous for defect-free fabrication of complex, shaped epoxy composites for structural applications by modern resin infusion techniques.

Thursday, April 11, 2013 11:15 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

564 - Photo-responsive mechanically adaptive bio-nanocomposites

***E. Johan Foster**, johan.foster@unifr.ch, Mahesh Biyani, Christoph Weder. Adolphe Merkle Institute, University Of Fribourg, Fribourg, Switzerland*

Stimuli-responsive nanocomposite materials which change their mechanical properties in response to external stimuli have attracted significant interest for using in broad spectrum applications. The incorporation of high-stiffness, high-surface-area nanofibers with switchable interactions into a polymer matrix has rapidly emerged as a versatile design strategy to create nanocomposites properties that react to a variety of stimuli. We will present our experimental research focused on the design, synthesis and possible applications of photo-responsive cellulose nanofibers, which can act as an adaptive filler within a soft polymer matrix, as well as provide a handle to tune the interactions within the nanocomposite. Photoactive moieties have been covalently attached to cellulose nanofibers and we show that both irreversible and reversible changes can be optically induced as a result of altering the interactions between the nanofibers and therewith the mechanical properties of materials comprising these fillers.

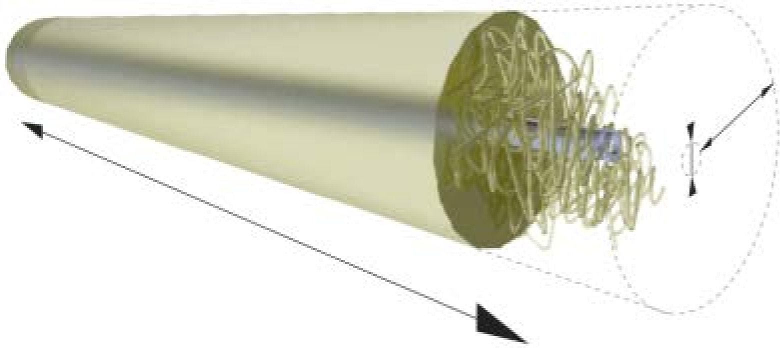


Thursday, April 11, 2013 11:35 AM
Natural and Renewable Polymers (08:00 AM - 12:05 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

565 - On the self assembly of (cyclic peptide)-polymers in the design of complex nanostructures

Ming Liang Koh[1], *m.koh@chem.usyd.edu.au, Katrina A Jolliffe*[2], *Sebastien Perrier*[1]. *(1) Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, The University of Sydney, NSW 2006, Australia, (2) School of Chemistry, The University of Sydney, The University of Sydney, NSW 2006, Australia*

We present the use of self assembling (cyclic peptide)-polymer conjugates as a means to obtain nanotubular structures of targeted dimensions with versatility to be functionalized. Adopting a convergent synthetic approach, microwave assisted copper(i) azide-alkyne cycloaddition was used in conjugating peptides to polymers and the subsequent self assembled structures were investigated. Here we report on our findings in achieving nanotubes of geometrically designed dimensions.



Thursday, April 11, 2013 09:00 AM

General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)

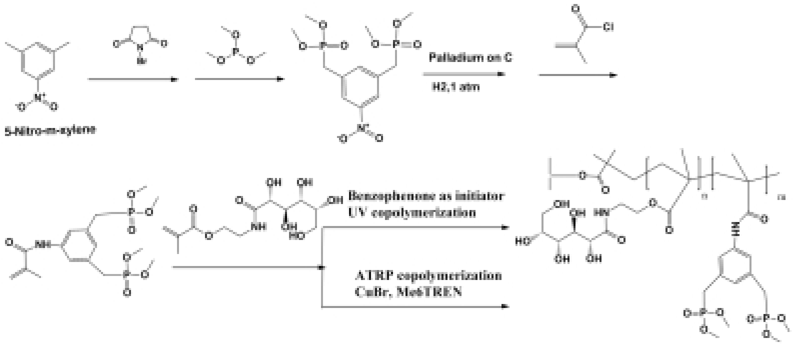
Location: Hilton Riverside

Room: Ste. C, Sec 15

566 - Developing synthetic high affinity membrane absorbers for protein separations

Zizhao Liu, *cscjlzz@hotmail.com, Qian Yang, Sumith R Wickramasinghe, Xianghong Qian. Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, United States*

Functional copolymerization provides an attractive strategy to generate novel surfaces and materials for specific separations. Bisphosphonate dendrimers and one of its copolymers have already demonstrated their high affinities for arginine rich proteins such as lysozyme. In order to further improve its potential for industrial bioseparation applications, copolymers of bisphosphonate with highly hydrophilic and flexible D-gluconamidoethyl methacrylate and other monomers were grafted from a membrane surface using both atom transfer radical polymerization and UV polymerization as shown



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Thursday, April 11, 2013 09:20 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

567 - Clickable nucleic acids

Weixian Xi, *Weixian.xi@colorado.edu, Chemical & Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303, United States*

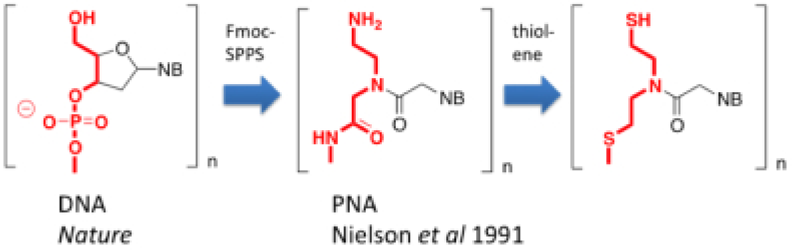
Clickable Nucleic Acids

Weixian Xi,[†] *Tao Gong,* [†] *Christopher J. Kloxin*[§], *Christopher N. Bowman*[†*]

[†]Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309 0424, United States

[§]Department of Materials Science & Engineering and Department of Chemical & Biomolecular Engineering, University of Delaware 150 Academy Street, Newark, Delaware 19716, United States

Abstract -A novel DNA homolog comprising clickable nucleic acids (CNAs) was developed based on thiol-ene 'click' chemistry. Four CNA monomers (A, T, G, C) were designed, synthesized and polymerized via the photo-initiated thiol-ene reaction. The preliminary results demonstrate the capacity of CNAs to bind with complementary DNA strands by Circular Dichroism spectroscopy. The melting temperature (*Tm*) determination results suggested that our CAN oligomers have higher affinity for the complimentary DNA strand than DNA itself does. Finally, surface modification experiments using CNA-DNA (fluorescence) showed one potential application of CNA-DNA hybrids.



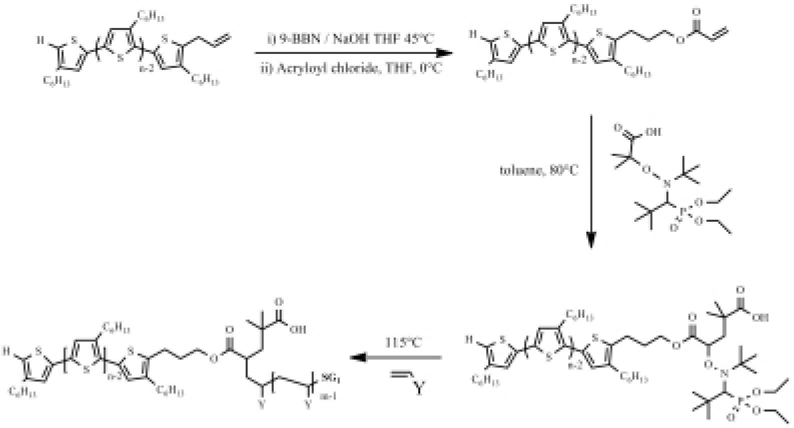
Thursday, April 11, 2013 09:40 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

568 - Design of semi-conducting graft and block copolymers through controlled radical polymerization: A tool box for nanostructured materials in organic electronic

Cyril Brochon[1,2], *cyril.brochon@enscbp.fr, Sébastien-Jun Mougnier*[1,2], *Eric Cloutet*[1,2], *Georges Hadziioannou*[1,2]. *(1) LCPO, Université de Bordeaux, Pessac, Select State 33607, France, (2) LCPO, CNRS, Pessac, Select State 33607, France*

Semi-conducting polymers are well soluble and processable at large scale. Among these materials, rod-coil block copolymers are very promising in organic electronic.

These copolymers can be obtained by various ways. In this contribution, we present recent results about the controlled synthesis of end-functionalized poly(3-hexylthiophene) (P3HT) and their use as building blocks for well-defined copolymers. Several synthetic routes have been developed (using mainly NMRP) in order to obtain pure materials for optoelectronic applications. Various P3HT based rod-coil copolymers have been synthesized.[1]



Recent results about more complex architectures are also presented.[2] Finally, as an example of application, the positive effect of the use of one of these copolymers in an organic photovoltaic solar cell is reported.[3]

1. S.-J. Mougnier, *et al.* J*ournal of Polymer Science part A* (2012) 50, 2463-2470

2. S.-J. Mougnier, *et al. Macromolecular Rapid Communications*(2012) 33, 703-709

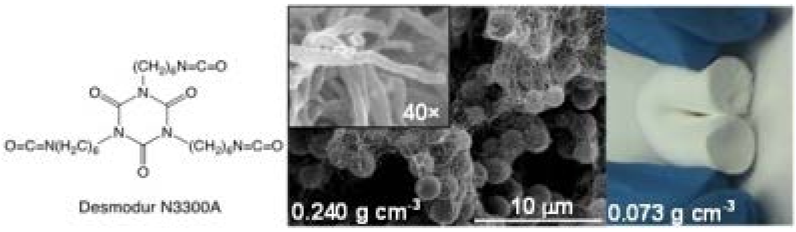
3 S.-J. Mougnier, *et al. Advanced Materials* (2012) 24, 2196-2201

Thursday, April 11, 2013 10:00 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

569 - Flexible polyurea aerogels: The effect of the polarity of the gelation medium on the nanomorphology

Chakkaravarthy Chidambareswarapattar, *ccxk4@mail.mst.edu, Chariklia Sotiriou-Leventis, Nicholas Leventis. Department of Chemistry, Missouri University of Science & Technology, Rolla, Missouri 65401, United States*

Mechanically strong polyurea (PUA) aerogels have been synthesized in acetone from Desmodur N3300A triisocyanate, water and triethylamine (TEA) as catalyst. Curiously, the nanomorphology of PUA aerogels varies from fibrous to particulate as the density increases. Reasoning that higher monomer concentrations (as high as 0.52 M) change the dielectric properties of the medium, herein we emulate that effect by changing the solvent polarity, and we report synthesis of PUA aerogels with nanomorphologies varying from similar to those obtained in acetone (e.g., in ethyl acetate), to cocoon-like structures embedded in a fiber web (e.g., see Figure below in acetonitrile). Some of those materials are flexible, while others demonstrate low speed of sound wave propagation (198 m s^{-1} at 0.340 g cm^{-3}) and are suitable for acoustic insulation.



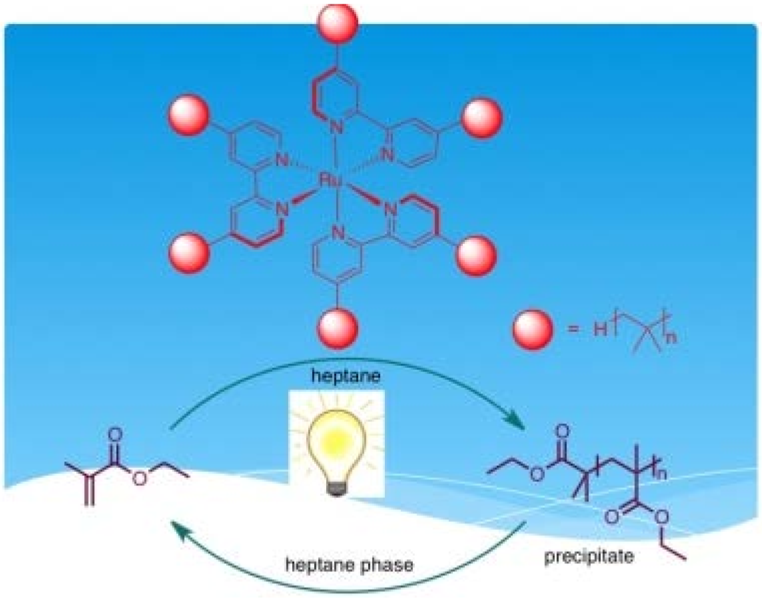
Thursday, April 11, 2013 10:20 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

570 - Greener reusable polyisobutylene bound ruthenium bispyridine photoredox catalyst

Nilusha Priyadarshani, *upriyadarshani@chem.tamu.edu, David Bergbreiter. Department of Chemistry, Texas A&M University, College Stataion, Texas 77842, United States*

By using polyisobutylene (PIB) alkylating agents that are highly soluble, bispyridine ligands capable of immobilizing transition metals have been immobilized on an easily separable soluble polymer support (polyisobutylene/ PIB). The resulting ligands were then used to synthesize a reusable homogeneous photoredox catalyst that can be used for visible light mediated free radical polymerization reactions at ambient temperature. In this chemistry, a 4, 4'-dimethyl bipyridine group was deprotonated at -78 °C and coupled to a PIB-bromide. The resulting PIB-bound bispyridine ligand was then used to form a ruthenium chloride complex that is analogous to low molecular weight $(bipy)_3RuCl_2$ catalysts others have used for a variety of photoredox catalytic reactions.

These PIB-bound photocatalysts are phase selectively soluble in non-polar solvents such as heptane, toluene and dichloromethane due to the PIB group and can be separated from polar solutions or polar products by a biphasic separation after a reaction. For example, this PIB-bound ruthenium photocatalyst shows excellent catalytic activity in free radical polymerizations of ethyl methacrylate monomers in a non-polar solvent such as heptane, under household fluorescent lamp irradiation. Upon polymerization the polymer precipitates from heptane solution while the catalyst remains in the solution. The catalyst then can be separated from the poly(ethyl methacrylate) product and reused without lost of catalytic activity.

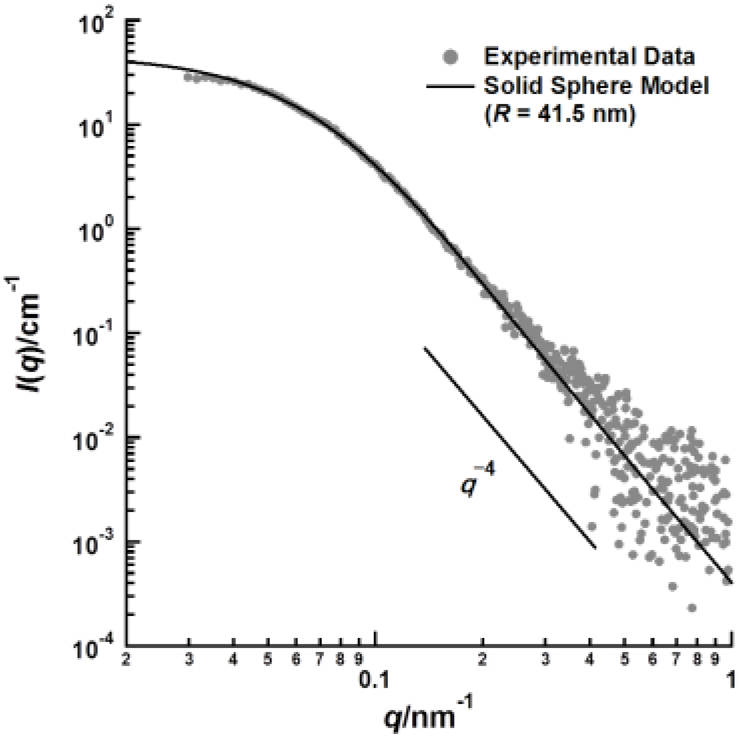


Thursday, April 11, 2013 10:40 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

571 - Characterization of molecular assembly in amphiphilic polymers with anomalous small-angle X-ray scattering

Isamu Akiba, *akiba@kitakyu-u.ac.jp, Megumi Sakou, Atsuro Takechi, Kazuo Sakurai. Department of Chemistry and Biochemistry, The University of Kitakyushu, Kitakyushu, Fukuoka 8080135, Japan*

Anomalous small-angle X-ray scattering (ASAXS) was applied for structural characterization of molecular assembly of poly(4-vinylphenol)-*block*-poly(p-bromostyrene) in alkaline solution. Figure 1 shows scattering contribution of hydrophobic domain composed of poly(4-bromostyrene) extracted from scattering profile of whole molecular assembly.



Numerical analysis for this profile reveals the hydrophobic domain forms spherical shape with smooth interface. Thus, using the ASAXS, we can separately obtain the scattering contributions of hydrophobic and hydrophilic domains in the molecular assembies and precisely characterize their internal structures.

Thursday, April 11, 2013 11:00 AM

General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)

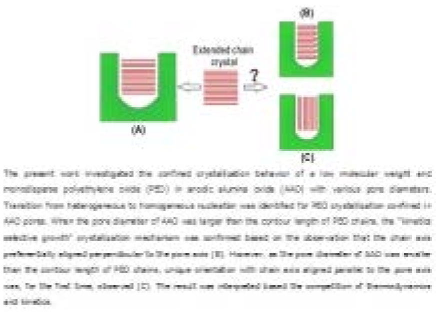
Location: Hilton Riverside

Room: Ste. C, Sec 15

572 - Nano-confined crystallization of polymer: from kinetics control to thermodynamics priority

*Yu Guan, Guoming Liu, **Dujin Wang**, djwang@iccas.ac.cn. Chinese Academy of Sciences, Institute of Chemistry, Beijing, China*

The present work investigated the confined crystallization behavior of a low molecular weight and monodisperse polyethylene oxide (PEO) in anodic alumina oxide (AAO) with various pore diameters. Transition from heterogeneous to homogeneous nucleation was identified for PEO crystallization confined in AAO pores. When the pore diameter of AAO was larger than the contour length of PEO chains, the “kinetics selective growth” crystallization mechanism was confirmed based on the observation that the chain axis preferentially aligned perpendicular to the pore axis. However, as the pore diameter of AAO was smaller than the contour length of PEO chains, unique orientation with chain axis aligned parallel to the pore axis was, for the first time, observed. The result was interpreted based the competition of thermodynamics and kinetics.



Thursday, April 11, 2013 11:20 AM

General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)

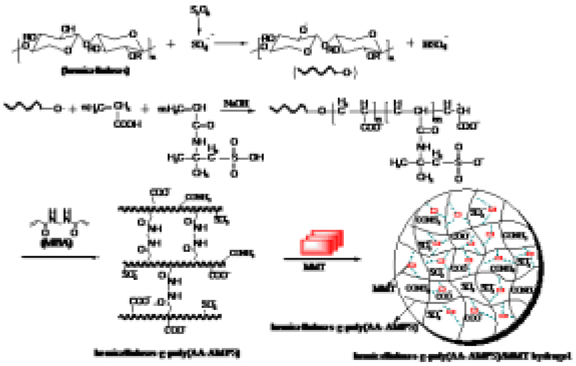
Location: Hilton Riverside

Room: Ste. C, Sec 15

573 - Synthesis and characterization of superabsorbent hydrogels based on hemicelluloses and montmorillonite

Feng Peng[1], *pengfeng0523@yahoo.com.cn*, *Yan Fang*[2], *Ying Guan*[1], *Jing BIan*[1], *Run-Cang Sun*[1,3]. *(1) Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing, China, (2) College of Chemistry and Molecular Sciences, College of Chemistry and Molecular Science, Wuhan, Hubei 430072, China, (3) State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China*

The unique organic/inorganic superabsorbent hydrogels based on hemicelluloses and inorganic caly montmorillonite (MMT) were prepared via grafting copolymerization of acrylic acid (AA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) with *N,N*-methylenebis-acrylamide (MBA) as a crosslinking agent and potassium persulfate (KPS) as an initiator. The network characteristics of the organic/inorganic hydrogels were investigated by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The effect of variables on the swelling capacity of the hydrogels, such as the weight ratios of MMT/hemicelluloses, MBA/hemicelluloses, AMPS/AA, and particle size, were systematically optimized. The results indicated that the superabsorbent hydrogels comprised a porous crosslinking structure of MMT and hemicelluloses with side chains that carry carboxylate, carboxamide, and sulfate. The maximum equilibrium swelling ratios of hydrogels in distilled water and 0.9 wt% sodium chloride solution were up to 1423 $g \cdot g^{-1}$ and 69 $g \cdot g^{-1}$, respectively. The effect of various cationic salt solutions ($LiCl$, $CaCl_2$, and $AlCl_3$) on the swelling has the following order: $Li^{+} > Ca^{2+} > Al^{3+}$. Furthermore, the influence of pH values on swelling behaviors showed that the superabsorbent composites retained around 1000 $g \cdot g^{-1}$ over a wide pH range of 6.0-10.0.

