APME'17

Advanced Polymers via Macromolecular Engineering

Ghent, Belgium | May 21-25, 2017

BOOK OF ABSTRACTS

ORGANISED BY

GHENT UNIVERSITY

UNDER THE AUSPICES OF

BELGIAN POLYMER GROUP

epf European Polymer Federation

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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CONTENT

WELCOME

Dear colleagues, dear friends, dear participants,

We are really delighted to welcome you in our historical city of Ghent in Belgium for the 12th International Conference on Advanced Polymers via Macromolecular Engineering, which is held under the auspices of IUPAC, European Polymer Federation (EPF) and the Belgian Polymer Group (BPG). APME2017 is the latest in a series of successful meetings, the most recent of which were held in Yokohama (Japan, 2015), Durham (UK, 2013), Cappadocia (Turkey, 2011) and Dresden (Germany, 2009).

To our surprise, the current edition turns out to be the largest APME-conference to date and one of the largest meetings on synthetic macromolecules this year. Indeed, APME2017 brings together around 500 participants from 43 countries. The program contains 97 oral presentations, organized in four parallel sessions, with contributions from many of the world's leading polymer scientists and also from numerous young polymer academics. There will also be around 250 posters presented in two poster sessions. Even though this will be a conference where you will need to make difficult choices between parallel top-lectures, we hope that you will remember it as a conference where you came home with numerous new ideas for your own projects.

The welcome reception on Sunday, the Belgian beer and fries tasting on Monday evening, the conference banquet on Tuesday evening, our special soccer game on Wednesday and touristic trips on Thursday should give all of you ample opportunities for networking and socializing while enjoying the very best of the Ghent city hospitality and beauty. The city of Ghent, with its origin around the year 630 and home of the spirit of Leo Baekeland, has been described as 'one of the world's top 10 cities to visit', 'Europe's best kept secret' and 'amongst the top 10 alternative city breaks in Europe' (Lonely Planet and Guardian). Ghent University - ranked as a top 100 university and celebrating its 200 year anniversary this year - accommodates 41,000 students, which results in a city that is filled with young people (and bikes).

We take the opportunity to express our sincere thanks to the founders of this APME-series, LD Organisation, the numerous sponsors/exhibitors, the session chairs and the many CMaC-volunteers for all efforts to make this 12th APME-conference possible!

We wish you a very pleasant stay and thank you for sharing your science and enthusiasm with us.

Prof. Filip Du Prez
Conference chairman

Prof. Richard Hoogenboom
Conference Co-chairman

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EXHIBITOR'S COMPANY PROFILES

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Biotage is a global leader in life science technology. With a broad scope of tools for synthesis, work-up, purification, evaporation and analysis, the company provides solutions, knowledge and expertise in the areas of analytical chemistry, medicinal chemistry, and process-development. Our focus is on developing technology to speed experimental procedures

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Sysmex Netherlands and Belgium

Sysmex (Benelux) is part of the international organisation, with headquarters in Kobe, Japan. Sysmex has a long history as supplier of hightech analytical systems for laboratory use. While the Sysmex products focussed mainly on haematology and urinalysis, several other reputable manufacturers are represented exclusively by us in the Benelux area.

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Vetex NV

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GENERAL INFORMATION

VENUE

Ghent University
Faculty of Economics and Business Administration
Tweekerkenstraat 2
(entrance left of Sint-Peter's Abbey)
9000 Ghent
Belgium

PUBLIC TRANSPORTATION:

- Buses 34, 35, 36, 55, 57, 58, 70, 71, 72, 73, 74, 76, 77, 78 (stop Heuvelpoort, then 5 minutes walking via Overpoortstraat)
- Bus 5 (stop Sint-Pietersplein)
- Tram, line 1 (stop Veergrep, then 7 minutes walking via Kannunikstraat and Kazernenstraat)

REGISTRATION & INFORMATION DESK

The Registration desk will be open on:

► Sunday, May 21	15:00 – 18:00
► Monday, May 22	08:00 – 17:45
► Tuesday, May 23	08:00 – 17:00
► Wednesday, May 24	08:30 – 16:00

POSTER PRESENTATIONS

Poster boards are located in the foyer of the Auditorium on the 2nd floor.

► **Poster Session 1:** Monday, May 22 at 17:45-19:15 – posters with odd numbers.

Related posters should be mounted on Monday during lunch or coffee breaks and should be removed by 10:00 on Tuesday. Posters which have not been removed by then will be removed and disposed of by the symposium staff.

► **Poster Session 2:** Tuesday, May 23 at 17:00-18:30 – posters with even number

Related posters should be mounted on Tuesday during lunch or coffee breaks and should be removed by 10:00 on Wednesday. Posters which have not been removed by then will be removed and disposed of by the symposium staff.

INTERNET ACCESS

WiFi internet is available for all participants during the symposium. Login credential are included in your welcome package.

CERTIFICATE OF ATTENDANCE

A certificate of attendance is provided in your registration package. Participants requiring an original stamp and signature should present their certificate at the Registration desk.

SOCIAL PROGRAMME

The social programme consists of the following activities:

WELCOME RECEPTION, SUNDAY MAY 21, AS FROM 18:00

In the entrance lobby

BELGIAN BEER TASTING AND FRIES, MONDAY MAY 22, AS FROM 19:00

In the entrance lobby

BANQUET, TUESDAY MAY 23, 19:30

The conference dinner will take place on Tuesday evening at the Oude Vismijn, located in the renovated Old Fish Market. After the dinner, you will enjoy the musical presence of «Luna6», a well-known pop-rock cover band in the Ghent region.
Participation at the banquet is optional with a contribution of €65. If you still wish to register, please check the availabilities at the registration desk.

SOCCER GAME, WEDNESDAY MAY 24

After the last plenary lecture on Wednesday, a soccer game is organised between the **"Belgian polymer team"** and the **"Rest of the World polymer team".**

- ► 17:15 Buses leaving to soccer tournament
- ► 17:45 Soccer game 'Belgian Polymer team' against 'Rest of the World Polymer team'

WORLD POLYMER TEAM	BELGIAN POLYMER TEAM
Yusuf Yagci - Captain (Turkey)	**Filip Du Prez - Captain**
Bruno Ameduri (France)	Stijn Dekeukeleire
Remzi Becer (United Kingdom)	David Fournier
Andres Ciolino (Argentina)	Jean-François Gohy
Lian Hutchings (United Kingdom)	Richard Hoogenboom
Makoto Ouchi (Japan)	Victor Jerca
Ali Gorkem Yilmaz (Turkey)	Wim Thielemans

- ► 19:00 Free drinks and snacks (until 20:00)

The participation to the soccer game is optional and free of charge but subject to registration. If you still wish to register, please check the availabilities at the registration desk.

EXCURSIONS, THURSDAY MAY 25

2 different excursions are proposed on Thursday May 25 to allow you to discover the two most charming cities in Flanders. If you still wish to register, please check for the availabilities at the registration desk.

GHENT, 10:00-12:30 (duration: about 2h30)

- **10:00: Boat tour to discover the medieval center of Ghent** - with an English speaking guide (45 minutes)
- **11:00: Visit of the STAM museum** with an English speaking guide (1h30): The boat will drop you off at the city museum STAM, which presents the story of the city of Ghent. A permanent circuit leads visitors along a chronological trail of objects and multimedia which trace the development and growth of Ghent.

Fee: 20 € (including boat ticket and STAM museum entrance.)

BRUGES, 10:00 - free duration

- **Buses** will leave Ghent at **10:00**, and will drop you off at **«De Halve Maan» brewery**, located in the historical centre of Bruges. The guided visit will start at 11:00 and should last about 45 minutes.
- After the visit, you will be **free to explore the lovely city of Bruges**. Listed on UNESCO World Heritage Sites, Bruges has the best-preserved example of a medieval city centre, with its bell tower leaving over the wide open market. With the centre closed off to cars, all the stunning beauty and culture of this unforgettable city can be easily explored on foot, although a boat ride along the quiet canals is something not to be missed.
- The largest religious procession, the **Procession of the Holy Blood**, will take place in Bruges on May 25 from 14:30 until 18:00. Up to 100,000 people witness the procession and its biblical stories. It is an event now included on the UNESCO World Heritage List. You can either leave Bruges before the procession or stay for this very typical event.
- A free time train ticket will allow you to return to Ghent at your best convenience.

Fee: 35 € (including ticket for brewery visit and train ticket)