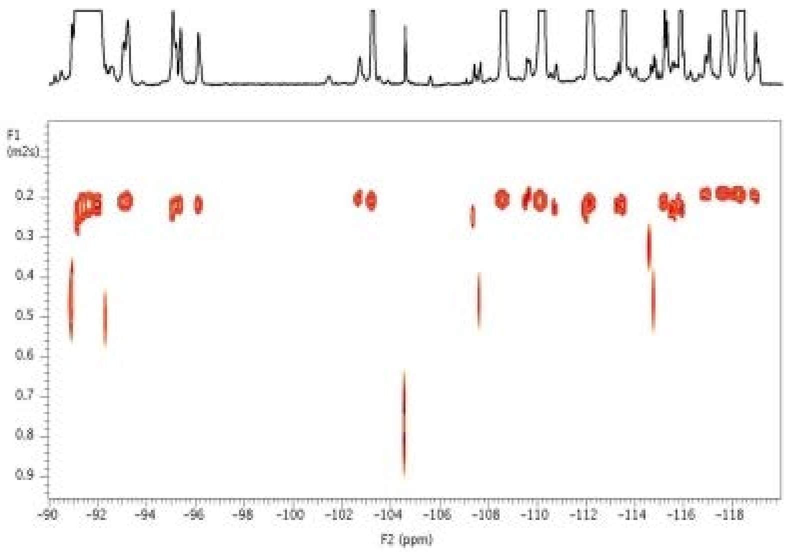


Thursday, April 11, 2013 11:40 AM
General Topics: New Synthesis and Characterization of Polymers (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

574 - Multidimensional NMR characterization of chain-end structures in P(VDF-HFP) copolymers and P(VDF-HFP-TFE) terpolymers

Eric B Twum[1], *ebt5@zips.uakron.edu, Elizabeth F McCord*[2]*, Peter A Fox*[2]*, Donald F Lyons*[2]*, Peter L Rinaldi*[1]*. (1) Department of Chemistry, The University of Akron, Akron, OH 44325, United States, (2) Experimental Station Laboratory, E. I. du Pont de Nemours and Co., Wilmington, DE 19880, United States*

^{19}F and ^{1}H NMRexperiments have been used to assign the resonances of chain-ends and chain branching structures in P(VDF-HFP) copolymers and P(VDF-HFP-TFE) terpolymers. Multidimensional NMR experiments, spin-lattice relaxation (T_1) analysis, and diffusion ordered spectroscopy (DOSY) NMR were used as complementary methods to identify and also to obtain the structure of the end groups in these polymers. Resonances of chain branching structures were also identified with T_1 and 2D DOSY NMR experiments; other 2D-NMR experiments, such as selective correlation spectroscopy (COSY) and gradient heteronuclear single quantum coherence (gHSQC) were used to provide atomic connectivity information thereby obtaining their resonance assignments. Furthermore, the compositions of each monomer involved in these polymers were calculated. Finally, the amount of each end group in the P(VDF-HFP) copolymer was quantified with the aid of an internal standard (1,4-dichloro-2-(trifluoromethyl)benzene). The end group -CH_2CF_2H is found to be the most prevalent in the copolymer under study.

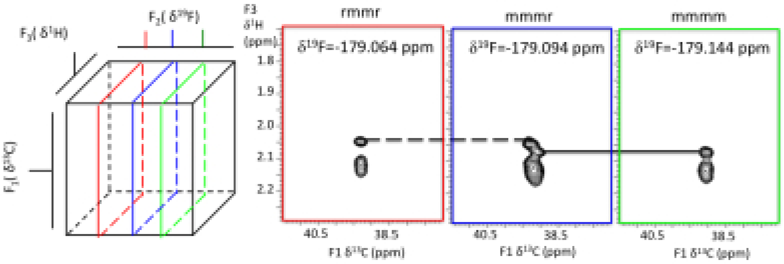


Thursday, April 11, 2013 09:00 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

575 - Characterization of stereo-sequences in poly(vinyl fluoride) by $^1H/^{13}C/^{19}F$ 3D-NMR

Linlin Li[1], *ll29@zips.uakron.edu, Bo Zhang*[1]*, Faith Wyzgoski*[2]*, Elizabeth F. McCord*[3]*, Xiaohong Li*[1]*, Peter A. Fox*[3]*, Donald F. Lyons*[3]*, Peter L. Rinaldi*[1]*. (1) Department of Chemistry, University of Akron, Akron, OH 44325, United States, (2) Department of Chemistry, Ohio State University, Mansfield, OH 44906, United States, (3) Experimental Station Laboratory, E. I. du Pont de Nemours and Co., Wilmington, DE 19880, United States*

Tacticity has an enormous influence on the physical and chemical properties of polymers. There is considerable work using 1D-NMR and empirical rules to study the stereo-sequences in polymers. This work suggests that $^1H/^{13}C/^{19}F$ 3D-NMR experiments can provide superior resolution and atomic connectivity information, so that unambiguous resonance assignment can be made for poly(vinyl fluoride) (PVF). Compared to prior work on 3D-NMR studies of stereosequence effects in fluoropolymers, the 3D-NMR pulse sequence used in this work is based on single quantum coherence transfer, which eliminates the complicated splitting patterns resulting from evolution of multi-quantum coherence. In addition, selective excitation of the ^{19}F nuclei of interest significantly reduces the folding of peaks from other spectral regions. This greatly simplifies the spectra and makes the assignment of resonances much easier. Based on our results, it is possible to assign the ^{19}F resonance to the pentad level. For example, consider the resonances of mm-centered sequences, which are not well resolved in ^{19}F-^{19}F COSY 2D-NMR spectrum, $^1H/^{13}C/^{19}F$ 3D-NMR data provide clear evidences for all of the three pentad structures: mmmm, mmmr and rmmr. Examples showing the resonance assignments of head-to-tail and head-to-head sequences will be presented.



Thursday, April 11, 2013 09:25 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

Location: Hilton Riverside

Room: Ste. C, Sec 18

576 - Stereoregularity analysis of poly lactic acid by solution NMR

Koto Suganuma[1,2], *ko.suganuma@teijin.co.jp, Ken Horiuchi*[2], *Hironori Matsuda*[2], *H.N. Cheng*[3], *Koichi Ute*[4], *Tetsuo Asakura*[1]. *(1) Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, (2) Material analysis research laboratories, Teijin limited, Hino, Tokyo 191-8512, Japan, (3) Southern Regional Research Center, United States Department of Agriculture, New Orleans, Louisiana 70124, United States, (4) Department of Chemical Science and Technology, The University of Tokushima, Tokushima, Tokushima 770-8506, Japan*

In order to understand the origin of the tacticity splitting in the NMR spectra of poly(lactic acid), monomer, dimer and trimer model compounds were synthesized and their ^{1}H and ^{13}C NMR chemical shifts were observed. And the chemical shifts for dimer model compounds were calculated by averaging the occurrence probabilities obtained from the optimized conformational energies and the calculated chemical shift of each conformation. As shown in Figure 1, a good agreement between observed and calculated chemical shifts was obtained.

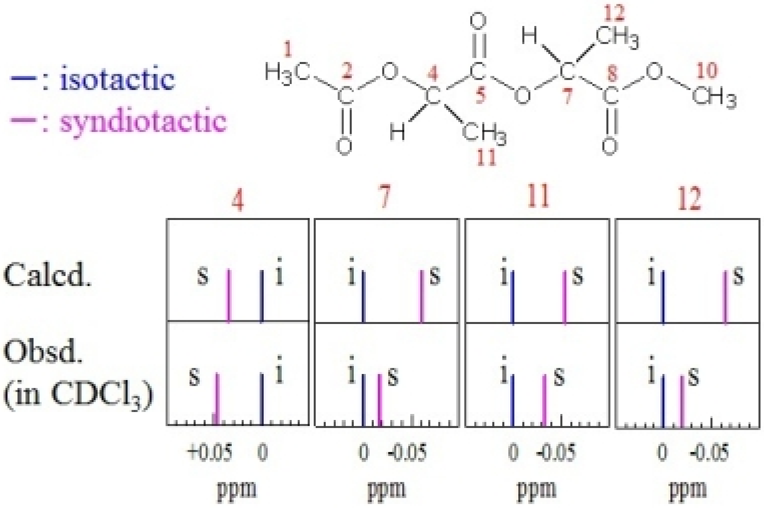


Fig.1 Comparison of the observed and calculated ^{1}H chemical shifts (in ppm) of dimer model compound of poly(lactic acid) shown as stick spectra.

Thursday, April 11, 2013 09:50 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

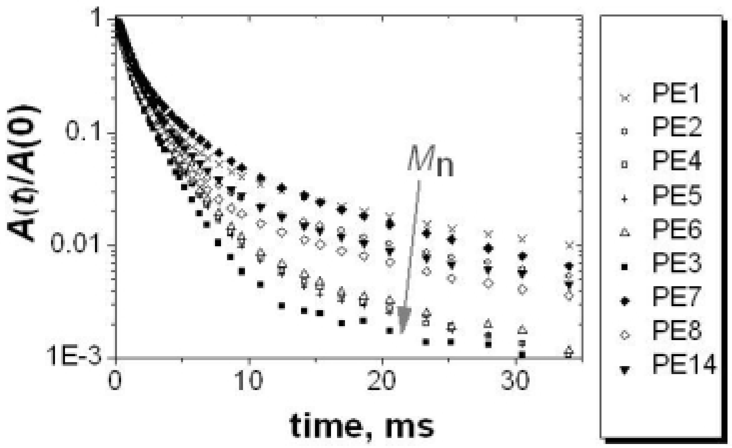
Location: Hilton Riverside

Room: Ste. C, Sec 18

577 - Chain entanglements in polyethylene melts: Why it is studied again?

Travis W Baughman[1], *travis.baughman@dsm.com, Victor Litvinov*[2]*, Mike E Reis*[3]*, Artur Henke*[2]*, Piotr P Matloka*[1]*. (1) DSM Ahead, Geleen, The Netherlands, (2) DSM Resolve, Geleen, The Netherlands, (3) School of Physics & Astronomy, University of Leeds, Leeds, United Kingdom*

Entanglement density of polymers is important characteristic of long chain molecules that largely determines melt viscoelasticity, the strength of interfacial adhesion in polymer composites, and dynamic and fracture properties among other critical aspects of macromolecular morphology and material performance. Two structural characteristics affect the entanglement density: 1) the primary chemical structure of polymer chains and 2) the molecular architecture, both of which are typically defined by the number- and weight-average molecular weight of polymer chains (M_n and M_w), molecular weight distribution, and the amount, average length and distribution of long chain branches. Several methods have been applied for the quantification of the entanglement density including numerous rheological methods, neutron spin-echo experiments, and NMR relaxation methods among computational treatments via Monte Carlo simulations. The aim of the present study is to revisit the characterization of entanglement density in polyethylene melts by studying a series of well-defined, high molecular weight polyethylene materials via transverse NMR relaxometry at 150^{o}C. The comparison of the relaxometry data with high temperature SEC-MALLS characterization allows the measurement and correlation of the fraction of chain-end fragments by two independent methods. As compared with rheological methods that measure volume average characteristics, the NMR method described here offers advantages for studying entanglement molecular weight (M_e) and chain dynamics in entangled polyethylene melts due to the high selectivity to dynamics of entangled chain fragments and disentangled chain end blocks.

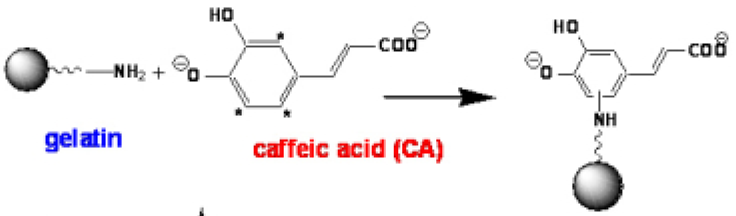


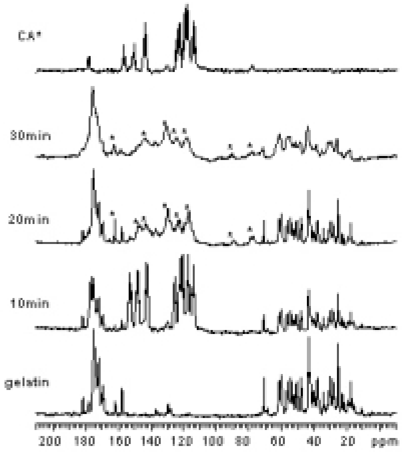
Thursday, April 11, 2013 10:30 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

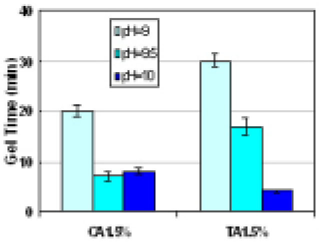
578 - Chemical crosslinking gelatin with natural phenolic compounds as studied by high-resolution NMR spectroscopy

Xiaoqing Zhang, *Xiaoqing.Zhang@csiro.au, Materials Science and Engineering, CSIRO, Melbourne, VIC 3168, Australia*

Crosslinking gelatin with natural phenolic compound such as caffeic acid (CA) or tannic acid (TA) resulted in formation of insoluble hydrogels. The crosslinking reactivity was controlled by variation of pH, the concentration of the gelatin solution, or the amount of CA or TA used in the reaction. Direct evidence was obtained from the NMR study to confirm that chemical reactions occurred between the phenolic reactive sites and the amino groups in gelatin to form C-N covalent bonds as crosslinking linkages. The crosslinking resulted in a significant decrease in the molecular mobility of the hydrogels, and the modulus of the films remained at high values at high temperatures.







Thursday, April 11, 2013 10:55 AM

Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)

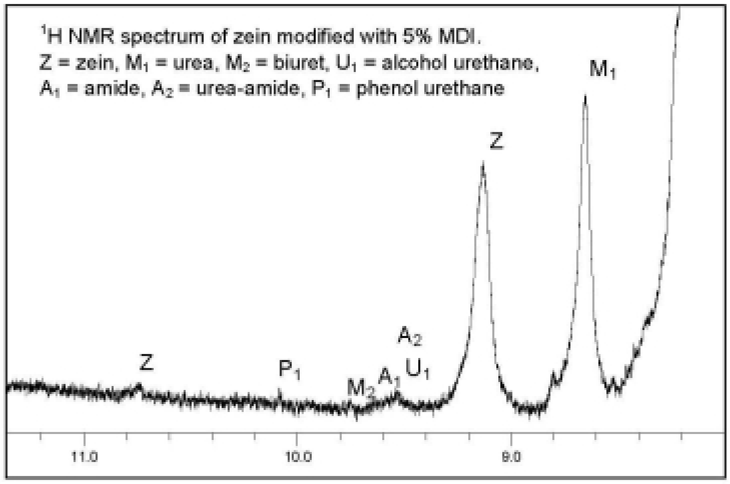
Location: Hilton Riverside

Room: Ste. C, Sec 18

579 - NMR studies of polymers from renewable materials

H. N. Cheng[1], *hn.cheng@ars.usda.gov, Atanu Biswas*[2]. *(1) Southern Regional Research Center, USDA Agricultural Research Service, New Orleans, Louisiana 70124, United States, (2) National Center for Agricultural Utilization Research, USDA Agricultural Research Service, Peoria, Illinois 61604, United States*

There has been a lot of recent interest in using agricultural products as raw materials to produce functional polymers. The motivation is to add value to agricultural products and to decrease the global dependence on petroleum-based feedstock. Moreover, agricultural materials are renewable, biodegradable, and sustainable. NMR is an excellent tool to characterize agricultural products, to monitor reactions, to elucidate reaction mechanisms, and to relate the polymer structures to end-use properties. Several examples where NMR has played an important role in new product development will be shown in this work. These include the production of cellulose derivatives from agricultural residues and the modifications of triglyceride oils using nitrogen-containing reagents. In all these cases, NMR has been used successfully to decipher the product structures and reaction mechanisms. Another example is the derivatization of zein, the main storage protein in corn. (The ^{1}H NMR spectrum of the zein-MDI product is shown in the attached figure.) The use of NMR on the reactions of isocyanates with zein in solution has permitted major reaction pathways to be identified. As a result of the modification reactions, the zein derivatives exhibit improved properties.



Thursday, April 11, 2013 11:20 AM
Understanding Complex Macromolecular and Supramolecular Systems using Innovative Magnetic Resonance Strategies (09:00 AM - 11:45 AM)
Location: Hilton Riverside
Room: Ste. C, Sec 18

580 - Carbon nanomaterials: Basics of mesopitch-derived nanofibers and graphene aerogels

Sadhan C. Jana[1], *janas@uakron.edu, Rafael Benavides*[1]*, Darrell Reneker*[2]*, Enrique Jimenez*[3]*, Senlong Gu*[1]*. (1) Department of Polymer Engineering, University of Akron, Akron, OH 44325, United States, (2) Department of Polymer Science, University of Akron, Akron, OH 44325-3297, United States, (3) Department of Mechanical Engineering and Materials, Technical University of Valencia, Valencia, Spain*

This talk presents new and unique results on synthesis of carbon nanofibers from mesopitch via nanofibers by gas jet (NGJ) method and aerogel structures from graphene. The study covers basic understanding of nanofiber formation from molten mesopitch by the action of tangential flow of air in a patented nozzle. The pitch nanofibers are then converted into graphitic structures by stabilization and graphitization. Graphene aerogels are obtained by reducing graphene oxide in several organic solvents and their bulk density, skeletal density, porosity are measured as function of the solvent used and the degree of reduction of graphene oxide. Results are presented on electrical conductivity and mechanical properties of compounds of carbon nanofibers and graphene aerogels.

Thursday, April 11, 2013 08:35 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

581 - Synthesis of carbon nanomaterials and their hybrids from carbonization of polymers via combined catalysis

TAO TANG, *ttang@ciac.jl.cn, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China*

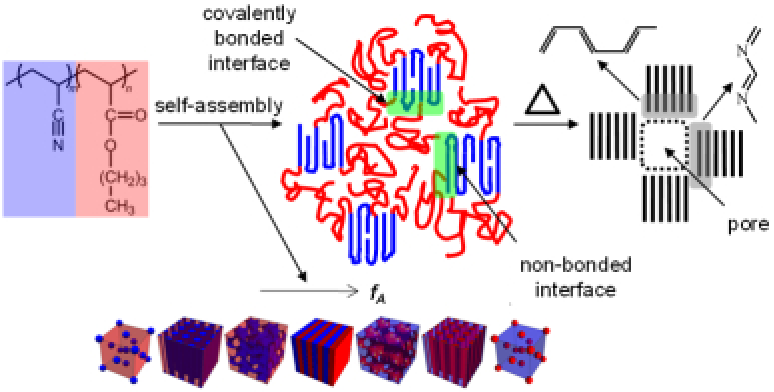
A one-pot method for synthesizing carbon nanomaterials was established. This method was based on the carbonization of polymers catalyzed by combined catalysts. Recently, we have found that nickel catalyst (Ni-Cat) could efficiently catalyze carbonization of the degradation products to form carbon nanotubes (CNTs) or other carbon materials during heating polypropylene (PP) or other polymers in the presence of solid acid (or halogen-containing compounds or active carbon). The mechanism on the combined catalysis of various combinations was investigated. Based on the same method, various kinds of carbon-based hybrids were also synthesized via a one-pot method, such as carbon/metal hybrids and carbon/clay hybrids, which showed potential application in adsorption and catalyst.

Thursday, April 11, 2013 09:05 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

582 - Block copolymer templating as a path to porous nanostructured carbons with highly accessible nitrogens for enhanced (electro)chemical performance

Tomasz Kowalewski, *tomek@andrew.cmu.edu, Mingjiang Zhong, Hunaid Nulwala, Krzysztof Matyjaszewski. Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States*

This presentation will describe the unique features of nitrogen enriched carbons synthesized by pyrolysis of block copolymers containing polyacrylonitrile (PAN) and a sacrificial block, e.g., poly(n-butyl acrylate) (PBA).



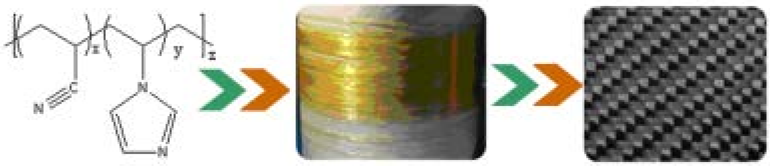
After thermal stabilization the copolymer precursor can be converted into a nitrogen doped carbon material with preservation of original nanostructure and abundance of highly accessible nitrogen heteroatoms originating from PAN. Such structure is particularly beneficial for applications in supercapacitors, electrocatalysis and CO_2 capture.

Thursday, April 11, 2013 09:25 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

583 - Carbon fiber for the masses: From synthesis to low temperature thermal extrusion

Benjamin L. Batchelor, *Ben.Batchelor@utdallas.edu, Samsuddin Faisal Mahmood, Rajneesh Verma, Dennis W Smith. Department of Chemistry and the Alan G. MacDiarmid Nanotech Institute, The University of Texas at Dallas, Richardson, TX 75080, United States*

Carbon fibers and composites are some of the strongest and most durable materials readily available to date. This amazing material has been excluded from mainstream applications such as automotive, aeronautical, and building structures is due to the cost hindrance. In order to address this problem, a copolymer was created known as poly(acrylonitrile-*co*-*N*-vinylimidazole). Due to the polymer's inherent glass transition temperature (T_g) of 110 ºC, the bulk polymer can be thermoformed into fibers at typical processing temperatures around 170 - 200 ºC. Combined with experimentation in the processing parameters and the use of additives, processing temperatures can be lowered due to a decrease in either the thermal properties of the polymer or the melt viscosity of the polymer, while showing negligible effects on mechanical strengths or modulus. The fibers being extruded at low temperatures allows for the retention of thermal properties such as the T_g, which helps in the ease in post extrusion processing and drawing of the fibers down to a lower diameter. The fibers can be drawn from a diameter of 1.5 mm to approximately 30 µm before any stabilization or carbonization even takes place to decrease the diameter even further. The fibers have been stabilized at varying amounts of oxygen concentrations and temperatures to determine the highest amount of strength retained in the material before carbonization to the well known carbon fiber.

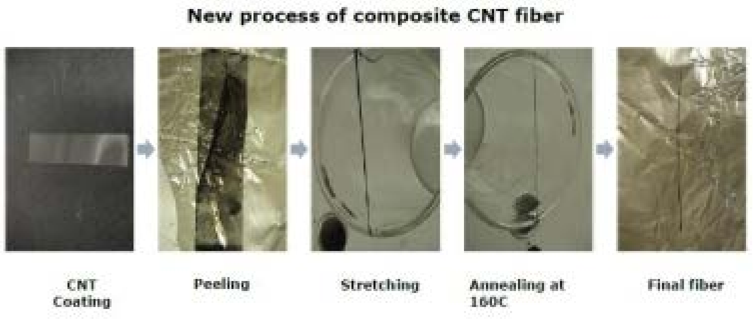


Thursday, April 11, 2013 09:45 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

584 - Novel process for the preparation of composite carbon nanotube fibers/yarns

Abdelaziz Rahy[1], Changheon Kim[1], Sungwoo Ryu[2], Jaewon Hwang[2], Soon Hyung Hong[2], ***Duck J. Yang[1]****, djyang@utdallas.edu. (1) The Alan G. MacDiarmid NanoTech Institute and Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75080, United States, (2) Institute of NanoCentury, Department of Material Science and Engineering, Korea Advanced Institute of Science, Daejeon, Republic of Korea*

A novel and versatile process for the preparation of composite carbon nanotube fibers/yarns having high mechanical properties was discovered. The process can be used for the preparation of various composite CNT fibers not only from single-walled nanotubes (SWNTs), double-walled nanotubes (DWNTs), or multi-walled nanotubes (MWNTs) but also from the mixtures thereof. The process utilizes a thin polymer (PVA: polyvinyl alcohol) layer coated on the PET film strip followed by CNT coating on it and delaminating the CNT coated PVA layer while applying stretching with spinning. Applying annealing at 160C increases its mechanical properties. Mechanical properties of 3.8 GPa tensile strength and 84 GPa Young's modulus using MWNTs with medium MW PVA, and 1.9 GPa of tensile strength and 117 GPa of modulus using MWNTs with High MW PVA as matrix polymer, were obtained.



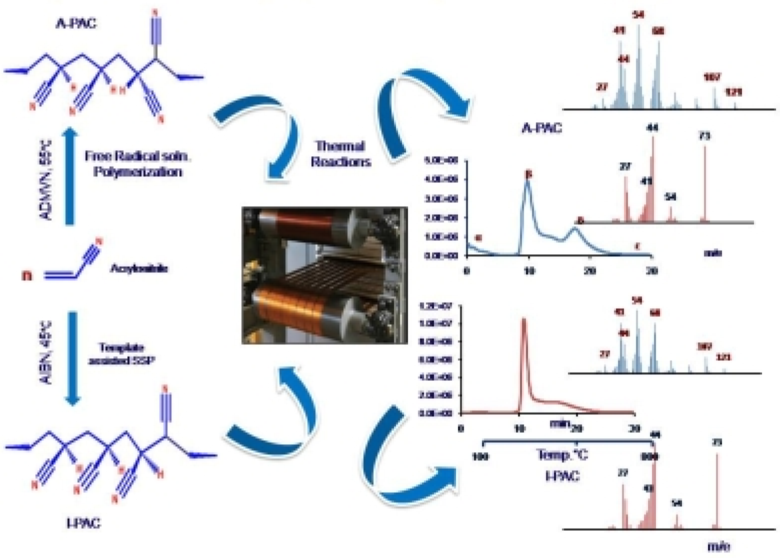
Thursday, April 11, 2013 10:20 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

585 - Studies on thermal degradation and stability of carbon fiber polymer precursors with different triad tacticity contents using hyphenated thermal techniques

Santhana Krishnan*, santhana@nal.res.in, Department of Materials Science, National Aerospace Laboratories, Bangalore, Karnataka 560017, India*

Carbon fiber polymer precursors such as poly (acrylonitrile) polymers (PAC) with different stereoregularities in terms of triad tacticity content i.e., predominantly isotactic (mm % > 40 Wt.) and atactic (mr % >45 Wt.) were synthesized.The molecular weight parameters viz., different average molecular weights (number, weight, size) were determined. The triad tacticity contents were estimated with ^{13}C-NMR techniques. The beneficial influence of higher isotactic triad content of polyacrylonitrile including the structural changes during the thermal oxidativedegradation reactions was investigated employing hyphenated thermal techniques namely Pyrolyzer-Gas Chromatography -Mass spectrometer, and thermal gravimetric analyzer-FT infrared spectrometer in the temperature range of 200-600°C. The thermal analysis results reveal that nitrile polymerization of pendant cyano functionalities precedes pyrolysis reaction in case of isotactic rich PAC leading to a steady and stable thermal oxidative degradation reactions as compared to atactic rich PAC. The mass loss during the thermal reactions was accounted for the evolution of hydrogen cyanide, ammonia and homologous of alkyl nitrile having molar mass between 47 and 147 m/z. The results of evolved gas analysis by simultaneous thermal gravimetric analyzer -Fourier transform infrared (TGA-FTIR) analysis also confirms the results of pyrolysis experiments.The [figure 1] represents experimental results graphically.

Fig. 1: The influence of stereoregularity on the thermal degradation of carbon fiber polymer precursors



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Thursday, April 11, 2013 10:50 AM

Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)

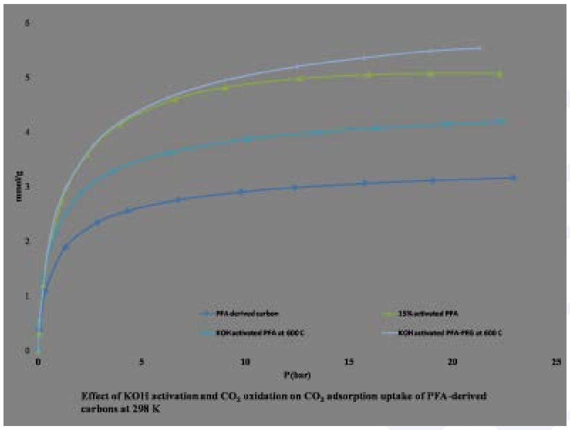
Location: Hilton Riverside

Room: Ste. B, Sec 7/10

586 - Studying the effect of CO_2 oxidation and KOH activation on the textural and gas adsorption properties of microporous polymer-derived carbons

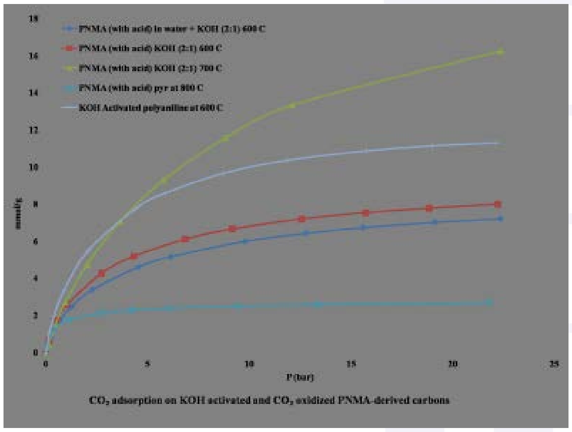
Ali Qajar[1], *axq106@psu.edu, Maryam Peer*[1], *Ramakrishnan Rajagopalan*[2], *Henry C Foley*[1,2]. *(1) Department of Chemical Engineering, Pennsylvania State University, State College, Pennsylvania 16802, United States, (2) Materials Research Lab, Pennsylvania State University, State College, Pennsylvania 16802, United States*

Polyfurfuryl alcohol (PFA) and poly n-methyl aniline (PNMA)-derived precursors are synthesized. The resulting polymer precursors are pyrolized under argon with and without KOH. The induced porosities and textural properties are determined via methyl chloride porosimetry method. Gas adsorption properties of the carbons are evaluated by measuring adsorption of CO_2 on the carbons at room temperature and elevated pressures. The PFA-derived carbons are essentially microporous with pore modes between 0.5 and 1 nm. Such a small pore size of the carbons enhances the CO_2 adsorption uptake



Effect of KOH activation and CO_2 oxidation on CO_2 adsorption uptake of PFA-derived carbons at 298 K

The effect of KOH activation and CO_2 oxidation on the poresize and also presence of nitrogen heteroatom in the carbon framework of PNMA-derived carbon on the CO_2 uptake is studied



CO_2 adsorption on KOH activated and CO_2 oxidized PNMA-derived carbons

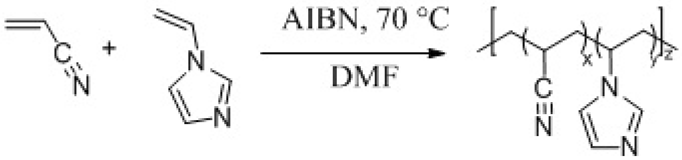
KOH activation method compared to CO_2 oxidation is showing higher adsorption capacities. This behavior cannot only be explained by the effect of poresize and presence of alkali metals inside the pores is expected to significantly contribute to the gas adsorption uptake.

Thursday, April 11, 2013 11:10 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

587 - New poly (acrylonitrile-co-1-vinylimidazole) copolymer: Applications and investigations on solvent and initiator affects

Samsuddin F Mahmood, *sfm093020@utdallas.edu, Wenjin Deng, Benjamin L Batchelor, Rajneesh Verma, Alysia Lowe, Kyung-Hye Jung, Kenneth J Balkus, John P Ferraris, Yang J Duck, Dennis W Smith. Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States*

Melt processable poly acrylonitrile(AN)-*co*-vinylimidazole(VIM) polymers of different compositions were successfully synthesized by free radical polymerization in N-N'-dimethylformamide (DMF) solvent system



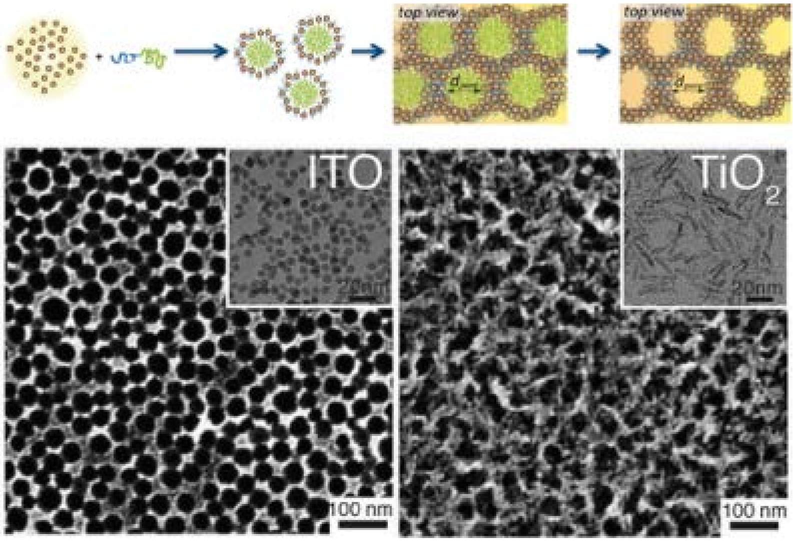
. The copolymers were characterized by attenuated total reflectance-Fourier transform Infrared (ATR-FTIR) spectroscopy, ^{1}H NMR spectroscopy, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). Suitable thermo-chemical properties of these copolymers showed their applicability as a melt processable carbon fiber precursor, nitric oxide releasing enhanced wound healing materials and supercapacitors. The effect on the molecular weights and thermo-chemical properties of the polymer with variable initiator concentrations was investigated for optimizing the reaction parameters for high molecular weights. The synthesis of the polymers was also carried out in different solvent systems to study their effect on thermo-chemical properties by comparing the results obtained from DMF system.

Thursday, April 11, 2013 11:30 AM
Polymer Precursor-Derived Carbon (08:30 AM - 11:55 AM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

588 - Polymer directed-assembly and infiltration of architectured nanocrystals for energy devices

Brett A. Helms, *bahelms@lbl.gov, Raffaella Buonsanti, Teresa E. Pick, Natacha Krins, Christina M. Chang, Bradley Williams, Thomas J. Richardson, Delia J. Milliron. The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

We will describe the design principles by which naked nanocrystals (i.e. those stripped of their native ligands) can be architectured into diverse 3-D mesoscale materials using block copolymers. Various polymer-architecturing paradigms will be discussed from a theoretical perspective alongside experimental results. Particular mention will be nanocrystal tethering domains that afford substantive enthalpic contribution to the free energy of co-assembly used to direct the nanocrystals into precision architectures at high volume fractions. We will also show how those various architectures are useful in high-power energy storage applications.



Thursday, April 11, 2013 09:05 AM

Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)

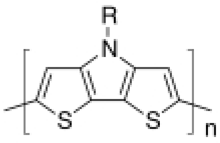
Location: Hilton Riverside

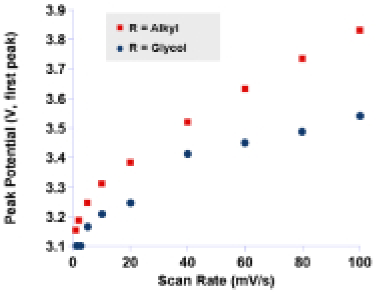
Room: Ste. C, Sec 13/16

589 - Effect of side-chain functionalization on novel conjugated polymers for energy storage

***Jared F. Mike**, jfmike@tamu.edu, Lin Shao, Jodie L. Lutkenhaus. Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States*

Conjugated polymers are promising electrode materials for cost-effective, light-weight, and flexible energy storage. They can be produced cheaply from a wide variety of starting materials and processed in solution. Synthetic tailoring can be used to fine-tune polymers to suit specific applications. The development of new materials with enhanced stability, cyclability, and response is essential to developing viable polymeric energy storage. For this purpose, we have focused our research on dithieno[3,2-b:2¢,3¢-d]pyrrole based conjugated polymers (polyDTPs) and studied their electrochemical storage performance as cathodes. PolyDTPs have stable oxidized states with higher than normal doping capacities and are not widely explored as materials for energy storage. Using targeted synthetic methods we have produced polyDTPs substituted with alkyl ether and alkyl side-chains in order to compare their electrochemical responses. Each polyDTP was characterized using UV-Vis spectroscopy and standard electrochemical testing (cyclic voltammetry, galvanostatic cycling, impedance spectroscopy) in nonaqueous media.



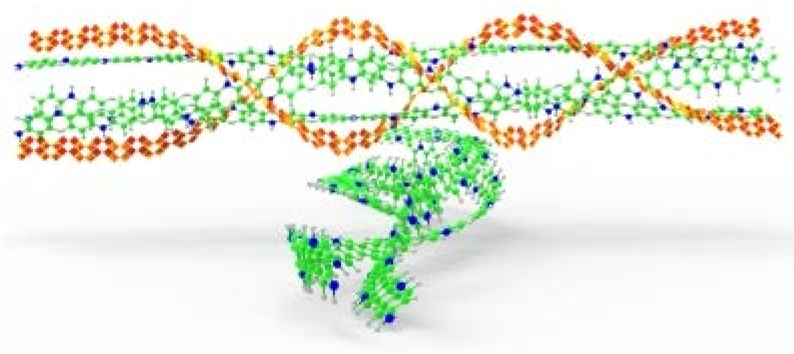


Thursday, April 11, 2013 09:35 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

590 - Polyaniline nanofiber/vanadium pentoxide layer-by-layer electrodes for energy storage

***Lin Shao**[1], l.shao@yale.edu, Ju-Won Jeon[2], Jodie Lutkenhaus[2]. (1) Chemical & Environmental Engineering, Yale University, New Haven, CT 06511, United States, (2) Chemical Engineering, Texas A&M University, College Station, TX 77840, United States*

Here, we report the layer-by-layer (LbL) assembly of polyaniline (PANI) nanofibers and V_2O_5 to form nanostructured electrodes for electrochemical energy storage. PANI nanofibers impart electronic conductivity to otherwise non-conductive V_2O_5 and assist in forming a highly porous structure**.** V_2O_5 imparts a large theoretical capacity. The non-aqueous electrochemical response of the electrode possessed contributions from both PANI nanofibers and V_2O_5. The maximum capacity was 233 mAh/g at a current of 2μA/cm^2, and no volumetric expansion was observed after charge/discharge cycling. V_2O_5 normally undergoes large expansions and contractions during cycling, but the porous structure of our electrode prevented degradation via volumetric expansion. The performance decreased only slightly after 100 cycles, which was attributed to the irreversible formation of the pernigraniline base form of polyaniline. This study indicates how LbL assembly can be used to fabricate high-performance electrodes.

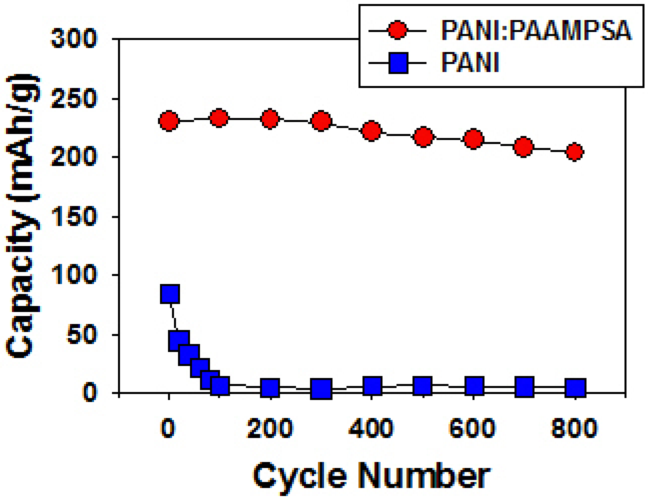


Thursday, April 11, 2013 09:55 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

591 - Oxidatively stable and water-processable polyaniline: Poly(2-acrylamido-2-methylpropane sulfonic acid) complexes for electrochemical energy storage

***Ju-Won Jeon**, jwjeon2010@gmail.com, Yuguang Ma, Jared F. Mike, Lin Shao, Perla B. Balbuena, Jodie L. Lutkenhaus. Department of Chemical Engineering, Texas A & M University, College Station, Texas 77840, United States*

Polyaniline, a conjugated polymer, has attracted great attention for electrode materials in the field of energy storage due to its good capacity, conductivity, and ease of synthesis. However, it is challenging to disperse the conductive form of polyaniline in many solvents. As an electrode in a non-aqueous energy storage system, polyaniline gradually loses its electrochemical activity due to its irreversible oxidation to pernigraniline base. Here, we present polyaniline: poly(2-acrylamido-2-methylpropane sulfonic acid) (PANI:PAAMPSA) colloids as a water-processable material for electrodes in non-aqueous energy storage systems. We demonstrate that PANI:PAAMPSA stores 230 mAh/g of polyaniline for over 800 cycles, while homopolymer polyaniline loses nearly all of its capacity after 100 cycles. PANI:PAAMPSA is stable up to 4.5 V vs Li/Li$^+$, the formation of pernigraniline base is prevented, and the resulting energy storage performance far exceeds that of polyaniline homopolymer. Instead PANI:PAAMPSA reversibly switches among leucoemeraldine base, emeraldine salt, and pernigraniline salt forms.