PROGRAMME

Sunday May 21, 2017	
15:00	Registration
18:00	Welcome reception

Monday May 22, 2017				
08:00	Registration			
	Auditorium Quatelet			
08:50	Introduction Filip DU PREZ (GHENT UNIVERSITY, Ghent, Belgium) Yusuf YAGCI (ISTANBUL TECHNICAL UNIVERSITY, Istanbul, Turkey)			
	Session Chair Krzysztof MATYJASZEWSKI (CARNEGIE MELLON UNIVERSITY, Pittsburgh, United States)			
09:10	**PL01 - Advanced Functional Polymers by Precision Polymerizations: A Perspective** Mitsuo SAWAMOTO (CHUBU UNIVERSITY, Kasugai, Aichi , Japan)			
10:00	Break			
	Auditorium Devreker	**Auditorium Vlerick**	**Auditorium Picard**	**Auditorium Van Vaerenbergh**
	Session Chair Martina STENZEL (UNSW, Sydney, Australia)	Session Chair Richard HOOGENBOOM (GHENT UNIVERSITY, Ghent, Belgium)	Session Chair Remzi BECER (QUEEN MARY UNIVERSITY OF LONDON, London, United Kingdom)	Session Chair Brigitte VOIT (LEIBNIZ INSTITUT DRESDEN, Dresden, Germany)
10:10	**IL01 - New ATRP Procedures for Macromolecular Engineering** Krzysztof MATYJASZEWSKI (CARNEGIE MELLON UNIVERSITY, Pittsburgh, United States)	**IL02 - Hydrogels as Synthetic ECM Analogs through Bio-Click Reactions** Kristi ANSETH (UNIVERSITY OF COLORADO BOULDER, Boulder, United States)	**IL03 - Polymerisation-induced Self-assembly** Steve ARMES (UNIVERSITY OF SHEFFIELD, Sheffield, United Kingdom)	**IL04 - Renewable Polymers a Supercritical Approach** Steven HOWDLE (UNIVERSITY OF NOTTINGHAM, Nottingham, United Kingdom)
10:40	Coffee break			
11:10	**IL05 - Sulfur-Free RAFT Polymerisation of Methacrylates in Emulsion Polymerisation** David HADDLETON (UNIVERSITY OF WARWICK, Coventry, United Kingdom)	**IL06 - Towards Polymer-peptide Conjugates as Potent Drugs** Bert KLUMPERMAN (STELLENBOSCH UNIVERSITY, Stellenbosch, South Africa)	**IL07 - Engineering Interfaces Using Controlled Radical Polymerization** Harm-Anton KLOK (EPFL, Lausanne, Switzerland)	**IL08 - Sustainable Polyurethanes: Reactivity Study and Challenges of Cyclic Carbonates** Sylvain CAILLOL (ICG MONTPELLIER, Montpellier, France)
11:40	**OC01 - RAFT/MADIX Emulsion Copolymerization of Vinyl Acetate and N-Vinylcaprolactam: Towards Waterborne Physically Crosslinked Thermoresponsive Particles** Maud SAVE (UNIVERSITY OF PAU, Pau, France)	**OC02 - An Injectable, Anisotropic Hydrogel for Directed Cell and Nerve Growth** Laura DE LAPORTE (DWI-LEIBNIZ INSTITUTE FOR INTERACTIVE MATERIALS E.V., Aachen, Germany)	**OC03 - Polymerization-Induced Self-Assembly for Reinforced Acrylic Coatings** Jutta RIEGER (PIERRE AND MARIE CURIE UNIVERSITY (UPMC) - CNRS, Paris, France)	**OC04 - Synthesis of Poly(Butylene Succinate) and Poly(Butylene Adipate) Copolymers Using Enzyme Catalysis** Miroslawa EL FRAY (WEST POMERANIAN UNIVERSITY OF TECHNOLOGY, SZCZECIN, Szczecin, Poland)
12:00	**OC05 - New Approaches to Controlled Synthesis of Polymers via "Living" Radical Polymerization** Mikhail ZAREMSKI (MOSCOW STATE UINIVERSITY, Moscow, Russia)	**OC06 - Functional Thin Hydrogel Layers** Dirk KUCKLING (UNI PADERBORN, Paderborn, Germany)	**OC07 - Single Chain Folding Engineering Toward Nanomedicine and Catalysis Applications** Jose A. POMPOSO (UNIVERSITY OF THE BASQUE COUNTRY, San Sebastian, Spain)	**OC08 - Biodegradable Protein-Polymer Supramolecular Assemblies: Synthetic Approaches and Properties** Kelly VELONIA (UNIVERSITY OF CRETE, Heraklion Crete, Greece)
12:20	Lunch			
	Auditorium Quatelet			
	Session chair Christopher BOWMAN (UNIVERSITY OF COLORADO, Colorado, United States)			
13:40	**PL02 - Principles of Vitrimer Chemistry and Physics** Ludwik LEIBLER (ESPCI, Paris, France)			
14:30	Break			
	Auditorium Devreker	**Auditorium Vlerick**	**Auditorium Picard**	**Auditorium Van Vaerenbergh**
	Session Chair David HADDLETON (UNIVERSITY OF WARWICK, Coventry, United Kingdom)	Session Chair Helmut SCHLAAD (UNIVERSITY OF POTSDAM, Potsdam, Germany)	Session Chair Andrew SLARK (HENKEL ADHESIVE TECHNOLOGIES, Wokingham, United Kingdom)	Session Chair: Guillaume DELAITTRE (KARLSRUHE INSTITUTE OF TECHNOLOGY, Eggenstein-Leopoldshafen, Germany)
14:35	**IL09 - Dynamic Chemistries in Smart Polymers** Christopher BOWMAN (UNIVERSITY OF COLORADO, Colorado, United States)	**IL10 - Polymer-surface Interactions from the Molecular Perspective by AFM Force Spectroscopy** Julius VANCSO G. (UNIVERSITY OF TWENTE, Enschede, The Netherlands)	**IL11 - Academic Research in a Chemical Company - Turning Contradiction into Common Ground** Bernd BRUCHMANN (BASF SE, Ludwigshafen am Rhein, Germany)	**IL12 - Design of Monomers Undergoing Radical Ring-Opening Polymerization and their Application to Functional Polymers** Takeshi ENDO (KINDAI UNIVERSITY, Osaka, Japan)
15:05	Coffee break			

15:35	**IL13 - Macromolecular Metamorphosis: An Alternative Approach to Stimuli-Responsive Polymers** Brent S. SUMERLIN (UNIVERSITY OF FLORIDA, Gainesville, United States)	**IL14 - Sequence-Specific Polymers Synthesized from Anionic Polymerizations of Template Monomers** Junpo HE (FUDAN UNIVERSITY, Shanghai, China)	**IL15 - Designed (and) Functional Polymer Networks ... New Approaches and Applications** Friedrich Georg SCHMIDT (EVONIK INDUSTRIES AG, Marl, Germany)	**IL16 - Polymer Assisted Housing of Actives for Designed Release** Munmaya MISHRA (ALTRIA RESEARCH CENTER, Virginia, United States)
16:05	**OC09 - Supramolecular Biomaterials: From Fundamentals to Advanced Healthcare Solutions** Eric APPEL (STANFORD UNIVERSITY, Stanford, United States)	**OC10 - New Polymerization Methodology of Amino-Acid Monomers** Youhua TAO (CHANGCHUN INSTITUTE OF APPLIED CHEMISTRY, Changchun, China)	**OC11 - Isosorbide as a Building Block for Polyesters and Polycarbonate, Challenges and Applications** René SAINT-LOUP (ROQUETTE, Lestrem, France)	**OC12 - Polymersomes and Multicompartment Systems for Synthetic Biology** Dietmar APPELHANS (LEIBNIZ INSTITUTE OF POLYMER RESEARCH DRESDEN, Dresden, Germany)
16:25	**Break**			
	Session Chair Steve ARMES (UNIVERSITY OF SHEFFIELD, Sheffield, United Kingdom)	**Session Chair** Eva M. HARTH (VANDERBILT UNIVERSITY, Nashville, United States)	**Session Chair** Friedrich Georg SCHMIDT (EVONIK INDUSTRIES AG, Marl, Germany)	**Session Chair** Mitsuo SAWAMOTO (CHUBU UNIVERSITY, Kasugai, Aichi , Japan)
16:30	**OC13 - «Colored» Multi-Stimuli Responsive Hydrogels** Patrice WOISEL (UNIVERSITY OF LILLE, Villeneuve d'ascq, France)	**OC14 - Recyclable Crosslinked Polymer Networks with Full Property Recovery via One-Step Controlled Radical Polymerization** John M. TORKELSON (NORTHWESTERN UNIVERSITY, Evanston, IL, United States)	**OC15 - The Synthesis and Characterization of Farnesene-Based Industrial Polymers** Anne-Laure JÉZÉQUEL (TOTAL, Saint-Avold, France)	**OC16 - Synthesis and Solution Properties of PHPMA Based Copolymers Containing Stable Nitroxyl Radicals** Sergey FILIPPOV (INSTITUTE OF MACROMOLECULAR CHEMISTRY, Prague, Czech Republic)
16:50	**OC17 - Polyampholyte Microgels: from Molecular Design to Ionic Traps and Switches** Andrij PICH (RWTH AACHEN UNIVERSITY, Aachen, Germany)	**OC18 - Alternatives to Conventional Polymerization Initiators** Didier GIGMES (AIX-MARSEILLE UNIVERSITY, Marseille, France)	**OC19 - Shape Recording Materials** Gerhard MAIER (POLYMATERIALS AG, Kaufbeuren, Germany)	**OC20 - Ring Opening of Sustainable Dioxolanone Monomers as a New Route to Functional, Degradable Polyesters** Michael SHAVER (UNIVERSITY OF EDINBURGH, Edinburgh, United Kingdom)
17:10	**IL17 - Functional Nanostructures through Polymerization Induced Microphase Separation** Marc A. HILLMYER (UNIVERSITY OF MINNESOTA, Minneapolis, United States)	**IL18 - Polymer Designs for Infrared Laser Responsive Material** Johan LOCCUFIER (AGFA GEVAERT NV, Mortsel, Belgium)	**IL19 - Solving Sticky Adhesive Problems with Polymer Chemistry: Linking Applied Properties with Polymer Architecture** Andrew SLARK (HENKEL ADHESIVE TECHNOLOGIES, Wokingham, United Kingdom)	**IL20 - Enzyme-Polymer Nanohybrids** Guillaume DELAITTRE (KARLSRUHE INSTITUTE OF TECHNOLOGY, Eggenstein-Leopoldshafen, Germany)
17:40	**Break**			
17:45	**Poster session 1 (until 19:15)**			
19:00	**Group picture**			
19:15	**Beer tasting and fries event**			

Tuesday May 23, 2017

	Auditorium Quatelet			
	Session Chair Kristi ANSETH (UNIVERSITY OF COLORADO BOULDER, Boulder, United States)			
08:40	**PL03 - The Power of Polymer Synthesis in Macromolecular Engineering** Craig HAWKER (UNIVERSITY OF CALIFORNIA, Santa Barbara, United States)			
09:30	**Break**			
	Auditorium Devreker	**Auditorium Vlerick**	**Auditorium Picard**	**Auditorium Van Vaerenbergh**
	Session Chair Jan C.M. VAN HEST (RADBOUD UNIVERSITY NIJMEGEN, Nijmegen, The Netherlands)	**Session Chair** Julius VANCSO G. (UNIVERSITY OF TWENTE, Enschede, The Netherlands)	**Session Chair** Harm-Anton KLOK (EPFL, Lausanne, Switzerland)	**Session Chair** Craig HAWKER (UNIVERSITY OF CALIFORNIA, Santa Barbara, United States)
09:35	**IL21 - Polymer-based Redox Flow Batteries: New Applications for Redox-active Functional Macromolecules** Ulrich SCHUBERT (UNIVERSITY OF JENA, Jena, Germany)	**IL22 - Using Crystallisation Driven Assembly for the Formation of 2D Nanomaterials** Rachel O'REILLY (THE UNIVERSITY OF WARWICK, Warwick, United Kingdom)	**IL23 - Introducing Mechanics into «click»-Chemistry: Force-induced Crosslinking and Self-healing of Polymers** Wolfgang BINDER (MARTIN-LUTHER UNIVERSITY HALLE-WITTENBERG, Halle, Germany)	**IL24 - Universal Conditions for the Controlled Polymerization of Acrylates, Methacrylates, and Styrene Via CU(0)-RDRP** Athina ANASTASAKI (UNIVERSITY OF CALIFORNIA, Santa Barbara, United States)
10:05	**Coffee break**			
10:25	**IL25 - Rational Design of ABC Triblock Terpolymer Solution Nanostructures with Controlled Patch Morphology** Axel MUELLER (UNIVERSITY OF MAINZ, Mainz, Germany)	**IL26 - Nanocelluloses and Well-defined Polymers – Hybrid Materials with Great Potential.** Eva MALMSTROM-JONSSON (ROYAL INSTITUTE OF TECHNOLOGY, Stockholm, Sweden)	**IL27 - Glycan Inspired Biomaterials; Targeting Bacterial Toxins** Matthew I. GIBSON (UNIVERSITY OF WARWICK, Coventry, United Kingdom)	**IL28 - H-bonding Activation for ROP: Enzymatic vs Organic Catalysis** Frederic PERUCH (LABORATOIRE DE CHIMIE DES POLYMARES ORGANIQUES, Pessac, France)
10:55	**IL29 - Macromolecular Materials via Precision Photochemistry** Christopher BARNER-KOWOLLIK (QUEENSLAND UNIVERSITY OF TECHNOLOGY (QUT), Brisbane, Australia)	**IL30 - Engineering of Fatty Acid Methyl Esters Towards Bio-based Polymers with Original Properties** Henri CRAMAIL (LCPO, UNIVERSITY OF BORDEAUX, Pessac, France)	**IL31 - Complex Glycopolymer Structures and their Interactions with Lectins** Remzi BECER (QUEEN MARY UNIVERSITY OF LONDON, London, United Kingdom)	**IL32 - Polypeptides by Light: Photo-Polymerisation Of N-Carboxyanydrides (NCA)** Andreas HEISE (ROYAL COLLEGE OF SURGEONS IN IRELAND, Dublin, Ireland)
11:25	**Break**			

	Auditorium Devreker	Auditorium Vlerick	Auditorium Picard	Auditorium Van Vaerenbergh
	Session Chair Axel MUELLER (UNIVERSITY OF MAINZ, Mainz, Germany)	**Session Chair** Eva MALMSTROM-JONSSON (ROYAL INSTITUTE OF TECHNOLOGY, Stockholm, Sweden)	**Session Chair** Rachel O'REILLY (THE UNIVERSITY OF WARWICK, Warwick, United Kingdom)	**Session Chair** Bruno AMEDURI (ENSC, Montpellier, France)
11:30	**IL33 - Benzodioxinone Photochemistry. A Versatile Root to Macromolecular Synthesis** Yusuf YAGCI (ISTANBUL TECHNICAL UNIVERSITY, Istanbul, Turkey)	**IL34 - Controlling Polymersome Shape and Function** Jan C.M. VAN HEST (RADBOUD UNIVERSITY NIJMEGEN, Nijmegen, The Netherlands)	**IL35 - Metathesis Polymerization of Amino acid Derivatives** Helmut SCHLAAD (UNIVERSITY OF POTSDAM, Potsdam, Germany)	**IL36 - Synthesis of Polyamide 6 with Aramide Units** Stephane CARLOTTI (UNIVERSITY OF BORDEAUX, Pessac, France)
12:00	**OC21 - Straightforward Synthesis of Substituted Thiolactones and their Application to Polymer Synthesis and Modification** Mathias DESTARAC (UNIVERSITY OF TOULOUSE, Toulouse, France)	**OC22 - Engineering Microbial Responses with Synthetic Polymers** Francisco FERNANDEZ-TRILLO (UNIVERSITY OF BIRMINGHAM, Birmingham, United Kingdom)	**OC23 - Synthesis of PH-Responsive Glycopolypeptides and their Interactions with Lectins** Henning MENZEL (BRAUNSCHWEIG UNIVERSITY OF TECHNOLOGY, Braunschweig, Germany)	**OC24 - Empowering Inert Polyethers with Functional Epoxides: Synthesis and Biological Applications** Byeong-Su KIM (UNIST, Ulsan, Korea, South)
12:20	**Lunch**			
	Session Chair Yusuf YAGCI (ISTANBUL TECHNICAL UNIVERSITY, Istanbul, Turkey)	**Session Chair** Junpo HE (FUDAN UNIVERSITY, Shanghai, China)	**Session Chair:** Brent S. SUMERLIN (UNIVERSITY OF FLORIDA, Gainesville, United States)	**Session Chair** Laura DE LAPORTE (DWI-LEIBNIZ INSTITUTE FOR INTERACTIVE MATERIALS E.V., Aachen, Germany)
13:40	**IL37 - Mechanisms of Solubility Enhancement for Hydrophobic Drugs in Polymeric Spray-Dried Dispersions** Timothy LODGE (UNIVERSITY OF MINNESOTA, Minneapolis, United States)	**IL38 - Living Radical Ring-opening Redox Polymerization (R3P) of Dithiols** Judit E. PUSKAS (UNIVERSITY OF AKRON, Akron, United States)	**IL39 - Synthetic Routes to Simplifying Molecular Complexity** Patrick THEATO (HAMBURG UNIVERSITY, Hamburg, Germany)	**IL40 - From Functionalized Polymers to Non-isocyanate Polyurethanes (NIPUs)** Sophie GUILLAUME (UNIVERSITY OF RENNES, Rennes, France)
14:10	**OC25 - Polymer Synthesis by Tandem Reaction of a-(Halomethyl)Acrylate via Addition-Fragmentation and Click Reactions** Yasuhiro KOHSAKA (SHINSHU UNIVERSITY, Ueda, Japan)	**OC26 - Fabrication of Polymer-Protein Hybrids Based on Thiol-Disulfide Exchange Reactions** Hanying ZHAO (NANKAI UNIVERSITY, Tianjin, China)	**OC27 - Triazolinedione-based Click and Transclick Reactions: a Macromolecular Relay** Hannes HOUCK (UNIVERSITY OF GHENT - KARLSRUHE INSTITUTE OF TECHNOLOGY, Ghent, Belgium)	**OC28 - Lassos and Loops: Topological Control over the Interfacial Physico-Chemical Properties of Polymer Assemblies** Edmondo Maria BENETTI (ETH ZÜRICH, Zürich, Switzerland)
14:30	**IL41 - Topological Polymer Chemistry toward Macromolecular Graph Constructions** Yasuyuki TEZUKA (TOKYO INSTITUTE OF TECHNOLOGY, Tokyo, Japan)	**IL42 - Stereochemical Control of Materials Properties through Nucleophilic Thiol-yne Additions** Andrew P. DOVE (WARWICK UNIVERSITY, Warwick, United Kingdom)	**IL43 - Linear Gradient Multi-Block Copolymers with Up to 14 Blocks: A Rapid and General Strategy for an Interesting Class of Materials with Excellent Mechanical Properties** Holger FREY (UNIVERSITY OF MAINZ, Mainz, Germany)	**IL44 - New Polymers and Strategies for Drug Delivery Applications** Julien NICOLAS (PARIS-SUD UNIVERSITY, CNRS, Châtenay-Malabry, France) - **Recipient of 2017 *Polymer Chemistry* Lectureship**
15:00	**Coffee break**			
	Session Chair Timothy LODGE (UNIVERSITY OF MINNESOTA, Minneapolis, United States)	**Session Chair** Bert KLUMPERMAN (STELLENBOSCH UNIVERSITY, Stellenbosch, South Africa)	**Session Chair** Christopher BARNER-KOWOLLIK (QUEENSLAND UNIVERSITY OF TECHNOLOGY (QUT), Brisbane, Australia)	**Session Chair** Bruno DE GEEST (GHENT UNIVERSITY, Ghent, Belgium)
15:20	**OC29 - Phosphorus Chemistry as a Tool for the Production of Metal-Containing Polymers and Polyelectrolytes** Joe GILROY (THE UNIVERSITY OF WESTERN ONTARIO, London, Canada)	**OC30 - (AB)N-Multiblock Copolymers via Simple One-Step Melt Condensation Chemistry** Theo DINGEMANS (UNC CHAPEL HILL, Chapel Hill, United States)	**OC31 - Multi-Responsive Coordination Polymers Utilising Metal-Stabilised, Dynamic Covalent Imine Bonds** Maarten SMULDERS (WAGENINGEN UNIVERSITY, Wageningen, The Netherlands)	**OC32 - Albumin-Polymer-Drug Conjugates - a Final End to the Molecular Weight Race** Camilla Frich RIBER (AARHUS UNIVERSITY, Aarhus C, Denmark)
15:40	**OC33 - Dancing in the Dark with Sulfur and Selenium: next Generation IR Optical Polymers for IR Thermal Imaging** Jeffrey PYUN (UNIVERSITY OF ARIZONA, Tucson, United States)	**OC34 - Twofold Helical Polymerization: thermal Solid-State Polymerization of 7-Cyano-7-Alkoxycarbonyl-P-Benzoquinone Methides** Takahito ITOH (MIE UNIVERSITY, Tsu, Japan)	**OC35 - Polymeric Arsenicals as Functional Polymer Scaffolds** Paul WILSON (UNIVERSITY OF WARWICK, Coventry, United Kingdom)	**OC36 - Poly(METHYL VINYL ETHER-alt-MALEIC ACID)-Based Hydrogels and their Biomedical Applications** Tianzhu ZHANG (SOUTHEAST UNIVERSITY, Nanjing, China)
16:05	**OC37 - Thin Films of Amphiphilic Block Copolymers Designed for Optical Sensor Application** Darinka CHRISTOVA (BULGARIAN ACADEMY OF SCIENCES, Sofia, Bulgaria)	**OC38 - Electrogenerated Thin Films of Microporous Polymer Networks with Remarkably Increased Electrochemical Response to Nitroaromatic Analytes** Ullrich SCHERF (UNIVERSITY OF WUPPERTAL, Wuppertal, Germany)	**OC39 - Teaching an Old Dog New Tricks - the Wonderful World of Azobenzenes** Hatice MUTLU (KARLSRUHE INSTITUTE OF TECHNOLOGY, Eggenstein-Leopoldshafen, Germany)	**OC40 - Increasing the Solubility Range of Polyesters by Tuning their Microstructure with Comonomers** Katrien BERNAERTS (MAASTRICHT UNIVERSITY, Geleen, The Netherlands)
16:25	**IL45 - Highly Aromatic Polymer Architectures Designed for Optoelectronic Applications** Brigitte VOIT (LEIBNIZ INSTITUT DRESDEN, Dresden, Germany)	**IL46 - Emulsion Templated Hydrogels: Superabsorbents, Stimulus-Response, Ion-exchange, and Self-crosslinking** Michael SILVERSTEIN (TECHNION - ISRAEL INSTITUTE OF TECHNOLOGY, Haifa, Israel)	**IL47 - New Spin on Old Polymers: Versatile Materials using Simple Chemistry and Electrospinning** Amitav SANYAL (BOGAZICI UNIVERSITY, Istanbul, Turkey)	**IL48 - Improvement of Nitinol Corrosion Resistance by SiATRP: the Key Role of Electrografting Process** Laetitia MESPOUILLE (UNIVERSITY OF MONS, Mons, Belgium)
16:55	**Break**			
17:00	**Poster session 2 (until 18:30)**			
19:30	**Banquet at Oude Vismijn**			