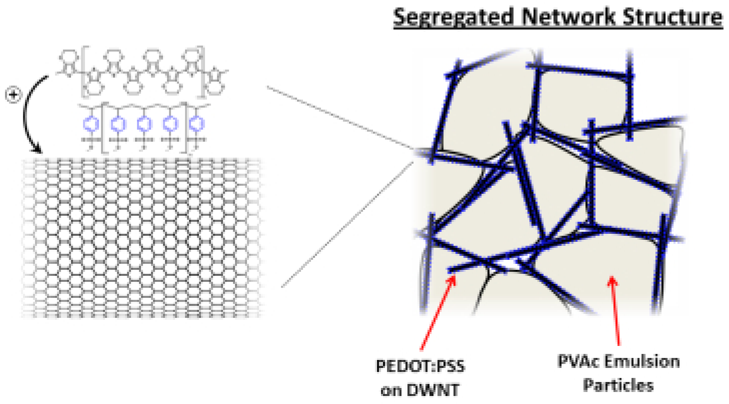


Thursday, April 11, 2013 10:15 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

592 - Promise of fully organic, high performance thermoelectric materials

Gregory Moriarty[2], ***Bart Stevens***[1], *bartstevens@tamu.edu, Jaime Grunlan*[1,2]. *(1) Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, United States, (2) Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3123, United States*

Segregated-network polymer nanocomposites have been shown to be viable fully organic thermoelectric materials in recent years. In the present work, a poly(vinyl acetate) (PVAc) latex, filled with 40 wt% double-wall carbon nanotubes (DWNT), stabilized by intrinsically conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), is shown to exhibit the highest reported electrical conductivity (s ~ 200,000 S/m) and power factor (PF) (S^2s ~ 400 µW/(m·K^2)), with moderate thermopower (S ~ 45 mV/K), at room temperature for a fully organic free-standing film. Despite displaying metal-like electrical conductivity, these organic composites exhibit polymer-like thermal conductivity, ranging from 0.2 - 0.4 W/(m·K). The overall thermoelectric figure of merit (ZT) can be calculated at room temperature to be ~0.35. These results indicate that flexible polymer nanocomposites, prepared from water under ambient conditions, can achieve thermoelectric behavior that is competitive with commonly used inorganic semiconductors, especially when considering their low density and ability to be applied like an ink or paint to any surface.

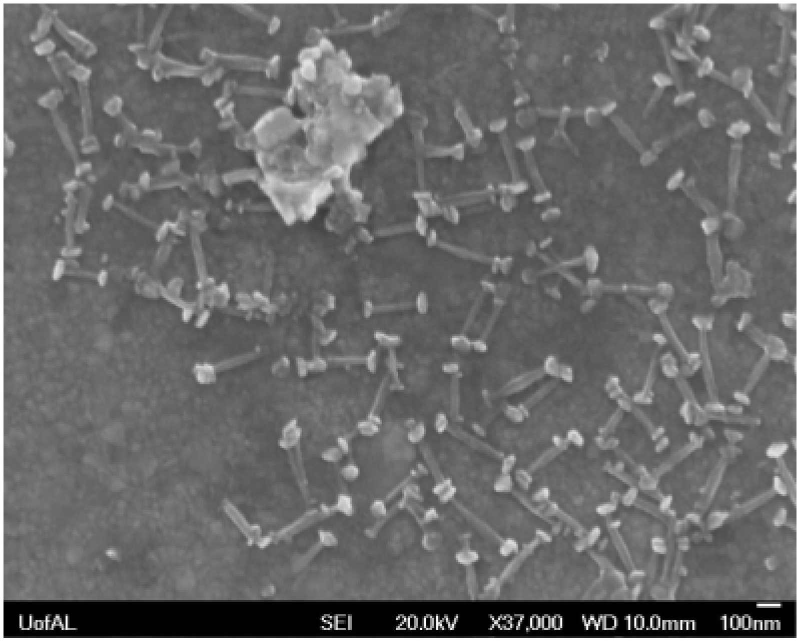


Thursday, April 11, 2013 10:50 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

593 - Conductivity studies on hybrid semiconductor nanowire/conducting polymer films for thermal energy conversion

Kimberly L. Anderson, *ander135@crimson.ua.edu, Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487, United States*

We report the synthesis and characterization of tellurium and bismuth telluride nanorods in a conducting polymer matrix as a potential thermoelectric material. The nanorods were prepared via a low-temperature, aqueous synthesis in the presence of PEDOT:PSS. The effects of reducing agents and thiol ligands on the morphology of the nanowires were studied.



Temperature-dependent conductivity of the thin films was measured and analyzed by Mott's variable range hopping model. We demonstrate the conductivity of the films can be increased with dopants.

Thursday, April 11, 2013 11:10 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

594 - Thermoelectric fabrics

David Carroll, *carroldl@wfu.edu, Department of Physics, Wake Forest University, Winston-Salem, NC 27109, United States*

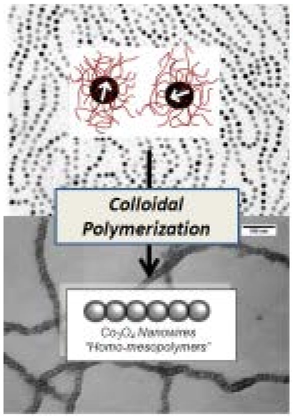
Thermoelectrics are materials capable of the solid state conversion between thermal and electrical energy. Traditional ceramic thermoelectrics, such as Bismuth Telluride (Bi2Te3), have been utilized commercially for more than a half century. Recent advancements in organic nanocomposite module thermoelectrics suggest that lower performance alternatives to ceramic materials may offer approaches to new applications. Using carbon nanotube/ polymer composite thin films assembled into multicomponent modules, we demonstrate that exceptionally good p/n junctions can be achieved. The resuting "farbic-like" applique can be used to scavenge heat energy over surprisingly large areas. It is flexible and robust, with no observable deterioration in performance over time. The thermoelectric voltage generated by these fabrics is the sum of contributions from each layer and although the thermoelectric figure of merit for each MWNT/PVDF layer is ZT ~ 0.02, considerably less than that for Bi2Te3 (ZT ~ 1), several other important factors such as cost, weight, and processability can make their use advantageous is a wide range of applications.

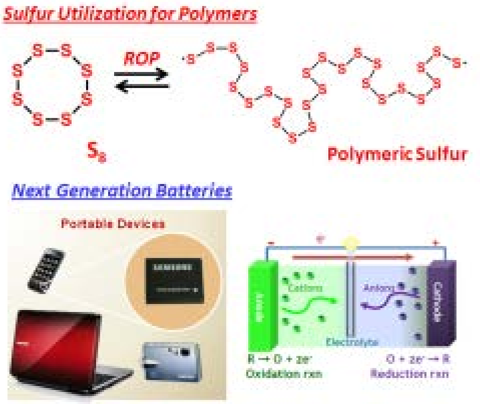
Thursday, April 11, 2013 11:30 AM
Polymer Composites for Energy Harvesting, Conversion and Storage (09:00 AM - 12:00 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

595 - Polymerizing nanoparticles and sulfur for energy applications

Jeffrey Pyun, *jpyun@email.arizona.edu, Department of Chemistry & Biochemistry, University of Arizona, Tucson, Arizona 85721, United States and School of Chemical & Biological Engineering, World Class University Program, Seoul National University, Gwanakgu, Seoul 151-744, Republic of Korea*

We will discuss our recent efforts the polymerization of a novel class of polymer-nanoparticle hybrid materials on dipolar cobalt nanoparticles, which were used as “colloidal monomers” in a process termed Colloidal Polymerization. From this process, we have been able to synthesis electroactive cobalt oxide nanowires and heterostructured nanocomposites with either noble metal, or semiconductor inclusions. We will discuss our recent efforts on the synthesis and characterization of these materials along with relevance to photocatalysis for water splitting and solar hydrogen generation. In the area of electrochemical energy storage, we will discuss our recent efforts on the polymerization of elemental sulfur to prepare novel polymeric and nanocomposite materials which we are exploring for utilization in next generation Li-S batteries. These unconventional systems both utilize either organic/inorganic hybrid nanoparticles, or inorganic polymers, which have strong relevance to future energy applications.



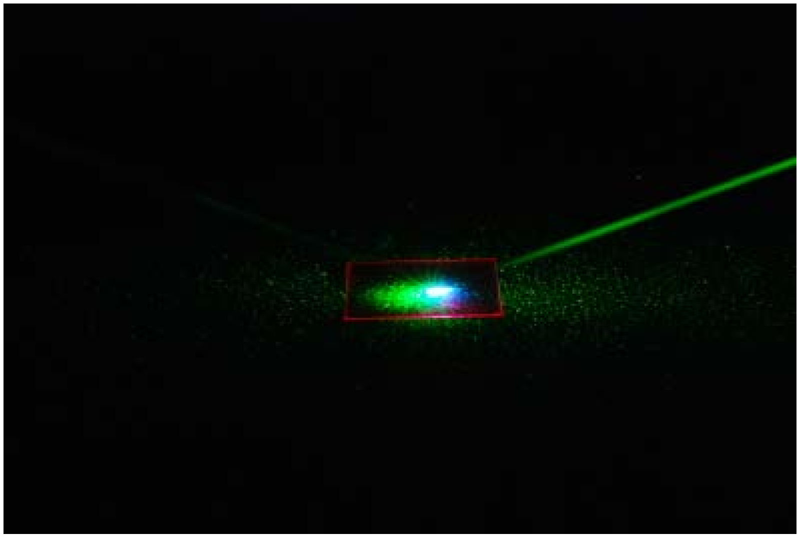


Thursday, April 11, 2013 01:30 PM
Hybrid Materials (01:30 PM - 03:40 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

596 - Sensitized upconversion in polymeric glasses

Roberto Vadrucci, Soo-Hyon Lee, Christoph Weder, ***Yoan C Simon****, yoan.simon@unifr.ch. Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland*

Materials capable of upconverting photons from lower to higher energy have the potential to impact many practical domains, such as bioimaging, solar harvesting or drug-delivery. In this context, sensitized upconversion is very promising due to its operational conditions at low-power densities and with polychromatic sources. While initial efforts have mostly focused on the utilization of rubbery polymers, we wish to report here new findings regarding the incorporation of organometallic moieties in glassy amorphous polymers to achieve highly efficient upconversion where constructive triplet-triplet annihilation is the preferred relaxation pathway. This efficacy is apparent through the linear relationship between laser intensity and upconverted emission intensity. The use of specific processing protocols to create blends of upconverting dyes and poly(methyl methacrylate) and the covalent tethering of the chromophores to polymer backbones allowed the incorporation of large concentration of dyes into the materials, which was essential to identify some of the governing parameters that influence energy transfer processes in the polymer matrix. Moreover, new observations about molecular glasses helped us to unravel important geometrical constraints in solid upconverting materials.



Thursday, April 11, 2013 02:00 PM
Hybrid Materials (01:30 PM - 03:40 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

597 - Hybrid PEDOT-Metal nanoparticles: New substitutes for PEDOT:PSS

Eric Cloutet[1,2], *cloutet@enscbp.fr, Marie-Hélène Delville*[3], *Muhammad Mumtaz*[1,2], *Henri Cramail*[1,2], *Georges Hadziioannou*[1,2]. *(1) Laboratoire de Chimie des Polymères Organiques, CNRS, Pessac, France, (2) Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux, Pessac, France, (3) ICMCB, CNRS, Pessac, France*

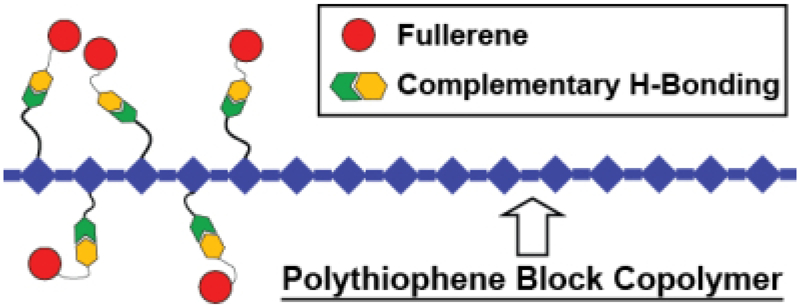
Hybrid PEDOT-metal nanoparticles were readily prepared in one-pot oxidative dispersion polymerization of EDOT together with the reduction of metals salts. The size and morphology of the final hybrid particles were finely tuned with a strict control of reaction conditions, the addition time of the co-oxidant ($HAuCl_4$ and $AgNO_3$) being a relevant parameter. The conductivity of such hybrid materials ranging from 0.1 to 1.3 S/cm makes them good candidates for electrode materials in opto-electronic devices. The most crucial point is that the resulting hybrid PEDOT-metal nanoparticles aqueous suspensions have been advantageously used to form a substitute layer replacing PEDOT:PSS. Electropolymerization of EDOT onto such PEDOT-metal nanocomposite layer gave rise to electrochromic layer with improved characteristics in terms of not only contrast ratio with a 3 to 4 times higher value and coloration efficiency but also of switching time response which is divided by five for coloration and four for bleaching.

Thursday, April 11, 2013 02:20 PM
Hybrid Materials (01:30 PM - 03:40 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

598 - Self-assembly of polythiophene block-copolymer and fullerene derivative via complementary hydrogen bonding

Fei Li, Jianzhong Yang, ***Yang Qin****, yangqin@unm.edu. Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States*

We report the synthesis and characterization of a polythiophene block copolymer selectively functionalized with diaminopyrimidine moieties (**P4**) and a thymine tethered fullerene derivative (**F1**). Self-assembly between **P4** and **F1** through “three-point” complementary hydrogen bonding is studied by NMR spectroscopy and differential scanning calorimetry. Fluorescence quenching measurements reveal strong complexation between these two components with a large Stern-Volmer constant (K_{SV}) of 1.2×10^5 M^{-1}. Such hybrid materials can potentially stabilize active layer morphologies in organic solar cells and thus enhance their durability.



Thursday, April 11, 2013 02:40 PM
Hybrid Materials (01:30 PM - 03:40 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

599 - Electrophoretic hybrid particles synthesis by dispersion polymerization: Toward electrophoretic display

Cyril Brochon[1,2], *cyril.brochon@enscbp.fr, Antoine Charbonnier*[1,2], *Eric Cloutet*[1,2], *Georges Hadziioannou*[1,2]. *(1) LCPO, Université de Bordeaux, Pessac, Select State 33607, France, (2) LCPO, CNRS, Pessac, Select State 33607, France*

Electronic paper based on the controlled motion of electrophoretic particles appears thus promising since it combines the advantages of the usual paper and the capacity to refresh information on the same support like the more common LCD or OLED technologies.

In this work the main goal is to rationalize and improve the ink synthesis. We performed the synthesis of hybrid particles by using an organic dispersion technique in aliphatic hydrocarbon solvents leading to electrophoretic particles with a good size control over a large range (from 75nm to 20µm) and a good stability. In order to obtain the full color panel, the encapsulation of several inorganic pigments was achieved by using the same technique.

pigment	**Initial Size (µm)**	**% of polymer (w/w)**	**Final Size (µm)**	**shape**
TiO_2	0.16	41	0.55	Raspberry
Fe_2O_3	0.13	61	0.70	Raspberry
$CoAl_2O_4$	0.55	24	1.50	Raspberry
Fe_3O_4	0.01	n. d.	0.09	Inverse core-shell

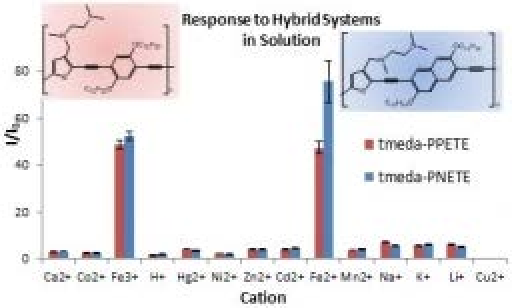
By this way, several inks, specially designed for electrophoretic measurements in organic media have been obtained through a one pot synthesis.

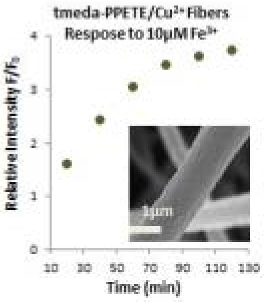
Thursday, April 11, 2013 03:00 PM
Hybrid Materials (01:30 PM - 03:40 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 9

600 - Photophysics of solution phase and solid-state fluorescent conjugated polymers as chemosensors for iron cations

Megan E. A. Fegley[1], *mfegley@binghamton.edu, Bo Song*[1], *Sarah Dill*[1], *Jetty Duffy-Matzner*[2], *Wayne E. Jones, Jr.*[1]. *(1) Department of Chemistry, Binghamton University, Binghamton, New York 13902, United States, (2) Department of Chemistry, Augustana College, Sioux Falls, South Dakota 57197, United States*

Fluorescent conjugated polymers (FCP's) can act as chemosensors to detect metals. Inorganic/organic hybrids, FCP's containing N,N,N'-trimethylethylenediamino (tmeda) receptors preloaded with Cu^{2+} are selective and sensitive fluorescence “turn-on” chemosensors for iron cations. To achieve greater portability and quicker at-source screening, FCPs were transitioned into the solid-state. Thin films and electrospun fibers containing tmeda FCP's have been fabricated using poly(methyl methacrylate), polyvinyl alcohol or polyethylene oxide matrices. Photophysical studies of solid-state materials have revealed time-dependent fluorescent response to metal cations.





Thursday, April 11, 2013 03:20 PM

Hybrid Materials (01:30 PM - 03:40 PM)

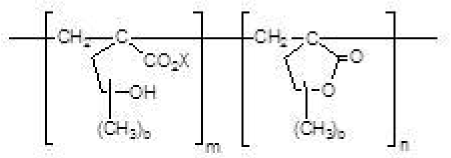
Location: Hilton Riverside

Room: Ste. B, Sec 9

601 - Superabsorbent polymers from nature

Brian Mullen, *brian_mullen@segetis.com, Marc Rodwogin, Dorie Yontz, Cora Leibig, Friederike Stollmaier. Segetis, Inc., Golden Valley, MN 55427, United States*

Superabsorbent polymers based on naturally-derived lactones have been demonstrated for the first time. These superabsorbent polymers are an example of one of the many commercially-promising products based upon the levulinic acid. These new polyelectrolytes were synthesized by emulsion polymerization and further modified by saponification of the polylactones to produce the final polymer. The superabsorbent polymers exhibited good properties, such as, good absorbency under load, which is a strict requirement for many superabsorbent applications.

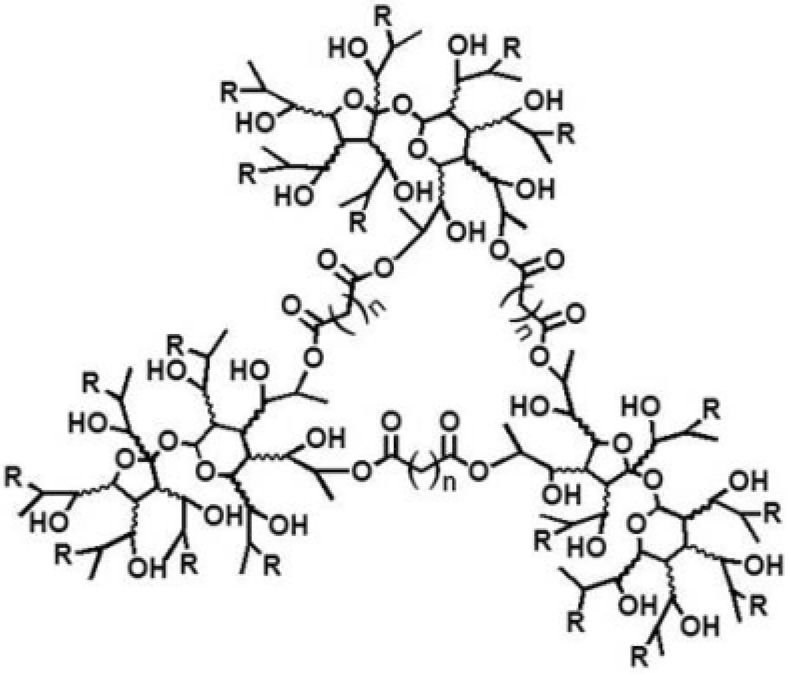


Thursday, April 11, 2013 01:30 PM
Natural and Renewable Polymers (01:30 PM - 04:25 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

602 - Vinyl ether blocked carboxylic acid compounds for use in biobased epoxy-acid thermosets

***Curtiss S Kovash, Jr**, curtiss.s.kovash@ndsu.edu, Erin Pavlacky, Dean C Webster. Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, United States*

Thermoset materials derived from epoxidized sucrose esters, a biobased product, have demonstrated excellent performance properties. The implementation of biobased multifunctional carboxylic acids as crosslinkers for these systems could lead to a 100% biobased coating being produced. The primary problem in realizing this system is that multifunctional carboxylic acids have a high degree of hydrogen bonding between molecules, resulting in high melting points and poor solubility in organic systems. A way to overcome these problems is to block the carboxylic acids by reacting them with vinyl ethers. The blocked carboxylic acids have four positive attributes: 1) the reaction to produce them can be performed without the need of a solvent nor an inert atmosphere, 2) the blocked acids are low viscosity liquids that are soluble in organics, 3) the deblocking reaction is thermally activated at moderate temperatures (170 °C), and 4) the vinyl ethers (which are not biobased) are volatile at these deblocking temperatures. Therefore, while the formulation is 92-95% biobased (depending on the multifunctional acid and the vinyl ether used), the final coating produced is 100% biobased. The synthesis of novel vinyl ether blocked carboxylic acids and their use with epoxidized sucrose soyate (ESS) in thermoset systems, which have shown both good surface adhesion and solvent resistance, will be presented.

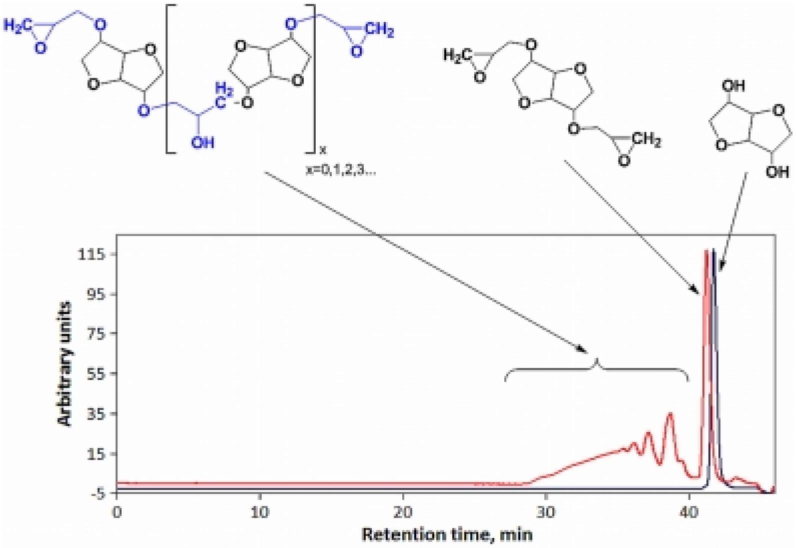


Thursday, April 11, 2013 02:00 PM
Natural and Renewable Polymers (01:30 PM - 04:25 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

603 - Curing and properties of isosorbide-based epoxy resins

Zoran S Petrovic[1], *zpetrovic@pittstate.edu, Mihail Ionescu*[1], *Jelena Milic*[1], *Eric Eastwood*[2]. *(1) Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS 66762, United States, (2) Honeywell FM&T, LLC, Kansas City, MO 64131-3095, United States*

Isosorbide or 1,4:3,6 dianhydrosorbitol is a solid compound with melting point of 60-62 ^{o}C derived from corn starch. It is thermally stable up to 270 ^{o}C, renewable, nontoxic and biodegradable and a potential alternative to Bisphenol A (BPA) in epoxy resins. We investigated the synthesis of diglycidyl ethers of isosorbide and compared their reactivity with BPA resins. The resins were cured with anhydrides and amines to give optically clear and colorless polymers. Curing of isosorbide epoxies was faster than with bisphenol A type epoxies. Ethylene diamine cured epoxy resins displayed excellent tensile and impact strength and low elongations, higher than in BPA resins. Glass transition of isosorbide resins was lower than in BPA resin. Isosorbide epoxy resins are a viable replacement for DGEBA resins.



GPC curve of diglycidyl ether of isosorbide

Thursday, April 11, 2013 02:20 PM

Natural and Renewable Polymers (01:30 PM - 04:25 PM)

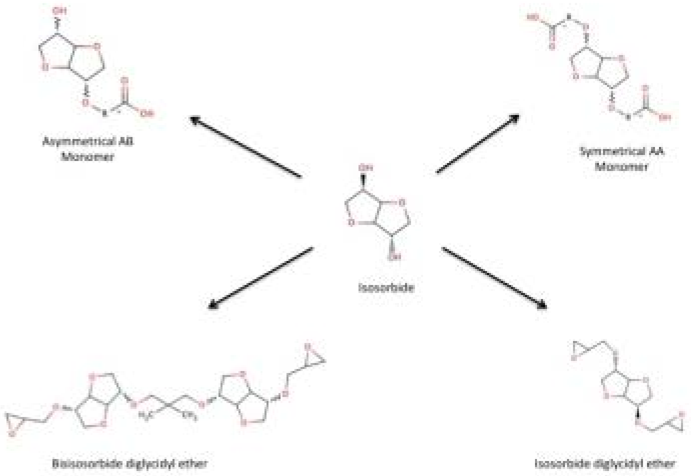
Location: Hilton Riverside

Room: Ste. A, Sec 6

604 - Isosorbide based polymers: Thermoplastics and thermosets

Prabhjot Saini, *pks23@njit.edu, Anthony J East, Willis Hammond, Michael Jaffe. Department of Biomedical Engineering, New Jersey Institute of Technology, Newark, New Jersey 07103, United States*

A glucose-derived chiral diol, isosorbide, has the potential to become the building block for various polymers. The unequal reactivity of its pendent hydroxyls allows selective substitution with desired moieties for different polymers.



Isosorbide-derived symmetric and asymmetric monomers have been developed by substituting one or both hydroxyls with moieties like terephthalate, biphenyl and naphthalene. This opens up avenues to synthesize various homo- and co-polymers. Isosorbide-based polymers exhibit high thermal-stability and mechanical-properties. Mesogenic polymers have been developed by attaching known mesogens to isosorbide. Isosorbide-derived monomers have been copolymerized with conventional polymers like PET and PLLA to improve their thermal and mechanical properties. Potentially biodegradable polymers synthesized from isosorbide linked with short alkyl-groups are being investigated. Such polymers are useful in biomedical and device-applications requiring biodegradation.

Epoxy resins have been synthesized by substituting the hydroxyls of isosorbide with glycidyl ethers. Due to the inherent highly hydrophilic nature of isosorbide, these epoxies tend to take up large amounts of water. However, water uptake can be tuned synthetically by selective substitution with hydrophobic moieties. High water affinity makes these resins ideal candidates for hydrogels. Thermosets have been developed by thermal-crosslinking of isosorbide-based glycidyl ethers with various natural carboxylic acids and amines to make hydrogels for biomedical and other humectant applications.

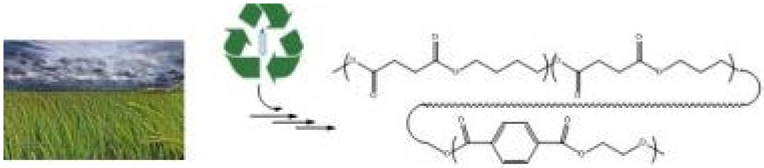
Isosorbide chemistry can be exploited to develop monomers to cover the entire range of polymers, making it an excellent platform for natural and renewable polymers.

Thursday, April 11, 2013 02:40 PM
Natural and Renewable Polymers (01:30 PM - 04:25 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

605 - Bio-based polyesters: Chemistry and properties

Hossein Ghassemi, *hxg30@cwru.edu, David A Schiraldi. Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44104, United States*

Bio-based polymers are a possible alternative to petroleum-based and synthetic products. This research concerns the chemistry, properties and applications of bio-based polyesters synthesized from succinate, butanediol, propanediol, tri-functional monomers and post-consumer PET with suitable properties for, applications such as coating, adhesives, fibers, packaging, paper, automotive, water treatment, pharmaceutical and biomedical. In this study, synthesis, physical and mechanical properties of some aliphatic (co)polyesters with mixed aliphatic and aromatic structures will be discussed. Combination of aromatic/aliphatic units in polyester is an approach to obtain products encompassing biodegradability and high-performance properties. Bio-based polyesters with chemically cross-linked structure were also prepared and studied.

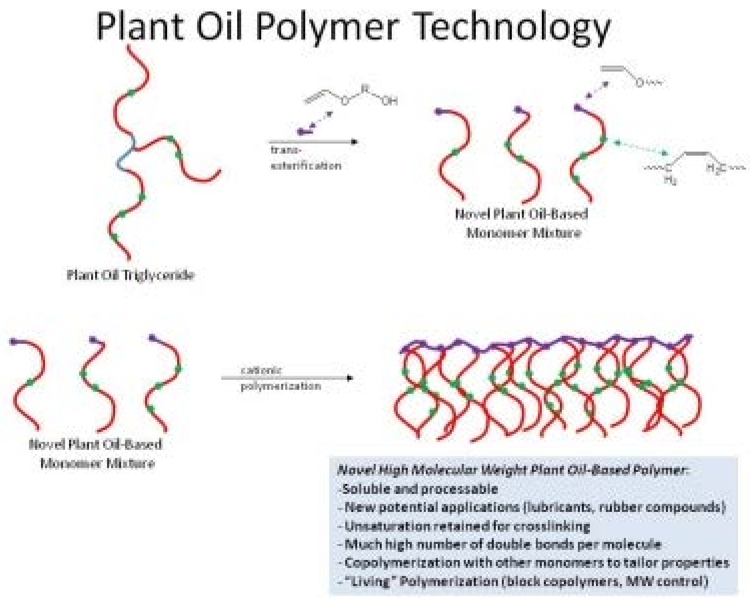


Thursday, April 11, 2013 03:15 PM
Natural and Renewable Polymers (01:30 PM - 04:25 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

606 - Novel polyvinylethers derived from plant oils

*Samim Alam[1], Harjyoti Kalita[2], Shashi Fernando[1], Anurad Jayasooriyamu[1], Satyabrata Samanta[1], Andriy Popadyuk[3], James Bahr[1], Andriy Voronov[3], Achintya Bezbaruah[4], Andrey Chernykh[1], **Bret J Chisholm**[1,2,3], Bret.Chisholm@ndsu.edu. (1) Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, ND 58102, United States, (2) Materials and Nanotechnology Program, North Dakota State University, Fargo, ND 58102, United States, (3) Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, United States, (4) Civil Engineering, North Dakota State University, Fargo, ND, United States*

A novel polymer platform technology was developed that involves the conversion of a plant oil to a mixture of vinyl ether monomers in which each monomer molecule contains a fatty acid ester group derived from the parent plant oil. The cationic polymerization system developed allows for living polymerization of the monomers exclusively through the vinyl ether groups. This characteristic enables double bonds present in the unsaturated pendent groups to be utilized for the production of thermosets either directly or by derivatization to other functional groups including epoxy, hydroxy, and acrylate groups. In addition to homopolymerization, the monomers have been copolymerized with other monomers to create a wide variety of functionalized polymers expected to have utility for a number of markets including coatings, composites, rubber compounds, and personnel-care products. An overview of the synthesis, characterization, and properties of key polymers will be presented along with the properties of various formulated materials.


Plant Oil Polymer Technology

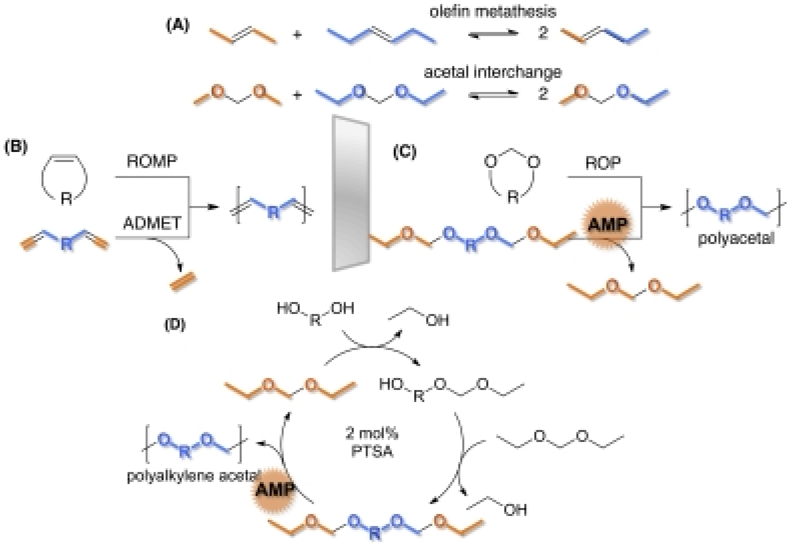
Novel High Molecular Weight Plant Oil-Based Polymer:
-Soluble and processable
-New potential applications (lubricants, rubber compounds)
-Unsaturation retained for crosslinking
-Much high number of double bonds per molecule
-Copolymerization with other monomers to tailor properties
-"Living" Polymerization (block copolymers, MW control)

Thursday, April 11, 2013 03:35 PM
Natural and Renewable Polymers (01:30 PM - 04:25 PM)
Location: Hilton Riverside
Room: Ste. A, Sec 6

607 - Acetal metathesis polymerization (AMP): Synthesis of biorenewable and (bio)degradable polyacetals from simple diols

***Alexander G. Pemba**, PEMBA@CHEM.UFL.EDU, Jeniree A Flores, Stephen A. Miller. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States*

Biodegradable and biorenewable polymers are an answer to many of the problems that commodity plastics have created. By utilizing Acetal Metathesis Polymerization (AMP), it is possible to create a new class of materials that derive solely from biomass. Acetal interchange mirrors the key olefin metathesis step in ADMET quite closely as illustrated in Figure 1A. This analogy is taken a step further in Figures 1B and 1C. Through the AMP method, simple diol monomers are linked with acetals to produce polyalkylene acetals of respectable molecular weights in a single pot, Figure 1D. By varying the methylene-spacer length between consecutive acetal subunits, the thermal properties of the polymers have been probed. Work to investigate the utility of more complex diols as monomers is currently underway.



Thursday, April 11, 2013 04:05 PM

Natural and Renewable Polymers (01:30 PM - 04:25 PM)

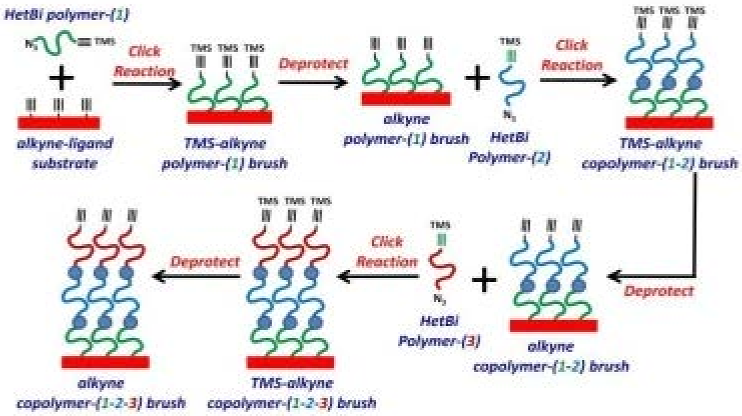
Location: Hilton Riverside

Room: Ste. A, Sec 6

608 - Modular approach for solid phase synthesis of structured polymers: Molecular tinker toys

Jeffrey T Koberstein, *jk1191@columbia.edu, Department of Chemical Engineering, Columbia University, New York, NY 10027, United States*

We describe a new modular system for preparing complex polymers from simple building blocks like molecular Tinker Toys. Building blocks are heterobifunctional molecules with azide and protected-alkyne termini and may be macromonomers or small molecules with a specific function like cleavage or chain branching. The figure illustrates preparation of a segmented copolymacromer.

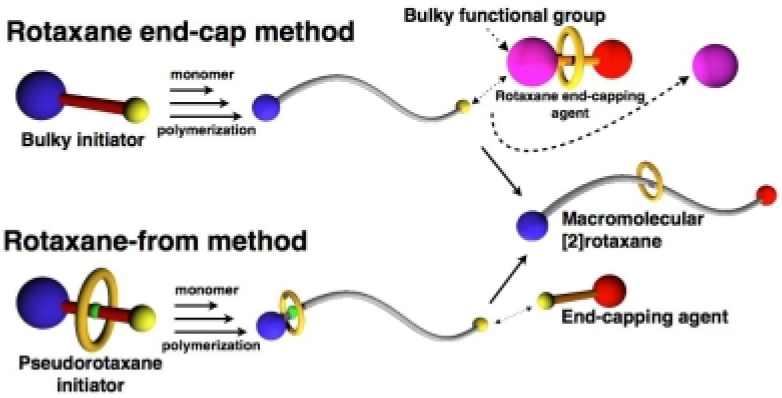


Thursday, April 11, 2013 01:00 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

609 - Synthesis and characterization of macromolecular [2]rotaxane having polymer chain as the axle component

Daisuke Aoki, *daoki@polymer.titech.ac.jp, Yasuhito Koyama, Satoshi Uchida, Toshikazu Takata. Department of Organic and Polymeric Materials, Tokyo institute of technology, Meguro-ku, Tokyo 152-8552, Japan*

In order to synthesize macromolecular [2]rotaxanes consisting of a polymer chain as an axle component and one crown ether as a wheel component, two synthetic methods were investigated. One is the end-cap method via introduction of polymer chain to the axle end of rotaxane having a reactive group at the axle terminal. The other is the rotaxane-from method via polymerization initiated by axle-terminal group of pseudorotaxane.



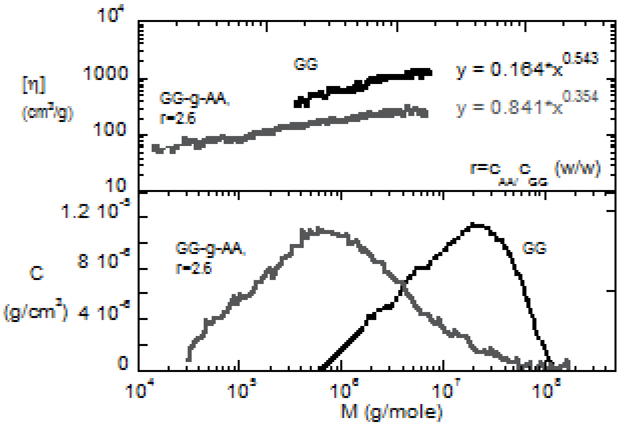
Monday, April 8, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Morial Convention Center
Room: Hall D

Thursday, April 11, 2013 01:20 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

610 - Synthesis and characterization of guar gum-g-poly(acrylic acid) copolymers

Zifu Zhu, ***Alina M Alb***, *aalb@tulane.edu. Department of Physics, Tulane University, New Orleans, Louisiana 70118, United States*

Graft copolymerization has been widely used as a method for modifying the structure of natural polymers, leading to multiple applications in various fields. In this study, the graft copolymerization of acrylic acid (AA) onto guar gum (GG) is followed by multi-detector size exclusion chromatography (SEC) and cross-checked by additional techniques. The effects of various factors such as reaction temperature, initiator concentration, and AA/GG ratio, on the polymer molecular weight, molar dispersity, and on the grafting efficiency are investigated. While the increase in AA concentration leads to a higher amount of polymer formed due to Tromsdorff effect, care has to be taken in choosing the initial parameters and the AA/GG ratio since a higher amount of AA added could lead to a blend of GG-g-AA and polyacrylic acid.



Molecular weight distribution (MWD) determined from SEC multi-angle light scattering data and intrinsic viscosity vs. polymer mass illustrate the incorporation of the acrylic acid into the guar gum chains. In the same time, the Mark-Houwink coefficient values from the power-laws used to fit viscosity data allow the efficiency of the grafting process to be quantified.

Due to the acrylic acid unique characteristics, it is hoped that the control of the grafting on the guar gum will enhance the polymer applicability.