Wednesday May 24, 2017

	Auditorium Devreker	Auditorium Vlerick	Auditorium Picard	Auditorium Van Vaerenbergh
	Session Chair Judit E. PUSKAS (UNIVERSITY OF AKRON, Akron, United States)	**Session Chair** Philippe DUBOIS (LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY, Hautcharage, Luxembourg)	**Session Chair** Eric DROCKENMULLER (UNIVERSITY CLAUDE BERNARD LYON 1, Villeurbanne, France)	**Session Chair** Michael MONTEIRO (THE UNIVERSITY OF QUEENSLAND, Queensland, Australia)
09:00	**IL49 - Multicomponent Reactions in Polymer Science: from Versatile Tuning of Structure and Properties to Sequence Defined Macromolecules** Michael A. R. MEIER (KARLSRUHE INSTITUTE OF TECHNOLOGY (KIT), Karlsruhe, Germany)	**IL50 - Molecular Engineering with Living Anionic Copolymerisation** Lian HUTCHINGS (DURHAM UNIVERSITY, Durham, United Kingdom)	**IL51 - Innovative Polymer Electrolytes for Energy and Bioelectronics** David MECERREYES (POLYMAT, INSTITUTE OF POLYMERIC MATERIALS, San Sebastian, Spain)	**IL52 - Engineering the Immune Sytem with Polymeric Nanomaterials** Bruno DE GEEST (GHENT UNIVERSITY, Ghent, Belgium)
09:30	**IL53 - Precision Polymer Chemistry for BioNano Applications** Sebastien PERRIER (UNIVERSITY OF WARWICK, Warwick, United Kingdom)	**IL54 - Polyphosphoesters: New Trends in Synthesis and Drug Delivery Applications** Christine JEROME (UNIVERSITY OF LIEGE, Liege, Belgium)	**IL55 - Redox Polymers: the Future for Li-ion Batteries?** Jean-François GOHY (Catholic University of Louvain, Louvain-la-Neuve, Belgium)	**IL56 - Designer Molecules in Precision Polymerizations toward Advanced Macromolecular Engineering** Makoto OUCHI (KYOTO UNIVERSITY, Kyoto, Japan)
10:00	**IL57 - Design and Applications of Digital Polymers** Jean-Francois LUTZ (CHARLES SADRON INSTITUTE, CNRS, Strasbourg, France)	**IL58 - Specifically Interacting Polymers: Can Polymer Chemists still Learn Anything from Mussels?** Hans BÖRNER (HUMBOLDT UNIVERSITY OF BERLIN, Berlin, Germany)	**IL59 - Multifunctional Poly(ionic liquid)s: from Synthesis to Applications in Energy and Environment** Christophe DETREMBLEUR (UNIVERSITY OF LIEGE, Liege, Belgium)	**IL60 - Controlling the Functionality and Topology of Polymers Prepared by Radical Polymerization thanks to Thiol Chemistry** Renaud NICOLAY (ESPCI, Paris, France)
10:30	**Coffee break**			
	Session Chair Henri CRAMAIL (LCPO, UNIVERSITY OF BORDEAUX, Pessac, France)	**Session Chair** Michael A. R. MEIER (KARLSRUHE INSTITUTE OF TECHNOLOGY (KIT), Karlsruhe, Germany)	**Session Chair** Jean-François GOHY (Catholic University of Louvain, Louvain-la-Neuve, Belgium)	**Session Chair** Christine JEROME (UNIVERSITY OF LIEGE, Liege, Belgium)
10:50	**IL61 - Polybenzoxazine-based Nanocomposites: from Synthesis to High Performance Materials** Philippe DUBOIS (LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY, Hautcharage, Luxembourg)	**IL62 - Conjugated Polymers: Versatile Organic Semiconductors with a Plethora of Applications** Dirk VANDERZANDE (UNIVERSITY OF HASSELT, Hasselt, Belgium)	**IL63 - Poly(1,2,3-triazolium)s: Functional and Dynamic Polymer Electrolytes** Eric DROCKENMULLER (UNIVERSITY CLAUDE BERNARD LYON 1, Villeurbanne, France)	**IL64 - Urethane-containing Macromonomers as Novel Hydrogel Building Blocks for Solvent- and Initiator Free 3D Printing Applications: the Ultimate Solution?** Peter DUBRUEL (GHENT UNIVERSITY, Ghent, Belgium)
11:20	**OC41 - Design of Multiblock Polymers by Chain Shuttling Polymerization** Philippe ZINCK (UNIVERSITY OF LILLE, Villeneuve d'Ascq, France)	**OC42 - Conjugated Surface-Grafted Polymer Brushes** Szczepan ZAPOTOCZNY (JAGIELLONIAN UNIVERSITY, Krakow, Poland)	**OC43 - Synthesis of Polycarbosilanes Having 5-Membered Cyclic Carbonate Groups and their Properties as Solid Polymer Electrolytes** Matsumoto KOZO (KINDAI UNIVERSITY, Lizuka, Japan)	**OC44 - Chain and Step Growth Polymerisations of Cyclic Imino Ethers – from Poly(2-Oxazoline)S to Poly(Ester Amide)s** Kristian KEMPE (MONASH UNIVERSITY, Melbourne, Australia)
11:40	**Break**			
11:45	**OC45 - Self-Assembly and Responsiveness of Polypeptide-Based Star and Triblock Copolymers** Daniel SAVIN (UNIVERSITY OF FLORIDA, Gainesville, United States)	**OC46 - Semi-crystalline Vitrimers via Solid-state Polymerization** Hans HEUTS (TECHNICAL UNIVERSITY OF EINDHOVEN, Eindhoven, The Netherlands)	**OC47 - The Application of Selenolactone In Polymer Synthesis** Xiangqiang PAN (SOOCHOW UNIVERSITY, Suzhou, China & & GHENT UNIVERSITY, Ghent, Belgium)	**OC48 - Poly(2-Oxazoline)s: from Fundamental Research to Biomedical Applications** Victor RETAMERO DE LA ROSA (GHENT UNIVERSITY, Ghent, Belgium)
12:05	**OC49 - Development of High Performance Polymers from Naturally Occurring Myo-Inositol** Sudo ATSUSHI (KINKI UNIVERSITY, Osaka, Japan)	**OC50 - Vitrimers Based on Transalkylation of Sulfonium Salts** Benjamin HENDRIKS (GHENT UNIVERSITY, Ghent, Belgium)	**OC51 - Synthesis and Thermoresponsive Properties of Multi-Sensitive Linear and Cyclic Graft Copolymers** Youliang ZHAO (SOOCHOW UNIVERSITY, Suzhou, China)	**OC52 - Thermoresponsive PNIPAM Coated Gold Nanoparticles for Sensors, Coatings and Catalytic Applications** Samarendra MAJI (GHENT UNIVERSITY, Ghent, Belgium)
12:25	**Lunch**			
	Session Chair Yasuyuki TEZUKA (TOKYO INSTITUTE OF TECHNOLOGY, Tokyo, Japan)	**Session Chair** Lian HUTCHINGS (DURHAM UNIVERSITY, Durham, United Kingdom)	**Session Chair** Sebastien PERRIER (UNIVERSITY OF WARWICK, Warwick, United Kingdom)	**Session Chair** Peter DUBRUEL (GHENT UNIVERSITY, Ghent, Belgium)
13:50	**IL65 - New Frontiers for Controlled Networks in the Nano – and Macroscale** Eva M. HARTH (VANDERBILT UNIVERSITY, Nashville, United States)	**IL66 - Deeper Insight Into the RDRP Polymerization of Vinylidene Fluoride** Bruno AMEDURI (ENSC, Montpellier, France)	**IL67 - Amine-based and Amine-reactive Polymers: a Versatile Toolbox for Polymer Conjugation** Sagrario PASCUAL (UNIVERSITY OF MAINE, Le Mans, France)	**IL68 - Thermodynamics of the Interaction of Natural Polymers with Nanocellulose** Wim THIELEMANS (KU Leuven, Kortrijk, Belgium)
14:20	**OC53 - Fluoride Catalyzed Chemistry of Imidazolyl Monomers: a Robust Polymerization Strategy Toward Dendrimers and Polycarbonates** Michael MALKOCH (KTH ROYAL INSTITUTE OF TECHNOLOGY, Stockholm, Sweden)	**OC54 - Investigations into the Mechanisms of Photo-ATRP and Photo-RAFT** Julien POLY (MULHOUSE INSTITUTE OF MATERIALS SCIENCE, Mulhouse, France)	**OC55 - Well-Defined Semi-Interpenetrating Polymer Networks: the BIEE-Crosslinking Approach** Theodora KRASIA-CHRISTOFOROU (UNIVERSITY OF CYPRUS, Nicosia, Cyprus)	**OC56 - Fabrication of Anisotropic Microparticles via Double-Speed Seeded Swelling Polymerization** Qiuyu ZHANG (NORTHWESTERN POLYTECHNICAL UNIVERSITY, Xi'an, China)
14:40	**Break**			

14:45	**OC57 - Unique Biomaterials and Nanocomposites Based on Multifunctional PEG-Hydrogels** Marga LENSEN (TECHNICAL UNIVERSITY OF BERLIN, Berlin, Germany)	**OC58 - Propagation Rate for Radical Polymerization of Water-Soluble Monomers In Aqueous Solutions** Igor LACIK (POLYMER INSTITUTE SAS, Bratislava, Slovakia)	**OC59 - Controlling the Micro-Environment of Cells by Exploitation of Macromolecular Photochemistry** Stefan BAUDIS (TECHNICAL UNIVERSITY OF VIENNA, Vienna, Austria)	**OC60 - Biodegradable Polymer Networks via Triazolinedione Crosslinking of Oleyl-Functionalized Poly(Epsilon-Caprolactone)** Melania BEDNAREK (CENTRE OF MOLECULAR AND MACROMOLECULAR STUDIES POLISH ACADEMY OF SCIENCES, Lodz, Poland)
15:05	**IL69 - Building Dynamic and Functional Nanostructures in Water: Tadpoles to Toroidal Nanorattles** Michael MONTEIRO (THE UNIVERSITY OF QUEENSLAND, Queensland, Australia)	**IL70 - Microflow Reactions: From Controlled Polymerization to Sequence-Defined Oligomers** Tanja JUNKERS (UNIVERSITY OF HASSELT, Hasselt, Belgium)	**IL71 - Multi-stimuli Responsive Self-assembled Block Copolymers via a Catechol/boronic Acid Ligation** David FOURNIER (UNIVERSITY OF LILLE, Lille, France)	**IL72 - H-Bonding Driven Self-Assembly of Amphiphilic Polymers** Suhrit GHOSH (INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, Kolkata, India)
15:35	**Coffee break**			
	Auditorium Quatelet			
	Session Chair Matthew I. GIBSON (UNIVERSITY OF WARWICK, Coventry, United Kingdom)			
16:00	**PL04 - Self-assembled Nanoparticles of Different Shapes and their Role in Drug Delivery** Martina STENZEL (UNIVERSITY OF NEW SOUTH WALES, Sydney, Australia)			
16:50	**Closing remarks**			
17:15	**Buses leaving to soccer tournament**			
17:45	**Soccer game 'Belgian Polymer team' against 'Rest of the World Polymer team'**			
18:45	**Free drinks and light dinner (until 20:00)**			

Thursday May 25, 2017	
10:00	**Touristic activities in Bruges or Ghent**

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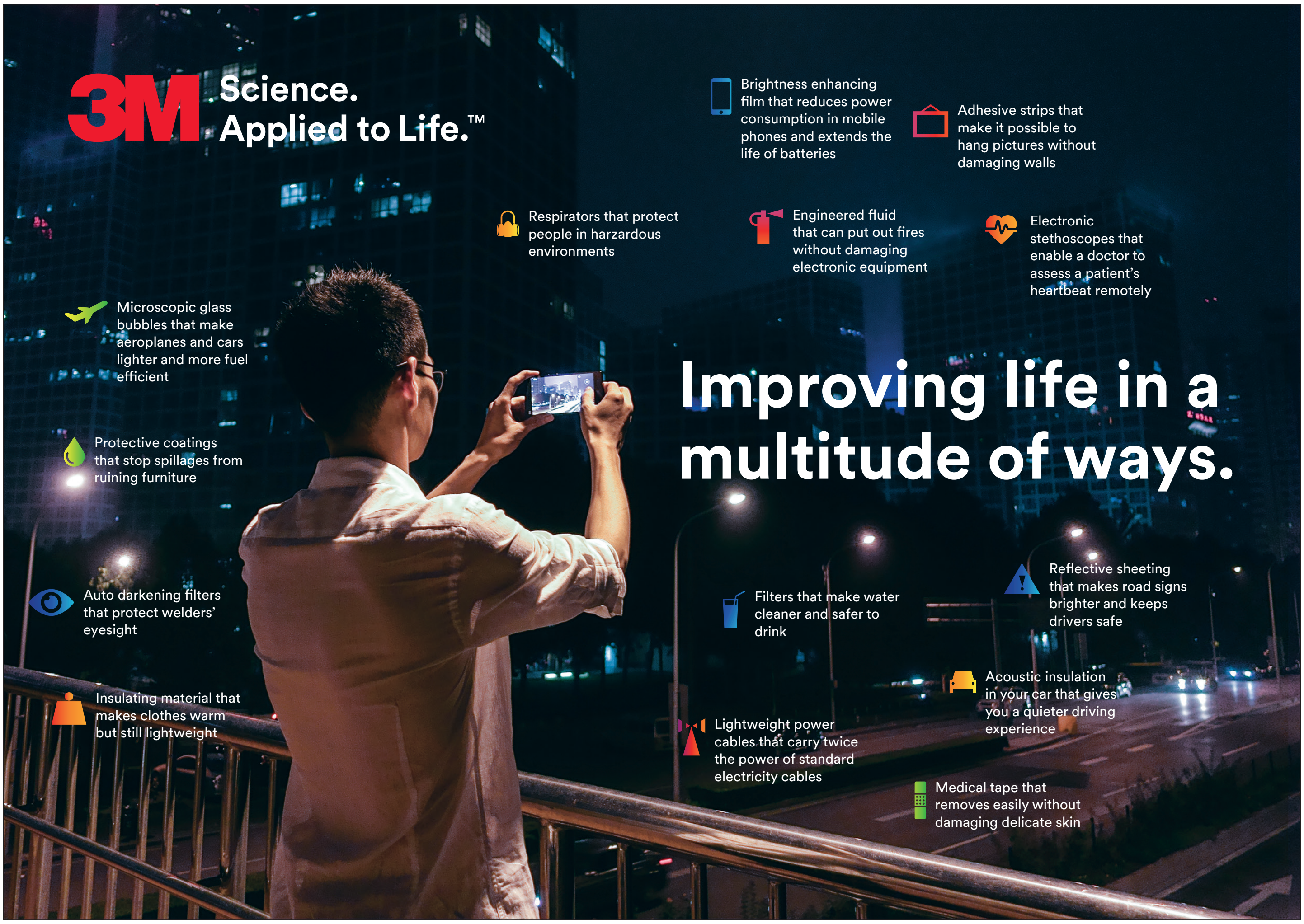

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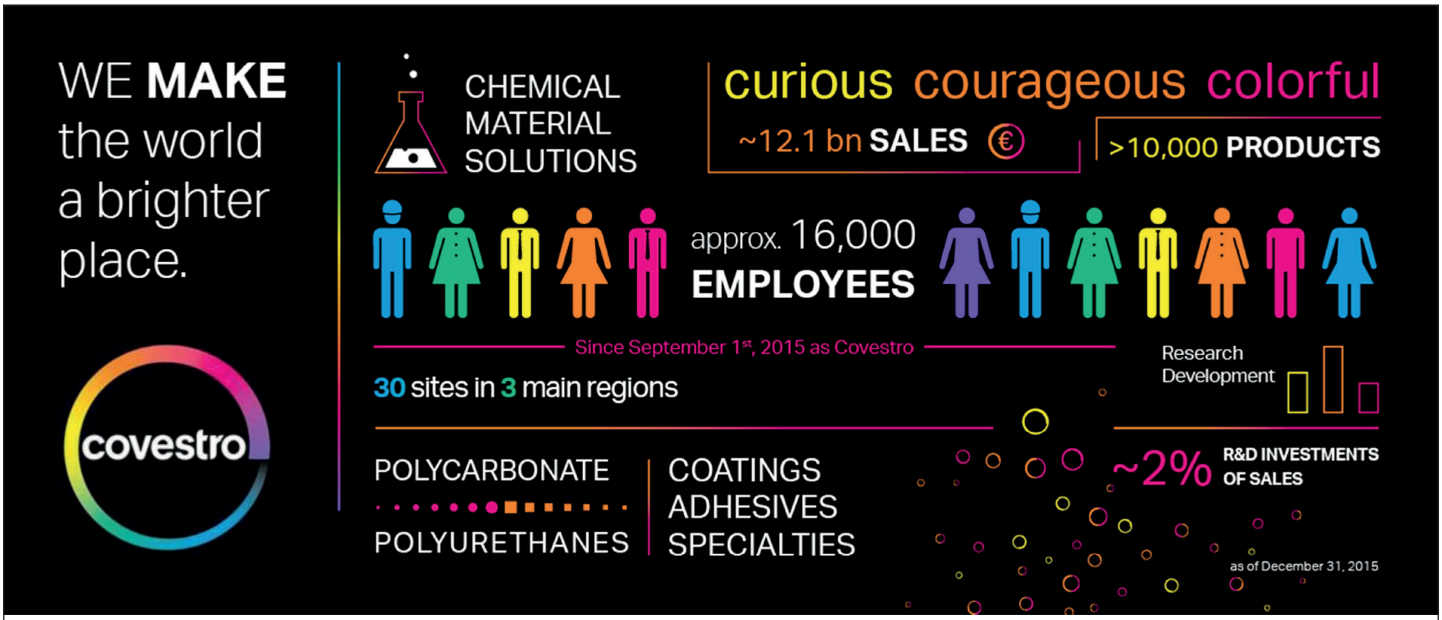
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PLENARY LECTURES
BIOGRAPHIES & ABSTRACTS

MITSUO SAWAMOTO

Mitsuo Sawamoto (b. 1951, Japan) received his B.S. (1974), M.S. (1976), and Ph.D. degrees (1979) in polymer chemistry from Kyoto University. After a postdoctoral research at The University of Akron, U. S. A. (1980–81), he joined the Department of Polymer Chemistry, Kyoto University in 1981 and was Professor of Polymer Chemistry since 1994. In 2017, he retired from Kyoto and now Professor of the Institute of Science and Technology Research, Chubu University.

Appointments. He is an executive member of the Science Council of Japan (2005–), a titular member of IUPAC Polymer Division (2008–), the immediate past President of the Society of Polymer Science, Japan (SPSJ) (2008–2010), and one of the Editors of the Journal of Polymer Science, Part A, Polymer Chemistry (1995–2015). He was also the leader of the Kyoto University Global Center of Excellence (GCOE) Project “Integrated Materials Science” (2007–2011).