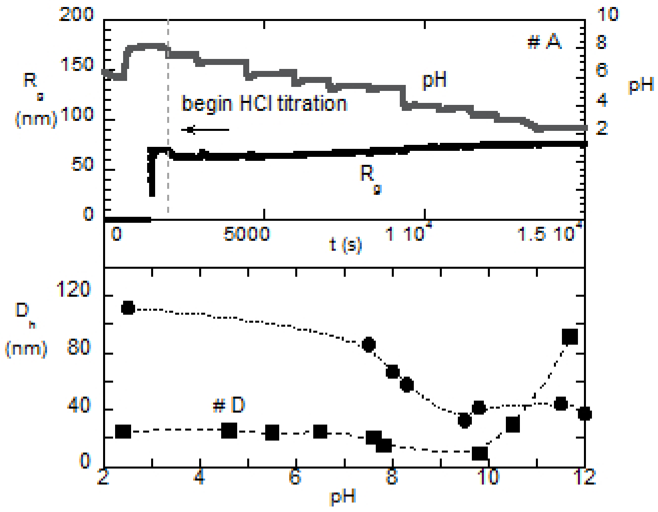
Thursday, April 11, 2013 01:40 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

611 - pH dependent self-assembly behavior of amphiphilic diblock copolymers by RAFT studied by light scattering-based methods

*Evelyn F de Melo[1], **Alina M Alb**[2], aalb@tulane.edu. (1) Department of Biochemistry, Federal University of Alfenas, Alfenas, Minas Gerais 37130-000, Brazil, (2) Department of Physics, Tulane University, New Orleans, Louisiana 70118, United States*

Inspired from nature, polymeric materials that respond to pH, ionic strength, light, temperature, and other external stimuli represent an important category of materials synthesized by reversible addition fragmentation transfer (RAFT) polymerization.

The focus of this study is on the self-assembly behavior in aqueous solutions of pH responsive amphiphilic diblock copolymers. 2-(Dimethylamino)ethyl methacrylate (DMAEMA)/styrene diblock copolymers with different hydrophilic block/hydrophobic block ratios were successfully synthesized via RAFT polymerization. The self-assembly properties of the diblock copolymers were studied by light scattering based techniques (automatic continuous mixing and dynamic light scattering) and transmission electron microscopy. Due to the hydrophilic/hydrophobic interactions, in aqueous environment, the copolymers undergo pH-dependent self-assembly, forming core-shell polymeric micelle-like structures, with styrene block being the hydrophobic core, stabilized by the hydrophilic DMAEMA corona.



The way the polymer conformation was affected by the change in pH and ionic strength, stability, aggregation/micellization phenomena were correlated to the degree of polymerization and block lengths of the components. The size of the polymeric structures and their response to the pH of the environment can be tuned by adjusting the block copolymer composition, molecular mass and degree of hydrophobicity.

Thursday, April 11, 2013 02:00 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

612 - Combining anionic polymerization and click-chemistry: Poly(glycerol)-based macromonomers for bioconjugation

Anja Thomas[1], *thomasan@uni-mainz.de, Tobias Steinbach*[1], *Frederik Wurm*[2], *Holger Frey*[1]. *(1) Department of Organic Chemistry, Johannes Gutenberg University, Mainz, RLP 55128, Germany, (2) Max Planck Institute for Polymer Research (MPI-P), Mainz, RLP 55128, Germany*

Polyether polyols like poly(glycerol) (PG) can be used as very potent and multifunctional alternatives to conventional monofunctional PEG. By transferring this analogy to macromonomers, we developed two different protocols for the synthesis of PG-based macromonomers, ranging from direct end-capping of oligo(glycerol) synthesized by anionic ring-opening polymerization to amphiphilic macromonomers prepared by click chemistry. The combination of the biocompatible polyether polyol structure with polymerizable methacrylate endgroups gives access to diverse macromolecular architectures or biohybrids via controlled radical polymerization techniques, e.g., ATRP.

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General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
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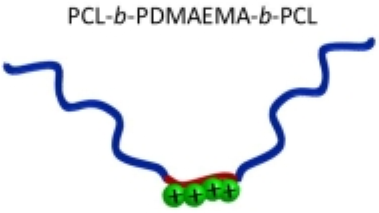
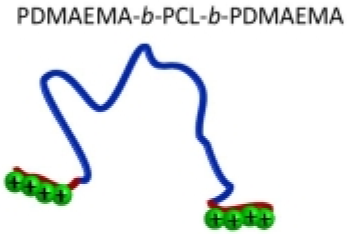
613 - Preparation and evaluation of triblock copolymers based on poly(2-(dimethylamino)ethyl methacrylate) and poly(e-caprolactone)

Carl Bruce[1,2], *cbruce@kth.se, Irakli Javakhishvili*[3], *Linda Fogelström*[1,2], *Anna Carlmark*[1,2], *Søren Hvilsted*[3], *Eva Malmström*[1,2]. *(1) Dept. of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden, (2) BiMaC Innovation, KTH Royal Institute of Technology, Stockholm, Sweden, (3) Department of Chemical and Biochemical Engineering, Danish Polymer Centre, Technical University of Denmark, Kongens Lyngby, Denmark*

In this work, the preparation of two block copolymers based on poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(e-caprolactone) (PCL) has been conducted, creating the triblock copolymers PDMAEMA-*b*-PCL-b-PDMAEMA and PCL-*b*-PDMAEMA-*b*-PCL. The PDMAEMA-part was then quaternized, to give polyelectrolytes with either one or two charged block(s). Subsequently, differences in properties were studied in the solid state, in solution and in water dispersion with techniques including differential scanning calorimetry, size exclusion chromatography and dynamic light scattering.





Thursday, April 11, 2013 02:40 PM

General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)

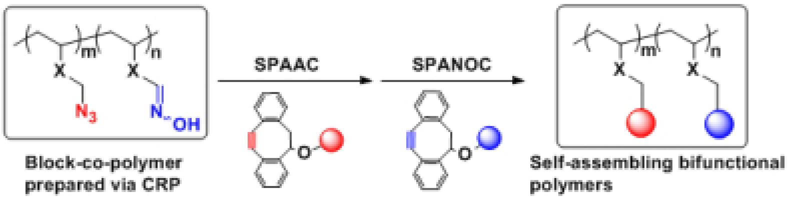
Location: Hilton Riverside

Room: Ste. C, Sec 15

614 - Multifunctionalization of polymers through sequential copper-free click reactions

Petr A. Ledin[1,2], *ledpet@uga.edu, Nagesh Kolishetti*[2], *Geert-Jan Boons*[1,2]. *(1) Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States, (2) Complex Carbohydrate Research Center, University of Georgia, Athens, Georgia 30602, United States*

Functional polymers with reactive side chain groups provide a versatile platform for development of new materials. Using RAFT polymerization we have prepared block-co-polymers containing azide and oxime moieties.



The resulting polymers served as scaffolds for sequential SPAAC (strain promoted alkyne-azide cycloaddition) and SPANOC (strain promoted alkyne-nitrile oxide cycloaddition) reactions with hydrophilic (carbohydrate, peptide, PEG) and hydrophobic dibenzocyclooctynol derivatives. Solution self-assembly of the resulting amphiphilic polymers has been studied by DLS and TEM techniques.

Thursday, April 11, 2013 03:00 PM

General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)

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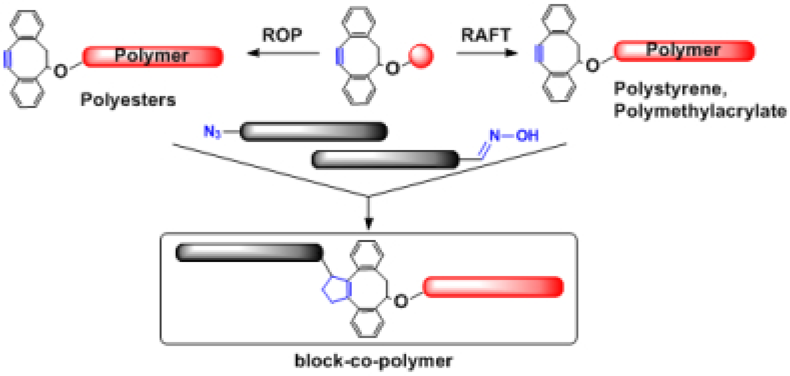
615 - Copper-free clickable initiators and chain transfer agents for ROP and RAFT polymerizations.

Nagesh Kolishetti[2], ***Petr A. Ledin***[1,2], *ledpet@uga.edu, Geert-Jan Boons*[1,2]. *(1) Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States, (2) Complex Carbohydrate Research Center, University of Georgia, Athens, Georgia 30602, United States*

Clickable initiators and chain transfer agents offer a novel route to end-functional polymers. We have prepared several ROP initiators and RAFT agents containing strained dibenzocyclooctynol (DIBO). These agents were used to synthesize various polymers (polyesters, polystyrene, polymethylacrylate) containing DIBO on a-chain end.



The resulting polymers were coupled with azide and oxime containing moieties (PEG, peptide and carbohydrate) via strain promoted alkyne-azide or nitrile oxide cycloaddition reaction giving block-co-polymers. The synthesis, characterization and self-assembly properties of these polymers will be discussed.

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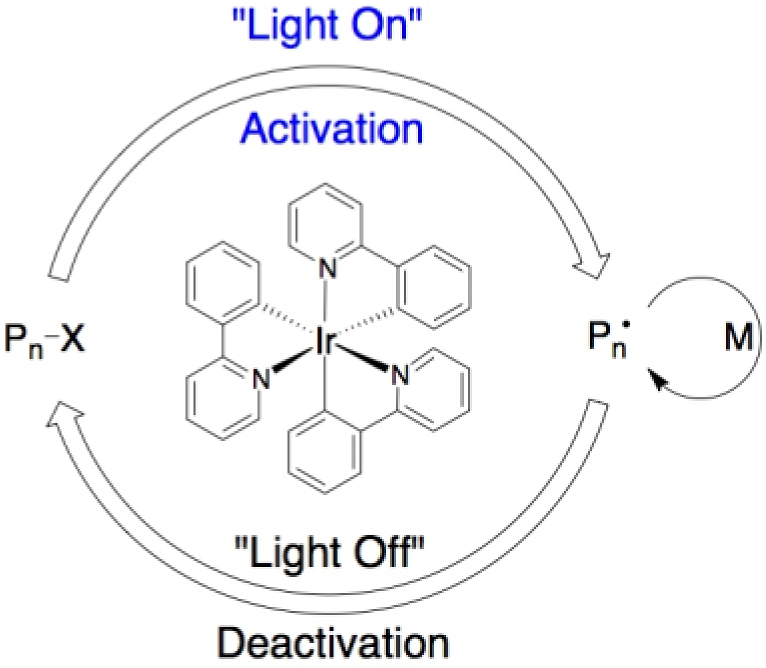
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

616 - Spatial and temporal control of a living radical polymerization by light

Brett P. Fors, *fors@mrl.ucsb.edu, Justin E. Poelma, Chien-Yang Chiu, John W. Kramer, Craig J. Hawker. Materials Research Laboratory, California NanoSystems Institute, Department of Materials, and Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Living radical polymerization processes have emerged as one of the most powerful synthetic strategies for the preparation of functional materials. The ability to regulate these processes with an external stimulus would dramatically increase their utility and facilitate an even greater range of applications. This presentation will detail the development and applications of a practical living free radical polymerization process that affords both spatial and temporal control over the chain growth process through mediation by light. Insight into catalyst structure activity relationships for this reaction, as well as applications that take advantage of the spatial and temporal control allowed by this system will be discussed.



Thursday, April 11, 2013 03:40 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

617 - Solution processable polyacetylenes through ADMET polymerization

Keda Hu, Robert Sparks, ***Yang Qin****, yangqin@unm.edu. Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States*

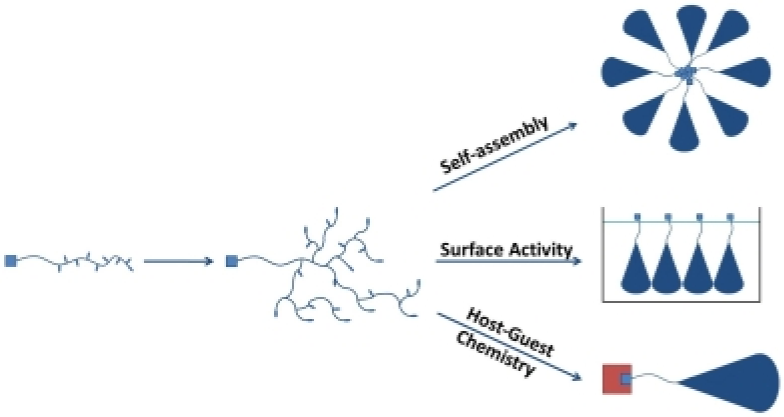
We describe a facile methodology for the synthesis of soluble polyacetylenes (PAs) with novel substitution patterns through acyclic diene metathesis (ADMET). PAs obtained from our method have substituents precisely placed on every other double bond along the backbone, which is not possible using previously established methods. The nature of the substituents can be easily modified and the electronic properties of resulting PAs can be customized and fine-tuned via cross-conjugation in order to meet specific requirements for different applications.

Thursday, April 11, 2013 04:00 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 15

618 - Hyperbranched amphiphiles bearing guest moieties for inclusion complex formation

Christian Moers[1,2], *moersc@uni-mainz.de, Anja Thomas*[1], *Holger Frey*[1]. *(1) Department of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Rhineland-Palatinate D-55128, Germany, (2) Graduate School Materials Science in Mainz, Mainz, Rhineland-Palatinate D-55128, Germany*

Linear polyhydroxy-functional amphiphiles bearing a guest moiety for inclusion complex formation were synthesized via anionic ring opening polymerization using protected glycidol derivatives followed by subsequent cleavage of the protection group. In a next step, these amphiphiles were used as macroinitiators for hypergrafting reactions leading to hyperbranched polyhydroxy-functional amphiphiles. Investigations concerning self-assembly, surface activity and ability to form inclusion complexes were conducted.



Thursday, April 11, 2013 04:20 PM

General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)

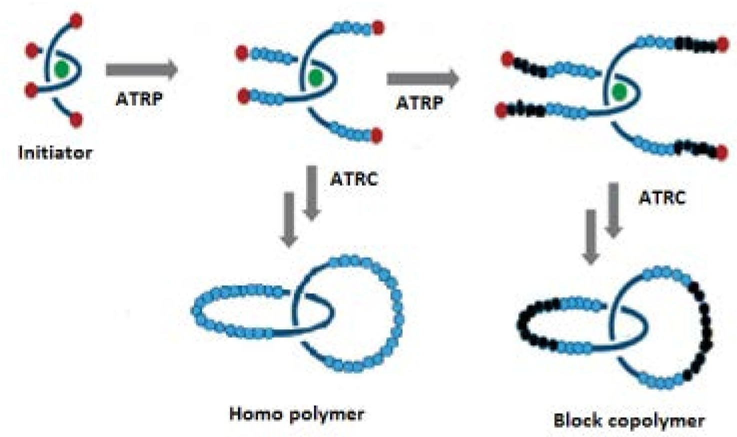
Location: Hilton Riverside

Room: Ste. C, Sec 15

619 - Synthesis of catenated homopolymer and block copolymer via a supramolecularly templated ATRP Initiator and ring closing approach

Ajaykumar Bunha[1], *avbunha@uh.edu, Maria Celeste Tria*[1]*, Joey Mangadlao*[2]*, Mary Jane Felipe*[1]*, Katrina Pangilinan*[2]*. (1) Department of Chemistry, University of Houston, Houston, TX 77204-5003, United States, (2) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States*

The topologically self-constrained structures of catenated polymers are of high interest for the study of its unique physical properties. A versatile approach for the synthesis of catenated homo and blockcopolymers was demonstrated via (1) growing the polymer chain from ATRP initiators templated in phenanthroline Cu(I) complex and (2) ring closing of resulting four arm type polymers via intra-molecular atom transfer radical coupling. The formation of the interlocked topology of desired polymers was confirmed by GPC and AFM analysis.



Thursday, April 11, 2013 04:40 PM

General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)

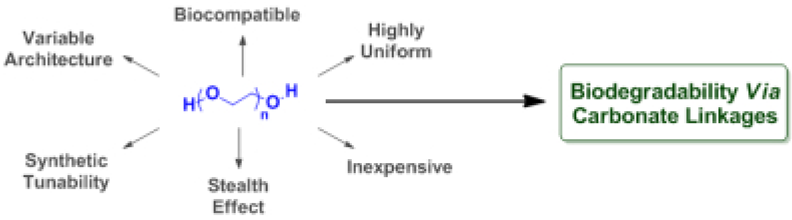
Location: Hilton Riverside

Room: Ste. C, Sec 15

620 - Biodegradable water soluble polymers as an alternative to PEG

Daniel J. Coady[1], *dcoady5@gmail.com, Haritiz Sardon*[3], *Yi Y. Yang*[2], *James L Hedrick*[1]. *(1) IBM - Almaden, United States, (2) Institute of Bioengineering and Nanotechnology, Singapore, (3) POLYMAT, Spain*

Nanomedical therapies have extensively employed PEG for a plethora of applications. Its primacy within current biomedical research has stemmed from PEGs ability to solubilize organic compounds within aqueous solutions while exhibiting biocompatibility and exceptional *in vivo* stability. Furthermore, PEG has been shown to decrease opsonization creating a “stealth” effect for itself and associated compounds. These features combined with its tremendous commercial availability and synthetic amenability has made PEG an ideal choice for therapeutic delivery systems, hydrogels and many other biological applications. However, since PEG lacks natural remediation clinicians are now beginning to demand a biodegradable analogue. Herein, progress towards creation of water soluble degradable controlled polymers is presented.



Thursday, April 11, 2013 05:00 PM

General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:20 PM)

Location: Hilton Riverside

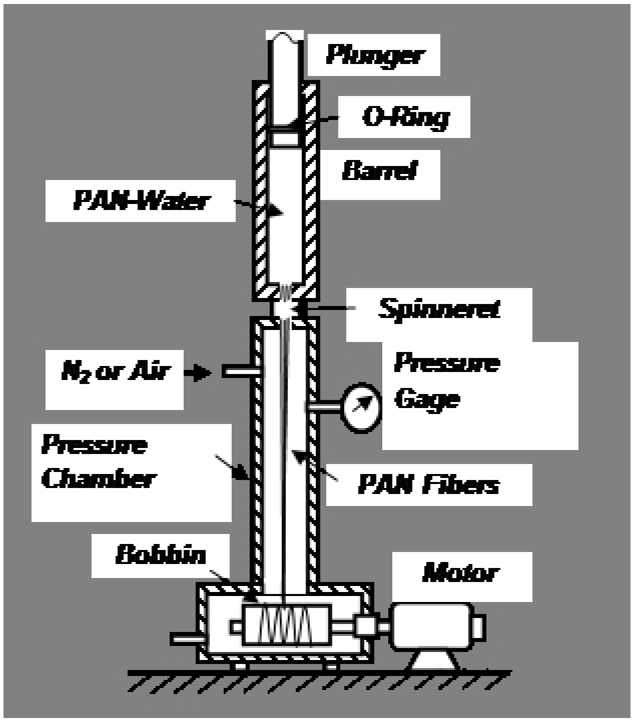
Room: Ste. C, Sec 15

621 - Melt spinning of polyacrylonitrile fibers as carbon fiber precursors

*Jianhua Huang, **Donald G Baird**, dbaird@vt.edu. Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States*

Carbon fibers are derived from precursors, with polyacrylonitrile (PAN) fibers being the predominant precursors used today. All commercial PAN fibers are presently wet or dry spun with expensive, environmentally harmful solvents. Over the past several decades efforts have been made to generate PAN fibers using the melt-spinning process. Melt-spun fibers were generated successfully from PAN copolymers plasticized with water. However, the fibers were found to have too many voids and other flaws to be used as carbon fiber precursors.

Our current work has centered on reducing the voids and flaws of melt-spun fibers with the goal of making them suitable for precursor applications. Fiber spinning was carried out using PAN copolymers containing 93 mol-% or more AN mixed with about 20 wt% of water. Differing from all previous work reported in the literature, we pressurized the fiber formation zone with nitrogen and increased the gas pressure to a level equal to or above the saturated steam pressure at the extrusion temperature as shown in the figure. This was done to eliminate or minimize the formation of bubbles or voids when the fibers solidify. It was found that the PAN fibers generated in such conditions have less voids, more uniform internal structure, and great potential to be used as carbon fiber precursors. The mechanical properties of the fibers were reported and compared with that of existing PAN fibers.