Research and Publications. His research interest includes development of precision cationic and radical polymerizations and catalysts, the synthesis of designed functional polymers, and most recently the sequence regulation in chain-growth polymerization, leading to: over 380 original papers, >40 reviews, >20 named and plenary lectures, >175 invited lectures, and >19,000 total citations (2016). The first paper on his living radical polymerization has been cited over 2500 times (Macromolecules #3 most cited), and a review over 2600 times [Chemical Reviews top <1% ACS Highly Cited Papers (1998–2007)].

Awards and Honors. For these achievements, Sawamoto has received the Award of The Society of Polymer Science, Japan (1992); the Divisional Research Award of the Chemical Society of Japan (1999); the Arthur K. Doolittle Award of PMSE Division, the American Chemical Society (2002); the Macro Group UK Medal for Outstanding Achievement in Polymer Science, the Royal Society of Chemistry (2012); the SPSJ Award for Outstanding Achievement in Polymer Science and Technology (2013); Alexander von Humboldt Research Award (2016); and Benjamin Franklin Medal in Chemistry (2017); along with the Medal of Honor with Purple Ribbon presented by the Emperor of Japan (2015).

PL01

ADVANCED FUNCTIONAL POLYMERS BY PRECISION POLYMERIZATIONS: A PERSPECTIVE

Mitsuo Sawamoto

Kyoto University, Department of Polymer Chemistry,
Graduate School of Engineering, Katsura, Nishikyo-ku,
Kyoto 615-8510, Japan

This Plenary Lecture will discuss the development of precision polymerizations (radical and cationic) and the precision synthesis of advanced functional polymers thereby. More specific topics will include:

Development of Precision Polymerizations

(a) Development of living radical polymerization – A perspective

(b) The advance in transition metal catalysts for metal-mediated living radical polymerization – active, user-friendly, versatile, and sustainable

Precision Synthesis of Advanced Functional Polymers

(a) Precision amphiphilic random copolymers that undergo unique single-chain folding and nano-space formation

(b) Microgel star polymers with a designed functional core for molecular recognition and catalysis

(c) Cyclic polymers by ring-expansion living cationic polymerization

(d) Sequence-controlled macromolecules with defined functionality by varying strategies based on precision polymerizations

LUDWIK LEIBLER

Dr Leibler, Research Director at CNRS (Centre National de la Recherche Scientifique) and Distinguished Professor at ESPCI Paris (Ecole Supérieure de Physique et Chimie Industrielles, is the director of Soft Matter and Chemistry Laboratory at ESPCI Paris. He received his PhD in 1976 in theoretical physics from Warsaw University and then was a post-doctoral fellow with Professor P-G de Gennes at Collège de France. He is a researcher at CNRS initially in Strasbourg (1979-1984) then in Paris (1984-1996). From 1996 to 2003 he was the founding director of a joint laboratory between CNRS and chemical company Arkema. He holds his present position from 2003.

Dr Leibler is a member of French Academy of Sciences and of National Academy of Engineering (USA), he has received number of honours and awards from various organizations including 2015 European Inventor Award, Polymer Physics Prize of American Physical Society, American Chemical Society Award in Polymer Chemistry, Tartufari International Prize in Physics and Chemistry from Accademia Nazionale Dei Lincei, Grand Prix of Fondation de la Maison de Chimie, Grand Prix IFP of the French Academy of Sciences and Grand Prix Pierre Süe of the French Chemical Society.

PL02

PRINCIPLES OF VITRIMER PHYSICS AND CHEMISTRY

Ludwik Leibler

Matière Molle et Chimie, ESPCI Paris, 10 rue Vauquelin, 75005 Paris, France

In 2011 we introduced the concept and synthesized, vitrimers, polymer materials that are insoluble and undergo gradual solidification just like amorphous silica. Insoluble whatever the temperature, solid at low temperatures yet processable when heated, vitrimers constitute the third class of polymers along with thermoplastics and thermosets (elastomers). Vitrimers are polymer networks that are able to change their topology without changing the total number of bonds through thermo-activated associative exchange reactions. First vitrimers were made from epoxy resins and used catalyzed transesterication to achieve networks with exchangeable links. Today most plastics and rubbers can be transformed into vitrimers. Since vitrimers can be shaped, assembled, repaired and recycled while showing exquisite chemical and thermomechanical resistance they should rapidly find applications in automotive, electronics, airplane, and coatings industries. Functional vitrimers (e.g. liquid crystalline or responsive and shape memory materials) are also expected to open new exciting applications.

CRAIG J. HAWKER

Professor Craig J. Hawker, FRS is Clarke Professor and holds the Alan and Ruth Heeger Chair of Interdisciplinary Science at UCSB where he directs the California Nanosystems Institute and the Dow Materials Institute.

He came to UCSB in 2004 after eleven years as a Research Staff Member at the IBM Almaden Research Center in San Jose, CA. Professor Hawker's research activities focus on synthetic polymer chemistry and nanotechnology, integrating fundamental studies with the development of nanostructured materials for advanced properties and functions in microelectronics and biotechnology.

This work has led to over 450 peer-reviewed papers and 60 patents with Professor Hawker helping to establish a range of start-up companies - Relypsa, Intermolecular, Olaplex, Tricida. For his pioneering studies, Professor Hawker's recent honors include the 2013 American Chemical Society Award in Polymer Chemistry, the 2012 Centenary Prize from the Royal Society of Chemistry and an Arthur C. Cope Scholar Award from the American Chemical Society in 2011. Professor Hawker has been honored with election to the Royal Society as well as being named a Fellow of the National Academy of Inventors and American Association for the Advancement of Science.

PL03

THE POWER OF POLYMER SYNTHESIS IN MACROMOLECULAR ENGINEERING

Craig Hawker

Materials Research Laboratory
University of California
Santa Barbara, CA, 93106
USA

The orthogonal functionalization of polymeric materials is a critical design strategy for the "bottom-up" fabrication of nanostructured systems. In synthesizing these nanostructures, functional group interconversion and efficient organic transformations are key.

MARTINA STENZEL

Martina Stenzel studied chemistry at the University of Bayreuth, Germany, before completing her PhD in 1999 at the Institute of Applied Macromolecular Chemistry, University of Stuttgart, Germany. She started as a postdoctoral fellow at UNSW in 1999 and is now a full Professor in the school of chemistry as well as co-director of the Centre for Advanced Macromolecular Design (CAMD).

Martina Stenzel published more than 260 peer reviewed papers mainly on polymer and nanoparticle design. Her research interest is focused on the synthesis of functional nanoparticles for drug delivery applications. She is in particular interested in combining synthetic polymers with nature's building such as sugars and proteins to create biocompatible and bioactive carriers for delivery of a range of drugs. She is especially passionate about developing synthetic strategies to deliver metal-based drugs.

She is scientific editor of Materials Horizons and the Beilstein Journal of Nanotechnology and serves currently on a range of editorial boards. She received a range of awards including the 2011 Le Fèvre Memorial Prize of the Australian Academy of Science. She is currently the chair of the National Chemistry Committee of the Australian Academy of Science.

PL04

HOLLOW SPHERES, PANCAKES, BAMBOO-STICKS? THE WORLD OF SELF-ASSEMBLED POLYMERS

Martina Stenzel, Sylvia Ganda, Fumi Ishizuka, Per Zetterlund, Jiachen Zhao, Sandy Wong

Center for Advanced Macromolecular Design (CAMD), University of New South Wales, Sydney, Australia

Material scientists have long turned to nature for inspiration. Many self-assembled systems such as cells are the result of millions of years of evolution and have been optimized over the course. Scientists have aimed at creating similar structures using self-assembled amphiphilic structures such as polymers. Self-assembly of amphiphilic block copolymers in selective solvents is a well-known process and the parameters determining the resulting structures have been studied in detail. Most commonly, micelles are obtained, but also the formation of cylindrical micelles and vesicles is possible. Self-assembly in the presence of additional forces such as crystallization, stacking forces, an additional polymers block or self-assembly in an emulsion system can lead to superimposed structures that lead to nanoobjects beyond traditional micelles.

In this presentation, we will discuss how additional forces can create new nanoparticles that may be suitable for therapeutic purposes. Motivation is to create nanoparticles that can have resemblance of virus-like structures, which are often non-spehrical and carry patterned surfaces with bioactive groups.

INVITED LECTURE'S ABSTRACTS

IL01

NEW ATRP PROCEDURES FOR MACROMOLECULAR ENGINEERING

Krzysztof Matyjaszewski

Carnegie Mellon University, Center for Macromolecular Engineering, Pittsburgh, PA, 15213, USA

Precise macromolecular engineering has been enabled by many controlled radical polymerization procedures. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among most efficient controlled/living radical polymerization systems.By applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. The activators are regenerated by light, reducing agents, electrical current or mechanical forces. By employing these systems, ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers was employed for macromolecular engineering of polymers with precisely controlled molecular weights, tuned dispersities, designed shape, composition and functionality. Examples of block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates prepared with high precision will be presented.

IL02

HYDROGELS AS SYNTHETIC ECM ANALOGS THROUGH BIO-CLICK REACTIONS

Kristi Anseth, Tobin Brown, Ian Marozas, Alex Caldwell, Hao Ma, Malar Azagarsamy

Department of Chemical and Biological Engineering and the BioFrontiers Institute
University of Colorado, Boulder, CO 80303 USA

Our group designs synthetic extracellular matrix (ECM) analogs that capture key features of the unique chemistry and physical properties of a cell's niche—an environment that is not only tissue specific, but can be strikingly heterogeneous and dynamic. Unique to our approach is the ability to create cell-laden matrices in three-dimensional space in which the matrix properties can be changed on demand—so-called 4D biology. Specifically, our groups has focused on the application of bio-click reactions to create tunable cell-laden matrices using strain-promoted azide alkyne cycloaddition, photoinitiated thiol-ene polymerizations, and bio-orthogonal tetrazine-norbornene coupling through inverse electron demand Diels-Alder. This talk will illustrate how we leverage these chemistries to present bioactive peptides, signaling ligands, small molecules, and biomechanical properties at will. We employ these biomaterial systems to study the effects of matricellular signaling on diverse cellular functions and processes.

IL03

POLYMERISATION-INDUCED SELF-ASSEMBLY

Steven Armes

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, Yorkshire, S3 7HF, UK

Polymerisation-induced self-assembly (PISA) enables the efficient synthesis of various types of sterically-stabilised block copolymer nano-objects, including spheres, worms, vesicles and framboidal vesicles. Moreover, these nano-objects can be prepared directly at high solids (20 to 50 % w/w) in either aqueous media or polar solvents (e.g. ethanol) or non-polar solvents (e.g. *n*-alkanes).[1]

In PISA, a soluble polymer is chain-extended using a second monomer that forms an insoluble polymer under the reaction conditions. This leads to nucleation at some critical degree of polymerisation to form sterically-stabilised spheres. Whether or not the copolymer morphology evolves further during the PISA synthesis depends on the precise formulation.

We have utilised this versatile technique for the design of many types of bespoke nanoparticles which can be used for various potential applications. These include: (i) nanoparticle lubricants; (ii) anti-reflective coatings; (iii) thickeners; (iv) flocculation aids; (v) Pickering emulsifiers; (vi) biocompatible hydrogels for cell growth; (vii)biocompatible hydrogels for cell storage; (viii) occlusion within host crystals such as calcite or ZnO.

References

1) Macromolecules, 2016, 49, 1985.

IL04

RENEWABLE POLYMERS; A SUPERCRITICAL APPROACH

Steve Howdle, Mariana Gamiero, Katie Pepper, Payal Baheti, Amy Goddard

School of Chemistry, University of Nottingham, UK

We have exploited the low viscosity and high diffusivity of $scCO_2$ to create a highly efficient and reversible plasticizer. We have lowered the viscosity of growing polymer melts to enhance the progress of both polycondensation and ring opening polymerisations. The plasticization also ensures that the reactions can thus be performed at much lower temperatures than is possible under conventional operating conditions. In some cases, these lower temperature operating conditions have opened up the opportunity to use enzymatic catalysts to yield new polymeric materials. We will report on polymers that are synthesized from renewable resources such as sorbitol, lactide, caprolactone and other materials that have been derived directly from nature including sources such as tree bark and oils from waste seeds.

References

1) Sainz, M. F.; Souto, J. A.; Regentova, D.; Johansson, M. K. G.; Timhagen, S. T.; Irvine, D. J.; Buijsen, P.; Koning, C. E.; Stockman, R. A.; Howdle, S. M., A facile and green route to terpene derived acrylate and methacrylate monomers and simple free radical polymerisation to yield new renewable polymers and coatings. Polymer Chemistry 2016, 7 (16), 2882-2887.
2) Goddard, A. R.; Perez-Nieto, S.; Passos, T. M.; Quilty, B.; Carmichael, K.; Irvine, D. J.; Howdle, S. M., Controlled polymerisation and purification of branched poly(lactic acid) surfactants in supercritical carbon dioxide. Green Chemistry 2016, 18, 4772 - 4786.
3) Curia, S.; Howdle, S. M., Towards sustainable polymeric nano-carriers and surfactants: facile low temperature enzymatic synthesis of bio-based amphiphilic copolymers in scCO2. Polymer Chemistry 2016, 7 (11), 2130-2142.

IL05

SULFUR FREE RAFT (SF RAFT) OF METHACRYLATES IN EMULSION POLYMERISATION

David Haddleton

Department of Chemistry, University of Warwick, Coventry, UK

We demonstrate the use of sulfur free reversible addition-fragmentation chain transfer polymerisation (RAFT as a versatile tool for the controlled synthesis of methacrylic block and comb-like copolymers. Sulfur free RAFT (SF-RAFT) utilises vinyl terminated macromonomers obtained *via* catalytic chain transfer polymerisation (CCTP) of methacrylates as a chain transfer agent (CTA), and thus precluding adverse aspects of the RAFT such as toxicity of dithioesters. We have synthesised a range of narrow dispersity block copolymers (Đ < 1.2) and comb-like macromolecules by employing emulsion polymerisation allowing for the preparation of relatively large quantities (~50 g) of the above mentioned copolymers promptly and straightforwardly. Copolymers were characterised using ^{1}H NMR, size exclusion chromatography (SEC), thermogravimetric analysis (TGA) and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) techniques.

IL06

TOWARDS POLYMER-PEPTIDE CONJUGATES AS POTENT DRUGS

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Peptides are promising candidates as drugs for a variety of conditions. However, they suffer from some inherent shortcomings that hamper their clinical use. Among these shortcomings are their tendency to trigger an immune response and their limited stability under physiological conditions. Polymer conjugation is seen as a promising way to stabilize peptides against proteolytic degradation, and to avoid an immune response. Poly(*N*-vinylpyrrolidone) (PVP) is an interesting candidate for the synthesis of peptide conjugates. In order to reliably link PVP to peptides, the introduction of chain-end functionalities is of great importance. In earlier work we have shown that the RAFT-mediated polymerization is susceptible to a range of side reactions. Optimization of polymerization conditions have now led to high chain-end fidelity, and the synthesis of hetero-telechelic PVP. The most recent progress in PVP synthesis, modification and conjugation will be discussed.

IL07

ENGINEERING INTERFACES USING CONTROLLED RADICAL POLYMERIZATION

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Surface-initiated polymerization (SIP) techniques are powerful tools for the preparation of thin, surface tethered polymer films. Surface grafted polymer films produced via SIP are often colloquially referred to as polymer brushes. SIP techniques are characterized by a number of unique features, which include the ability to (i) prepare polymer brushes with precise control over chemical composition and film thickness; (ii) generate polymer films that present very high surface concentrations of functional groups; (iii) conformally coat both simple, planar substrates as well as complex, 3D structured or porous substrates and (iv) tune the conformation of the surface grafted polymer chains by engineering the average distance between neighboring anchoring points. This presentation will highlight recent work from our laboratory that illustrates the use of SIP to generate thin polymer films with sensory or responsive properties as well as results from recent work, which shows that the stretched conformation of these surface grafted polymer chains also has an impact of their chemical reactivity, potentially opening avenues towards novel mechanically responsive surfaces.

IL08

SUSTAINABLE POLYURETHANES: REACTIVITY STUDY AND CHALLENGES OF CYCLIC CARBONATES

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Polyurethane is currently one of the most commonly used polymers worldwide for various applications such as rigid and flexible foams, coatings, elastomers, adhesives and sealants. However, isocyanate precursors are very harmful at each stages of the life cycle of the polymers. Hence, in recent years, intensive research and development were carried out for the design of isocyanate free polyurethanes from reaction between five-membered cyclic carbonates and amines which yields polyhydroxyurethanes (PHU). Nevertheless, this reaction presents a drawback: the low reactivity of cyclic carbonate aminolysis. Firstly, our works intended to propose comprehensive reactivity studies, in order to determine the influence of the structure of reactants. Secondly, we proposed innovative solutions to allow room temperature elaboration of a range of PHU materials, foams and hybrid PHU-epoxy with increased adhesion properties to meet thermo-mechanical properties required by potential applications.

IL09

DYNAMIC CHEMISTRIES IN SMART POLYMERS

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Dynamic bonds are covalent linkages which, if given specific stimuli, can form an equilibrium between exchanging reactants and their products. Recent work by our lab has developed dynamic functional groups which can be seemlessly incorporated into network or linear polymers and harnesses the supurb reactivity and chemoselectivity of thiyl radicals and thiolate anions. These dynamic functionalities act as crosslinks in network polymers or in the backbone of linear polymers and are easily adapted to various stimuli including light, heat, or chemical. Here we show recent developments towards the formation of dynamic liquid crystalline networks and thioester-based networks both responsive towards light in order to develop shape shifting and remoldable photopolymers. Additionally, we demonstrate a sequence shifting, dynamic thioester-linked DNA-like polymer by implementing an covalently exchangeable thioester backbone. We believe that the broad implementation of this chemistry demonstrates the breadth of this approach towards the formation of smart, responsive polymers.

IL10

POLYMER-SURFACE INTERACTIONS FROM THE MOLECULAR PERSPECTIVE BY AFM FORCE SPECTROSCOPY

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AFM based force spectroscopy approaches, which have been used with success to measure forces down to the level of single molecule interactions, have been used with success to study adsorption and binding strength, conformation, and supramolecular structure of surface attached polymers. In this presentation two examples will be used to show recent progress in this area. First we present results related to measuring the isoelectric point (pI) of proteins immobilized at AFM probe surfaces, using designer reference substrates with controlled charge over a broad pH range. This approach allowed us to determine pI values of still unsequenced adhesion proteins relevant for marine fouling, and available in minute amounts only. In the second example we focus on single polymer pull and show the first results related to direction dependence of the adhesion force for partially adsorbed chains, when the free end is pulled. We demonstrate direction-dependent chain pull and fingerprints in the adhesion force vs. pulling angle indicating adsorption-desorption transitions as a function of the pulling angle. A short account on anticipated future developments will conclude the presentation.

IL11

ACADEMIC RESEARCH IN A CHEMICAL COMPANY – TURNING CONTRADICTION INTO COMMON GROUND

Bernd Bruchmann

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For industrial research "Open Innovation" is a major source of inspiration in the quest for new business opportunities. An exhaustless pool for creative ideas is located in academia - universities are the perfect breeding ground for innovation on account of their academic flexibility and research freedom.

In close cooperation with selected universities BASF aims at cultivation of innovative thoughts and for generation of a solid basis for the development of futuristic materials and systems. In addition to conventional polymer topics, the themes to be explored include novel monomers and polymers, hybrid systems, nanostructured materials, and biobased and bioinspired systems.

In expanding its international research network BASF opens up as well the opportunity to motivated young academic researchers to explore highly interesting topics in industry-relevant fields in close collaboration with BASF scientists.

The talk will highlight how the spirit of creativity is cultivated within BASF´s daily research activities and how "Open Innovation" influences the selection of research topics in a globally operating company. Selected examples will demonstrate, how research projects and products are derived from recent collaborations with academia.

IL12

DESIGN OF MONOMERS UNDERGOING RADICAL RING-OPENING POLYMERIZATION AND THEIR APPLICATION TO FUNCTIONAL POLYMERS

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The radical ring-opening polymerization (RROP) has attracted considerable interest from the following viewpoints: 1) Its potential to afford polymers with functional groups in the main chains, i.e., ester, olefin, ether, inherited from the corresponding functional monomers. 2) Its potential applicability to copolymerization with conventional vinyl monomers such as styrenic and acrylic monomers.