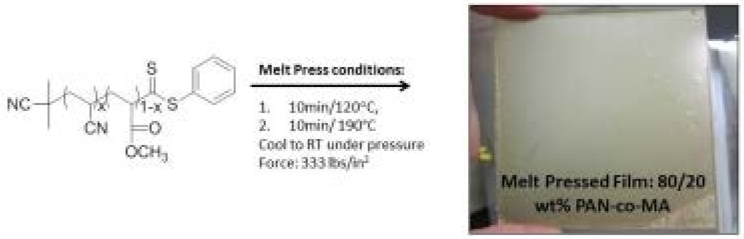


Thursday, April 11, 2013 01:35 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

622 - Synthesis and characterization of melt processible acrylonitrile copolymers via RAFT polymerization

Susan A Beck[1], *susanbeck@vt.edu, Devon Baker*[2], *Andrew Shaver*[3], *Justin Ryan*[4], *Sue Mecham*[3], *James E McGrath*[1,4]. *(1) Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States, (2) Department of Materials Engineering, Virginia Tech, Blacksburg, VA 24061, United States, (3) Macromolecular Science and Engineering, Virginia Tech, BLACKSBURG, VA 24061, United States, (4) Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States*

Acrylonitrile (AN) is well known to be an important fiber-forming material; however, high AN content copolymers are exclusively spun from solution on a commercial basis since thermooxidative degradation occurs well below appropriate melt processing temperatures due to the high temperature melting transition (T_m) of PAN. Our group at Virginia Tech has been investigating copolymers which could be designed to achieve melt fabrication even with high acrylonitrile content. We have synthesized 80%, 85%, 90% and 95% AN systems through RAFT copolymerization with methyl acrylate (MA) using 2-cyano-2-propyl dithiocarbonate as a chain transfer agent (CTA). ^{1}H-NMR and ^{13}C-NMR have been used to confirm the wt% of AN. Differential scanning calorimetry and parallel plate rheology have been utilized to determine the melt behavior of this series of polymers. Additionally, we have been able to melt press films using the 80% AN material.



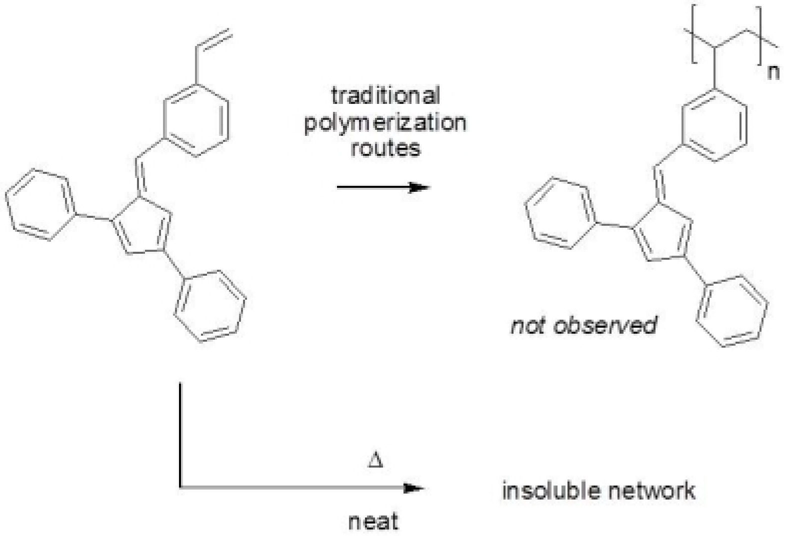
Due to the poor hydrolytic stability of dithiocarbonates and competing termination reactions which stop the polymerization at 65% monomer conversion, a series of 85 wt% PAN-co-MA polymers have been synthesized with cyanomethyl dodecyl trithiocarbonate as the CTA. This RAFT CTA has reduced the reaction times significantly as well as increased the monomer conversion. We are investigating the effect of altering monomer concentration, initiator concentration and CTA concentration to find the optimum conditions for making these copolymers to maximize monomer conversion as well compare the effect that these changes have on melt processibility.

Thursday, April 11, 2013 02:05 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

623 - Melt processable fulvene-derived glassy carbon

Russell E. Johnson, Gary J. Balaich, ***Scott T. Iacono****, scott.iacono@usafa.edu. Department of Chemistry, United States Air Force Academy, USAF Academy, Co 80840, United States*

The miniaturization of functional components is an evolving area of technology with profound implications, particularly in the microelectronics industry. Since the late 1990's, the Air Force Research Laboratory has developed a fugitive chemical vapor deposition (CVD) process that employs a sacrificial mandrel to develop nano- and micrometer-sized tubes. The process has substantial utility such that micrometer-sized tubes can be fabricated from a practically any material into a range of lengths with precise control of wall thickness, inner wall roughness, and internal diameters. This area can be further expanded to produce 3D glassy carbon components from melt-processable carbon precursors. In this sense, we have serendipitously discovered that a 1,3,6-trisubstituted fulvene possessing styryl functionality undergoes thermal crosslinking as opposed to the desired chain extension utilizing traditional polymerization routes. Thermal analysis reveals concurrent melt transition and onset of thermal crosslinking which would be ideal for the processing of shape-moldable carbon components. Various substituted fulvenes possessing extended arylene units at the 6-position produced networks with carbon yields approaching 40 wt %. The synthesis, characterization, and thermal properties of these fulvene precursors as templates for carbon systems are discussed.

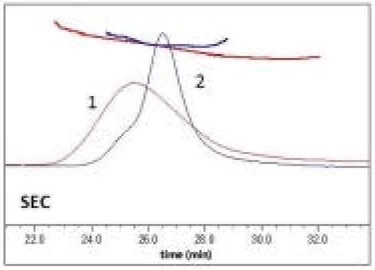


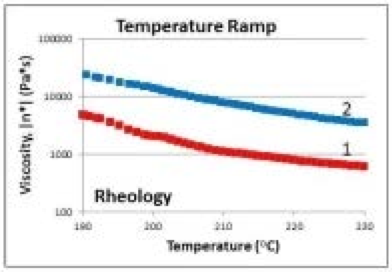
Thursday, April 11, 2013 02:25 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

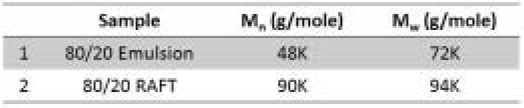
624 - Comparison of acrylonitrile/methyl acrylate (AN/MA) statistical copolymers synthesized via controlled RAFT and classical emulsion free radical polymerization for melt processing applications

__James E McGrath__[1], jmcgrath@vt.edu, Susan A Beck[1], Pryia Pisipati[4], Sue Mecham[4], Devon Baker[2], Andrew Shaver[4], Justin Ryan[3]. (1) Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States, (2) Department of Materials Engineering, Virginia Tech, Blacksburg, VA 24061, United States, (3) Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States, (4) Macromolecular Science and Engineering, Virginia Tech, Blacksburg, VA 24061, United States

Controlled RAFT and classical emulsion free radical copolymerization techniques have been used to make PAN-co-MA statistical copolymers with compositions ranging from 95 wt. % to 80 wt. %. The copolymer synthesis, characterization, and melt behavior of these materials will be described and contrasted in this presentation. These copolymers have been characterized by ^{1}H-NMR, ^{13}C-NMR, size exclusion chromatography, differential scanning calorimetry, and parallel plate rheology to investigate the structure-property differences between these polymerization techniques and resulting effects on melt-processibility.







	Sample	M_n (g/mole)	M_w (g/mole)
1	80/20 Emulsion	48K	72K
2	80/20 RAFT	90K	94K

Thursday, April 11, 2013 03:10 PM

Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)

Location: Hilton Riverside

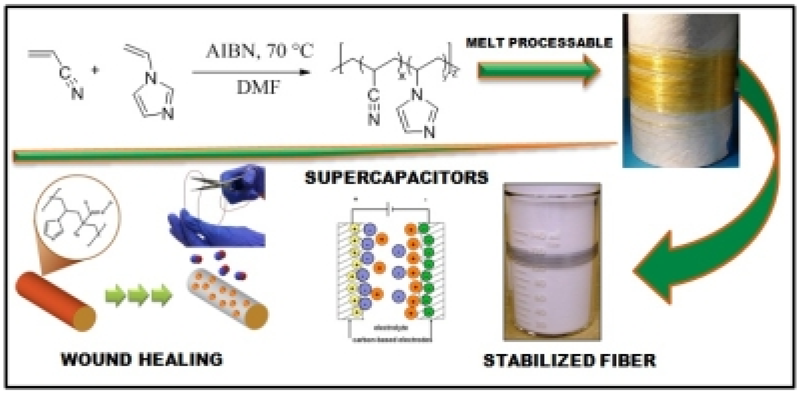
Room: Ste. B, Sec 7/10

625 - New poly (acrylonitrile-co-1-vinylimidazole) copolymer as a melt processable carbon fiber precursor and for nitric oxide releasing enhanced wound healing and supercapacitors

Samsuddin Faisal Mahmood, Wenjin Deng, Benjamin L. Batchelor, Rajneesh Verma, Alysia Lowe, Kyung-Hye Jung, Kenneth J. Balkus, John P. Ferraris, D. J. Yang, ***Dennis W. Smith,****, dwsmith@utdallas.edu. Department of Chemistry and the Alan G. MacDiarmid NanoTech Institute, The University of Texas at Dallas, Richardson, Texas, United States*

Poly acrylonitrile(AN)-*co*-vinylimidazole(VIM) polymers of different compositions were successfully synthesized by two different methods namely solution and dispersion polymerization[1,2]. Free radical solution polymerization was carried out in N-N'-dimethylformamide (DMF) solvent system whereas in dispersion system environmentally benign water was used as solvent. Suitable thermal properties like thermal stability and glass transition temperature (T_g) of the copolymers enable successful melt extrusion yielding melt extruded fiber. Melt processed and electrospun fibers were loaded with nitric oxide to make surgical suture and bandage respectively with enhanced wound healing property[3]. The results of thermal stabilization at 250 °C followed by carbonization at 1000 °C showed the applicability of AN/VIM fiber as carbon fiber precursors. Carbon nanofibers electrodes were prepared using electrospinning and thermal treatment of poly(acrylonitrile-co-vinylimidazole) followed by steam activation and annealing. Electrochemical study proved the possibility of poly(AN-*co*-VIM) as new carbon nanofiber precursor for supercapacitor electrodes[4].

References: [ol][li]Deng W.; Lobovsky A.; Iacono S.T.; Wu T.; Tomar N.; Budy S.M.; Long T.; Hoffman W.P. and Smith Jr., D.W. *Polymer*, **2011** , *52*, 622-628.[/li][li]Deng, W. and Smith Jr., D.W. Poly (Acrylonitrile-co-1-Vinylimidazole): A New Carbon Fiber Precursor: Melt Processable and Thermally Crosslinkable Carbon Fiber Precursor. LAP Lambert Academic Publishing, **2012** . pp 1-75.[/li][li]Lowe, A.; Deng, W.; Smith Jr., D.W.; Balkus Jr., K. *Macromolecules*, **2012** , *45*, 5894-5900.[/li][li]Jung K.-H., Deng w., Smith Jr., D.W. and Ferraris, J.P. *Electrochemistry Communications*, **2012,** *23,*149-152.[/li][/ol]

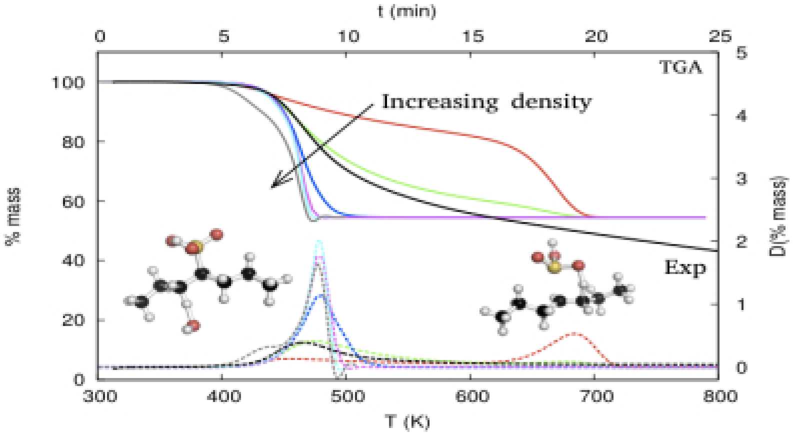


Thursday, April 11, 2013 03:40 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

626 - Pyrolysis pathways of sulfonated hydrocarbon

Jarod M Younker[1], *younkerjm@ornl.gov, Ariana Beste*[2]. *(1) Division of Computational Chemical & Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6164, United States, (2) Joint Institute for Computational Sciences, University of Tennessee, Oak Ridge, TN 37831-6164, United States*

In this work, we study the pyrolysis of sulfonated hydrocarbon, for which potential industrial applications have recently emerged. To understand the pyrolysis of these materials, *n*-heptane-4-sulfonic acid (H4S) was selected as a model compound for study. Density functional theory and transition state theory were used to determine the rate constants of pyrolysis for H4S from 300-1000K. Multiple reaction channels from two different mechanisms were explored: 1) internal five-centered elimination (E_i5), and 2) radical chain reaction. The pyrolysis of H4S was simulated with kinetic Monte Carlo (kMC) to obtain thermogravimetric analysis (TGA) plots that compared favorably to experiment. We observed that at temperatures < 550K, the radical mechanism was dominant and yielded the trans-alkene, whereas cis-alkene was formed at higher temperatures from the internal elimination. The maximum rates of %mass loss became independent of initial OH radical concentration at 440-480K. Experimentally, the maximum %mass loss occurred from 440-460K (heating rate dependent). Activation energies derived from the kMC-simulated TGAs (26-29 kcal/mol) agreed with experiment (~31 kcal/mol). The simulations revealed that in this region, decomposition of radical $HOSO_2$ became competitive to alpha-H abstraction by $HOSO_2$ radical, making OH the carrying radical for a chain of reactions. The maximum rate of %mass loss for internal elimination was observed at temperatures >630K; thus, internal elimination will not be competitive.



Thursday, April 11, 2013 04:10 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

627 - Chemistry of char forming polymers as potential precursors for carbon fibers

Amit K Naskar, *naskarak@ornl.gov, MSTD, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

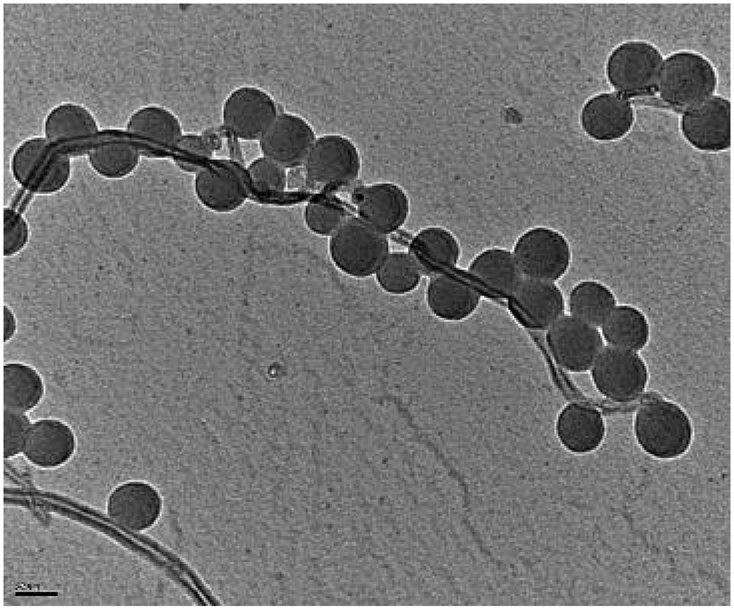
Carbon fibers are conducting and high performance materials used in a variety of structural composite applications. Historically, carbon fiber usage was limited to high end specialty applications. A lower end, high volume utilization, such as widespread use in passenger vehicles, will require significant cost reduction and new technology development. This presentation will give an overview of research approaches that are being conducted at Oak Ridge National Laboratory (ORNL). Cost analysis data on conventional polyacrylonitrile (PAN)-based carbon fibers shows that the precursor fiber contributes to 50% of the overall manufacturing cost of carbon fiber. Therefore, identifying suitable lower-cost precursors is a major objective to enable the widespread commercialization of carbon fibers. Inexpensive precursors that were considered include polyolefins, textile grade PAN, lignin, and melt-processible PAN. This presentation will also focus on melt-processible precursors that can produce nonwoven mats.

Thursday, April 11, 2013 04:30 PM
Polymer Precursor-Derived Carbon (01:30 PM - 04:55 PM)
Location: Hilton Riverside
Room: Ste. B, Sec 7/10

628 - New flexible transparent conductive electrodes based on carbon nanotubes/semi-conducting polymers composites

Eric Cloutet[1,2], *cloutet@enscbp.fr, Georges Hadziioannou*[1,2], *Usein Ismailov*[1,2], *Cyril Brochon*[1,2], *Muhammad Mumtaz*[1,2], *Wiljan Smaal*[1,2], *Gilles Pécastaings*[1,2]. *(1) LCPO, CNRS, Talence, France, (2) LCPO, Université de Bordeaux, Talence, France*

Indium Tin Oxide (ITO) and Fluorine-doped Tin Oxide (FTO) have been widely used as window electrodes in optoelectronic devices. However, when used in low-cost flexible organic device applications, these metal oxides appear to be increasingly problematic due to high cost and limited availability of indium, pooor mechanical features on flexible substrates, low chemical stability, etc. The search for novel electrode materials with good stability, high transparency and excellent conductivity is therefore a crucial goal for optoelectronics and organic optoelectronics in particular. Our strategy is based on the formulation of carbon nanotubes with polymer latexes. First we have developed an original one-pot method for synthesizing new semi-conductor polymer latexes with particle sizes below 50 nm. Then the polymer latexes were formulated with different concentrations of carbon nanotubes and deposited as films on various substrates. Characteristics (e.g. transmittance, roughness, sheet resistance, etc.) have been evaluated. One formulated product is shown below on a TEM picture discovering the first example of Bordeaux 'nano-grape'.

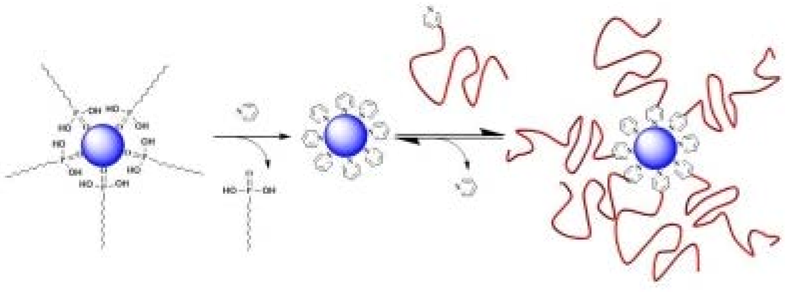


Thursday, April 11, 2013 01:35 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

629 - Tailoring nanoscale organization of CdSe/P3HT blends by ligand modification

W Michael Kochemba[1], *wkochemb@utk.edu, Deanna L Pickel*[2], *S Michael Kilbey*[1,2]. *(1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States, (2) Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States*

A method to tailor the donor/acceptor interface of bulk heterojunction organic photovoltaic devices by modifying the surface chemistry of semiconductor quantum dots (CdSe SQDs) will be presented. The ligands on CdSe SQD surfaces play an impactful role in their synthesis, solution properties and nanophase organization in a polymer matrix. In this work, we report a method to stabilize CdSe SQDs in a poly(3-hexylthiophene) (P3HT) matrix through ligand modification by successive ligand exchanges.



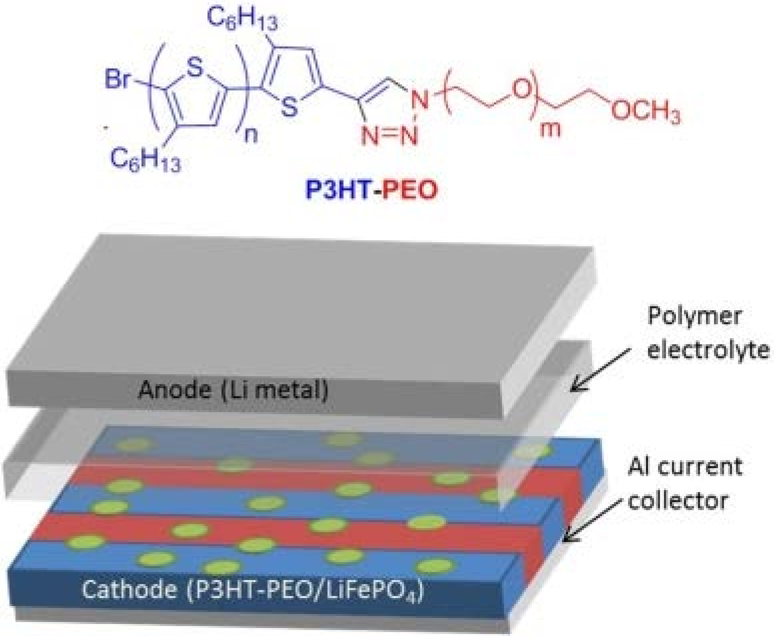
The surface ligands that were studied include dodecylphosphonic acid, pyridine, and pyridine end-functional P3HT. The pyridine end-group installed on P3HT has the propensity to coordinate to CdSe SQDs, thereby creating intimate contact between the donor and acceptor materials. Thin films of P3HT/CdSe blends were prepared under different annealing conditions and characterized using transmission electron microscopy and grazing incidence x-ray scattering techniques. The solution and electronic properties of the P3HT/CdSe blends will also be discussed.

Thursday, April 11, 2013 02:05 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

630 - Block copolymers with simultaneous ionic and electronic conduction for use in lithium battery cathodes as electrolyte

Anna E. Javier[1,2], *ajavier@lbl.gov, Shrayesh N. Patel*[2]*, Nitash P. Balsara*[1,2]*. (1) EETD, Lawrence Berkeley National Lab, Berkeley, California 94720, United States, (2) Department of Chemical Engineering, University of California, Berkeley, CA 94720, United States*

Increasing the energy density of rechargeable lithium batteries is a goal of considerable significance.[1,2] While most of the efforts thus far have focused on the energy producing components of the battery,[1-7] i.e. the active components in the electrodes that participate in the energy-producing redox reactions, improvements in the non-energy-producing battery components are essential if these targets are to be met. Current lithium-ion batteries contain several non-energy-producing components: (1) a liquid electrolyte to transport ions between the electrodes, (2) a polymeric separator to prevent contact between the electrodes, (3) an inactive polymer that binds the active particles in the electrodes, (4) an electronic conductor such as carbon to conduct electrons within the electrode, and (5) current collectors that deliver electrons to the external circuit. The non-energy producing components account for about 50% of the mass of a weight of a lithium battery. The purpose of this paper is to describe the synthesis and performance of a polymeric binder that simultaneously delivers both ions and electronic charge to active centers.

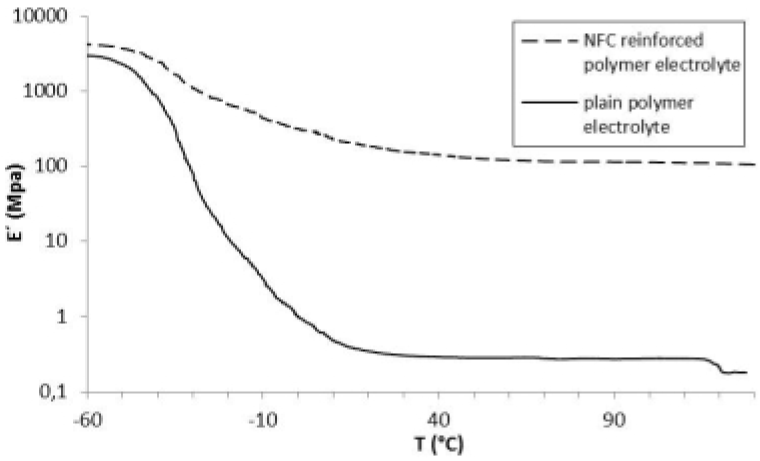


Thursday, April 11, 2013 02:25 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

631 - Structural electrolytes reinforced by NFC-aerogels

Markus Willgert, *markuswi@kth.se, Mats Johansson. Department of Fibre & Polymer Technology, Coating Technology, Stockholm, Stockholm SE-100 44, Sweden*

Polymer electrolyte composite containing a nano-fibrillated cellulose (NFC) aerogel as a mechanical reinforce have been manufactured to be used in structural lithium ion batteries. By incorporating NFC, initial studies show that the ionic conductivity drops around a factor of 10. However, the storage modulus at room temperature increases around 600 times (figure 1). Further studies will aim to covalently bond the polymer matrix to the NFC to avoid appearance of micro voids and polymer migration.



Thursday, April 11, 2013 02:45 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

632 - Polyelectrolyte multilayers stabilized catalytic nanoparticles for proton exchange membrane fuel cells

Chungyeon Cho[1], *chocy78@gmail.com, Deborah Myers*[3], *Nicole Zacharia*[1,2]. *(1) Materials Science & Engineering, Texas A&M University, College Station, Texas 77840, United States, (2) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77840, United States, (3) Chemical Science and Engineering, Argonne National Laboratory, Cass Avenue, Illinois 60439, United States*

The layer-by-layer technique for the formation of polyelectrolyte multilayers is a method of sequential exposure to oppositely charged polyelectrolyte solutions that forms a coating or even freestanding film. This technique is a versatile way to incorporate materials of different functionalities and chemistries for a range of proposed applications such as devices for energy conversion. One problem in the PEM fuel cell is the diffusion of Pt catalyst nanoparticles along their carbon black support and their eventual coalescence as the fuel cell is operated. This coalescence reduces available Pt surface area and is one of the failure modes of the catalyst in the PEM fuel cell. The work described here here is the formation of polyelectrolyte multilayers with available carboxylic acid groups used to bind Pt complexes. We incorporate Pt complex ions into LbL films by counterion exchange and use the multilayers as a nanoreactor to synthesize and a support for Pt NPs. The LbL films are used as a template for the synthesis and growth of Pt NPs, and act to immobilize the particle, preventing the further aggregation or detachment of the catalyst particles during electrochemical cycling. These materials are electrochemically characterized and present a possible method for improving PEM fuel cell life times.

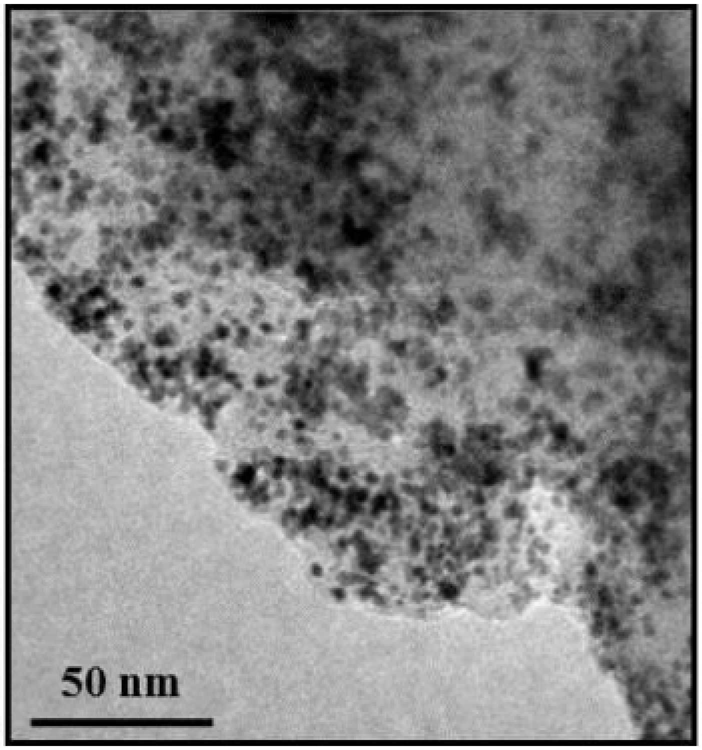


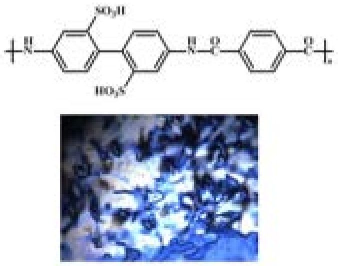
Figure 1. TEM image of PAH/PAA LbL films containing Pt NPs

Thursday, April 11, 2013 03:20 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

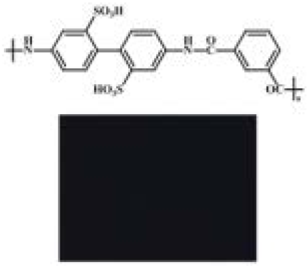
633 - Liquid crystal sulfonated aramids as proton exchange membranes for fuel cell applications

Jianwei Gao[1], *J.Gao@tudelft.nl, Ying Wang*[2], *Louis Madsen*[2], *Theo Dingemans*[1]. *(1) Faculty of Aerospace Engineering, Delft University of Technology, Delft, South Holland 2629 HS, The Netherlands, (2) Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, United States*

Two polyamides, PBDT and PBDI were successfully synthesized. Due to the different polymer structures, PBDT shows nematic liquid crystalline behavior in water, whereas PBDI forms an isotropic solution. PBDT exhibits excellent proton conductivity, comparable to Nafion^{TM}, which can be contributed to the close molecular packing of the molecules in the nematic phase, while the non-LC reference material, i.e. PBDI is significantly less. PBDT is currently under investigation as proton exchange membrane for fuel cell applications.



LC Polymer : PBDT



Non-LC Polymer: PBDI

Thursday, April 11, 2013 03:40 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

634 - 3M proton exchange membrane simulations with hetero poly acids for fuel cell applications

Somisetti V Sambasivarao, *vsomiset@mines.edu, Steve Tse, C Mark Maupin. Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States*

Classical and Multistate Empirical Valence Bond (MS-EVB) Molecular dynamics (MD) simulations have been performed on a 3M polymer with side chain -O$(CF_2)_4SO_3H$ and one H_3O^+ per sulfonic acid head group. Subsequent simulations on the 3M polymer incorporated hetero poly acids (HPAs), which are superacidic inorganic acids that have been shown to increase the overall proton conductivity. 3M-HPA systems have been simulated over various hydration and HPA loadings using classical MD in order to evaluate structural information while the MS-EVB simulations are utilized to study the aqueous proton solvation and transport phenomena. Typical transparent snapshot of 3M polymer with HPW, waters and hydronium ions from MD simulations is shown in Figure 1.

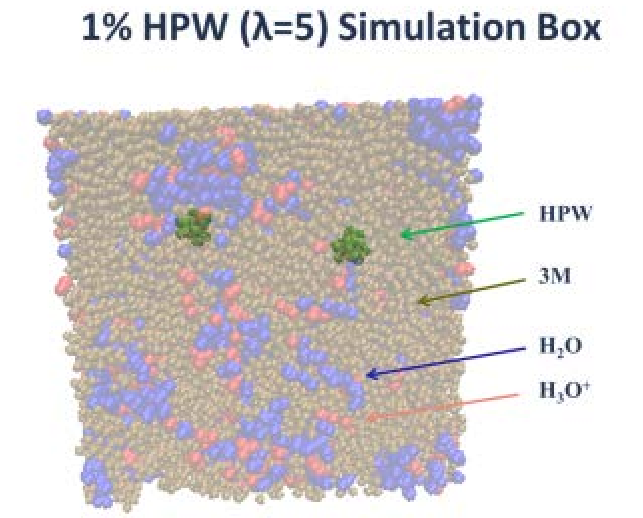


Figure 1: Snapshot of 3M showing HPW, waters and hydronium ions.

Thursday, April 11, 2013 04:00 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

635 - Novel metal-cations for anion exchange membranes

Greg Tew, *tew@mail.pse.umass.edu, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, United States*

Novel cations for anion exchange membranes remain of great importance. We report novel metal-cations based on supramolecular units capable of stability at 2 M KOH and 80 °C. These novel polymer cations have been fabricated into membranes and characterized. Their conductivity for hydroxide is 29 mS/cm at 30 °C and for bicarbonate is 10 mS/cm.

Thursday, April 11, 2013 04:30 PM
Polymer Composites for Energy Harvesting, Conversion and Storage (01:30 PM - 05:05 PM)
Location: Hilton Riverside
Room: Ste. C, Sec 13/16

POLY/PMSE Plenary Lecture and Awards Reception - EVE Session

Location:	Hilton Riverside
Room:	HEC C
Cosponsored by:	PMSE
Organizers:	Scott Iacono, Sheng Lin-Gibson, Jeffrey Youngblood
Presiders:	David Schiraldi
Duration:	5:30 pm - 8:00 pm

Pres Time	**Pub #**	**Presentation Title**
5:30 pm		Network
6:10 pm		Introductory Remarks
6:15 pm		3M Technologies and Applications Related to Energy Market Opportunities. Larry Wendling
7:00 pm		Award Reception

Sci-Mix Presentation

Sci-Mix - EVE Session

Location: Morial Convention Center
Room: Hall D
Organizers: Scott Iacono
Duration: 8:00 pm - 10:00 pm

Pub #	Presentation Title
377	From CO$_2$ to multifunctional poly(carbonate)s with controlled number of functional groups for grafting via click chemistry Jeannette Geschwind, Frederik Wurm, Holger Frey.
380	RAFT polymerization of sustainable triblock copolymers for applications as thermoplastic elastomers Shu Wang, Megan L Robertson, Kim M Le.
309	Synthesis of end-functionalized poly(β-butyrolactone) using super Brønsted acid Seiya Kikuchi, Kosuke Makiguchi, Harumi Kaga, Toshifumi satoh, Toyoji Kakuchi.
609	Synthesis and characterization of macromolecular [2]rotaxane having polymer chain as the axle component Daisuke Aoki, Yasuhito Koyama, Satoshi Uchida, Toshikazu Takata.
279	Star-dendritic-linear polymers as a modular platform to probe unimolecular micelles Brittany Myers, Scott Grayson.
282	Morphological tunability of pH-responsive, self-assembled polypeptide block copolymers through molecular design and polymer composition Ashley J Johnson, Jacob G Ray, Andrew C Holley, Charles P Easterling, Jack T Ly, Daniel A Savin.
283	HPMA-b-NCA copolymers with pH-responsive helical segments for membrane disruption Andrew C Holley, Jacob Ray, Wen M Wan, Brooks Able, Keith H Parsons, Daniel Savin, Charles L McCormick.
411	Preparation of thermally-responsive polyurethanes based upon Diels-Alder chemistry Craig A Machado, Philip J Costanzo.
402	Perfluorinated acrylate modified thiol-ene networks for highly water vapor breathable, waterproof materials Jacob M Schekman, James Goetz, Sergei Nazarenko.
406	Structure-property relationships of dual (tethered and intercalated) POSS modified montmorillonite in elastomeric nanocomposites Harold Owens, Mithun Bhattacharya, Elana C Lewis, Sarah E Morgan.
442	Multiple quantum NMR on deuterium and its application to melted homopolymers Joshua T Damron, Filipe Furtado, Marie-Luise Trutschel, Kay Saalwaechter.
446	Chemical modification effects on molecular dynamics of complex poly(rotaxane) investigated by solid-state NMR Chuan Tang, Aoi Inomata, Yasuhiro Sakai, Hideaki Yokoyama, Toshikazu Miyoshi, Kohzo Ito.
355	Synthesis, stability, and dielectric properties of polymer-functionalized SiO$_2$ nanoparticles Elizabeth Opsitnick, Chris Grabowski, Hilmar Koerner, Larry Drummy, Richard Vaia.
362	New room-temperature approach to hybrid materials: Polystyrene/silica from emulsion gels Tan Zhang, Gu Xu, Zhe-Fei Li, Oren Regev, Madhubhashini Maddumaarachchi, Frank D Blum.
360	Partially fluorinated bisphenol-A epoxy aluminized composite materials Hannah A Miller, James W Neat, Sharon C Kettwich, Scott T Iacono.
294	Self-assembly and optoelectronic properties of a rod-rod semiconducting liquid crystalline block copolymer containing poly(3-hexylthiophene) Mahesh P Bhatt, Mihaela C Stefan.
293	Non-covalent incorporation of specific binding sites onto organic transistors via block-copolymer templating Mallory L. Hammock, Oren S. Knopfmacher, Zhenan Bao.
292	Synthesis and crystallinity of all-conjugated poly(3-hexylthiophene) block copolymers Yen-Hao Lin, Rafael Verduzco.

373 Towards a low temperature biaxial nematic phase: Synthesis and phase behavior of oxazole based liquid crystals
Katie M. Gulliford, Eric Scharrer, Mary Packard.

376 Smart liquid crystalline polymers: Tuning gas permeability with external stimuli
Robinson Anandakathir, Margaret J Sobkowicz, Joey Mead, Syed Hassan, Bridgette M Budhlall.

374 Effects of nano-confinement on the structure and properties of liquid crystalline polymers
Paola A. Gonzalez Garza, Zhenpeng P. Li, Eric Baer, Christopher J. Ellison.

400 Synthesis meso-micoporous carbons using PVDC block copolymer as a carbon precursor via RAFT
yongzhong Bao, Jie Yang.

399 Impact of zeolite LTA functionalization on polyimide nanocomposite membrane properties for use in natural gas separations
Megan E. Lydon, Christopher W. Jones, Sankar Nair.

392 Thermal and mechanical properties of biodegradable epoxy resins derived from epoxidized soybean oil
Guozhen Yang, Megan L. Robertson.

2013 Fall - 246th NATIONAL ACS MEETING

Indianapolis, September 8-12, 2013

Program Meeting Chair Primary Contact: **Jeffrey Youngblood**

Program Meeting Chairs: **Sheng Lin-Gibson**, **Scott T. Iacono**

Call for papers

PACS will be open for author abstract submission on 1/21/2013 and close on 3/18/2013

THE POLY/PMSE PLENARY LECTURE AND AWARDS RECEPTION IS SCHEDULED FOR WEDNESDAY EVENING

PlenarySpeaker:

Theme: Chemistry in Motion

Program - Preliminary

Joint **POLY**/PMSE: AkzoNobel Award for Outstanding Graduate Research in Polymer Chemistry
Warren Ford

Biomacromolecules for Therapeutics and Diagnostics Delivery
Jianjun Cheng, Young Jik Kwon, Linda Shekhawat

Biomacromolecules/Macromolecules Lectureship in Creative Polymer Science
Joe Mabry

Charles Overberger Award
Rick Laine

DSM Science and Technology Award
Travis Baughman

General Topics: New Synthesis and Characterization of Polymers
Dana Garcia

Herman F. Mark Polymer Chemistry Award in honor of Ken Wagener, University of Florida

Mark Scholars Award in honor of Rigoberto Advincula, Case Western Reserve University

Mark Scholars Young Award in honor of Rachel O'Reilly, University of Warwick

Monomer and Polymer Mimicry with Renewables
Stephen Miller, Robert Mathers

Polymers for Transportation and Aerospace
Sarah Morgan, Elizabeth Jordan, Mary Ann Meador, Michael Meador

Rational Design of Advanced Capacitor Films (invited only)
Sanat Kumar, Rampi Ramprasad, Mike Chung

Joint **POLY**/PMSE: Sensing and Controlling Motion with Polymeric Materials
Christopher Wohl, Michael Dickey

Sequence-Controlled Polymers
Jean-François Lutz, Tara Meyer, Makoto Ouchi, Mitsuo Sawamoto

Structural Composites and Biomaterials: Modeling and Experiment
James Moller, Hendrick Heinz, Barry Farmer

POLY/PMSE Plenary Lecture & Awards Reception
Sheng Gibson-Lin, Jeff Youngblood, Scott Iacono

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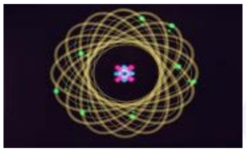
Workshops and POLY Sponsored Meetings



Complete details on upcoming POLY Workshops

For Technical Workshop Information and Registration, contact Lesia Linkous

Submit a proposal for a workshop

SUSTAINABLE POLYMERS

- May 20 - 23, 2013
- Safety Harbor Hotel and Conference Center
- Safety Harbor, Florida USA
- Co-Organizers: Dylan J. Boday and Marc A. Hillmyer

POLYMER COMPOSITES AND HIGH PERFORMANCE MATERIALS

- July 21 - 24, 2013
- Hilton Sonoma Conference Center
- Santa Rosa, California USA
- Organizers: Sara Morgan, Daniel Savin, Michael Meador, Mary Ann Meador, Jeffrey Gilman

POLYMERS IN MEDICINE AND BIOLOGY: 2013

- October 9-12, 2013
- Hilton Sonoma Conference Center
- Santa Rosa, California
- Organizers: Buddy D. Ratner, Kathryn E. Uhrich, Judy S. Riffle

ADVANCES IN POLYOLEFINS 2013

- October 13 – 16, 2013
- Hilton Sonoma Wine Country
- Santa Rosa, California
- Co-Organizers: Pal Arjunan, James E. McGrath

POLY Sponsored and Co-Sponsored Meetings

For Technical Program Information and Registration, contact: the organizers of the specific meeting

2015 Pacific Polymer Federation Conference

- Hyatt, Kauai, Hawaii
- December, 2015

2014 National Graduate Research Polymer Conference

- Louisiana State University, Baton Rouge, LA,
- May 21-23, 2014
- Organizers: W. H. Daly, J. Poyman, D. Zhang

Recently past meetings

The Southwest Regional Meeting of the American Chemical Society 2012

IUPAC World Polymer Congress 2012

MACROMEX 2011

Pacifichem 2010