In the molecular design of cyclic monomers that undergo radical ring-opening polymerization, there are four essential requirements: 1) Monomers should possess C-C double bond which can accept radical species. 2) They should possess highly distorted ring-structures. 3) Their ring-opening reaction should be accompanied by some isomerization process that can afford thermodynamically stable functional groups. 4) These ring-opening reactions should be promoted by giving the corresponding radical species stabilized by electron withdraw groups. Vinylcyclopropane and vinyloxirane are typical examples that fulfill these requirements. In this work, we report that RROPs of vinyloxirane and vinylcyclopropane give the corresponding polymers containing vinylether and internal olefin, respectively.

IL13

MACROMOLECULAR METAMORPHOSIS: AN ALTERNATIVE APPROACH TO STIMULI-RESPONSIVE POLYMERS

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Advances over the last two decades in the area of macromolecular engineering have allowed access to polymers with complex architectures, compositions, and functionality. While the composition and functionality of many polymers can be altered post-synthesis, for example by postpolymerization modification, the architecture of a polymer is typically considered a static inalterable feature that is predetermined by the functionality of the monomers or initiator used during polymerization. Our recent work has focused on macromolecules with dynamic architecture that undergo dramatic topological transformations via a process we term *macromolecular metamorphosis*. Examples include metamorphosis from a linear amphiphilic block copolymer or hyperbranched polymer into comb, star, and hydrophobic block copolymer architectures. This approach was also employed to obtain gels that undergo programmed crosslink exchange such that the molecular weight between crosslinks increases on heating. Topological transformations of this type represent an entirely new approach to stimuli-responsive materials.

References

1) Hao Sun, Christopher P. Kabb, Yuqiong Dai, Megan R. Hill, Ion Ghiviriga, Abhijeet P. Bapat, Brent S. Sumerlin "Macromolecular metamorphosis via stimulus-induced transformations of polymer architecture" Nature Chemistry 2017, in press.

IL14

SEQUENCE-SPECIFIC POLYMERS SYNTHESIZED FROM ANIONIC POLYMERIZATIONS OF TEMPLATE MONOMERS

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Recently, chain sequence control is attracting increasing interest in the research of polymer synthesis. A number of strategies have been developed to prepare sequence-specific polymers from both chain growth and step growth polymerizations.[1,2] With the purpose of simultaneous control over molecular weight, monomer sequence, and functionalities, we combined living anionic polymerization technique and template monomer approach for the synthesis of sequence-specific vinyl polymers and substituted polyacetylenes after respective hydrogenation and dehydrogenation of the polymerization products.

The template monomers are a series of di- or tri-substituted 1,3-butadienes, in which the substituents were attached at 1,3-, 2,3- or 1,2,3-position. These monomers were polymerized with the initiation of *sec*-butyllithium (*s*-BuLi) in living manner, yielding products with controlled molecular weight. Interestingly, spectroscopy characterization of the product microstructure demonstrated almost 100% 1,4-enchainment, indicating high regioselectivity by the single direction of monomer addition. After hydrogenation, the products became equivalent to exact alternating vinyl polymers, whereas after dehydrogenation, the products were transformed into polyacetylenes with alternating substituents.[3-6]

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References

1) Lutz, J.-F.; Ouchi, M.; Liu, D. R.; Sawamoto, M. Science, 2013, 341, 1238149.
2) Qu, C. K.; He, J. P. Sci. China Chem. 2015, 58, 1651-1662
3) Zhang, Y.; Li, J.; Li, X. H.; He, J. P. Macromolecules 2014, 47, 6260-6269
4) Li, J.; He, J. P. ACS Macro lett. 2015, 4, 372-376
5) Yu, Y. H.; He, J. P. Eur. Polym. J. 2017, 86, 58-67
6) Yu, Y. H.; He, J. P. Macromol. Chem. Phys. 2017 (accepted)

IL15

DESIGNED (AND) FUNCTIONAL POLYMER NETWORKS - NEW APPROACHES AND APPLICATIONS

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Polymer networks were used worldwide in various applications e.g. tires, paints and lacquers, adhesives, doming, endless-fibre reinforced composites and for many, many other uses. During the last decades the design of functional and/or smart polymeric networks with combined properties and cheap and easy application is a hot topic not only within the academic research labs but of the industrial developments as well. In this presentation it is shown that from new results out of the collaboration between industrial and academic research groups the use of reversible crosslinked polymeric networks opens up a wide field of smart applications.

By the variation of molecular weight, crosslink density, polymer composition and the type of crosslinking functionalities the properties of the polymeric network can be adjusted to the demands of new applications. Here the control of the gelling and de-crosslinking kinetic, the viscosity in the molten state combined with the application process requirements, the thermal and mechanical properties and the chemical resistance of the resulting network are important issues and a scientific challenge.

IL16

POLYMER ASSISTED HOUSING OF ACTIVES FOR DESIGNED RELEASE

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The control release of actives can be achieved via encapsulation–immobilization[1]. This talk will focus on our work in the area of encapsulation - immobilization of a flavor ingredient by a variety of techniques including controlled polymerization[2], coacervation[3ab], cocrystallization-complexation[3cd], capsules[4a], emulsification[4b], inclusion complexation[4c], porous materials[5ab], supercritical CO_2 assisted impregnation[5cd], etc. for controlled release applications. As an example the atom transfer radical polymerization of menthyl acrylate[2] was performed in a controlled / living manner. The pyrolysis of poly-(menthyl acrylate) released flavor compounds. In another approach we had prepared porous structures[5ab] using hot melt reactive extrusion blending of chitosan and poly (acrylic acid) without any process additives. These porous structures are capable of housing active ingredients for later use. As a different technique we had used near-critical and supercritical CO_2 to facilitate the impregnation of flavors such as, vanillin and l-menthol, into cellulose acetate[5cd]. These studies will be further elaborated during this talk.

References

1) M. Mishra (Ed); Handbook of Encapsulation Controlled Release; 2015, CRC Press, Boca Raton, USA
2) S. Liu, M. Mishra, P. Lipowicz, B. Duan: 2015, US Patent 9185925; M. Mishra, K. Paine, J. Paine III, S. Liu: 2015, US Patent 9089162; S. Liu and M. Mishra; Macromolecules, 40, 867 (2007)
3) a) T. Sengupta, M. Mishra, W. Sweeney, D. Fernandez: 2013, US Patent 8356606; b) T. Sengupta, D. Fernandez, M. Mishra, W. Sweeney, S-S. Yang: 2015, US Patent 9167847; c) B. Duan, M. Mishra, P. Lipowicz, S. Liu: 2013, US Patent 8361236; d) M. Mishra, S. Liu, D. Kellogg: 2013, US Patent 8541401
4) a) M. Mishra, J. Fournier, K. Paine: US Patent Application 20060144412; b) T. Sengupta, M. Mishra, D. Fernandez, W. Sweeney, T. Howell: US Patent Application 20120045553; c) M. Mishra, S. Wrenn, J. Fournier: 2014, US Patent 8864909
5) a) M. Mishra, H. Yu, J. Molnar, V. Baliga: Des. Monom. and Polym.; 12, 273 (2009); b) S. Jeung and M. Mishra; Int'l. J. of Polym. Mater.; 60, 102 (2011); c) M. McHugh, G. Karles, D. Gee, J. Banyasz, Z. Shen, M. Mishra: 2012, US Patent 8201564; d) Z. Shen, G. Huvard, S. Warriner, M. McHugh, J. Banyasz, M. Mishra: Polymer, 49, 1579 (2008)

IL17

FUNCTIONAL NANOSTRUCTURES THROUGH POLYMERIZATION INDUCED MICROPHASE SEPARATION

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Block polymers are remarkable hybrid materials that can self-assemble on nanoscopic length scales. By controlling the composition, architecture, connectivity and molar mass, synthetic chemists can finely tune the morphologies adopted by these materials. Of the typical morphologies accessible from block polymer, bicontinuous phases such as the gyroid structure have been targeted due to their special utility in various applications that require interpenetrating domains structured on the nanoscale. However, the window of thermodynamic stability for the gyroid phase is often quite narrow. In this presentation I will discuss the design, synthesis, self-assembly and applications of block polymers formed in situ using controlled polymerizations such that the chemical synthesis and their self-assembly occur in a single process. I will discuss how we discovered this approach, mechanistic consideration associated with the formation of bicontinuous structures, and applications of the resulting nanostructured materials in, for example, polymer electrolyte membranes for use in batteries, fuel cells, and separation membranes.

IL18

POLYMER DESIGN FOR INFRARED LASER RESPONSIVE MATERIALS

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Stimuli responsive polymers are of major interest in different fields of technology (1). Responsive systems reacting on a wide range of stimuli such as heat, light and pH have been intensively studied. Often very ingenious polymer designs with very well defined polymer architectures have been developed. In different technologies, NIR laser exposure is often used as external stimulus to generate changes in polymeric materials. However, in industrial applications, cost limitations and economical considerations often limit the complexity of the polymeric design. Making use of very simple principles in polymeric designs can create high performance stimuli responsive polymeric materials, also in industrial applications, as will be illustrated in four case studies.

- NIR laser induced reduction of surface area
- NIR laser induced rearrangement of non covalent interactions in polymers
- NIR laser induced barrier permeation
- NIR laser induced polymerization

References

1) Wei et al., Polymer Chemistry, 8(1), 127-143 (2017); Hu et al., Accounts of Chemical Research, 47(7), 2084-2094 (2014); Reineke T.M., ACS Macro Letters, 5(1), 14-18 (2016)

IL19

SOLVING STICKY ADHESIVE PROBLEMS WITH POLYMER CHEMISTRY: LINKING APPLIED PROPERTIES WITH POLYMER ARCHITECTURE

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Market needs for adhesives can be addressed by differentiating how they are applied/processed, the initial properties obtained immediately after joining substrates together or the final properties developed after the physical/chemical processes have equilibrated. Developing critical understanding between applied adhesive properties and basic material properties is important in order to define key product architectures which differentiate performance.

Hot melt adhesives allow fast processing. Cooling rates are extremely fast and the specific morphologies generated immediately after cooling are critical to performance. Rapid kinetics of crystallisation can be followed by synchrotron experiments, enabling polyolefin formulations to be designed for controlling the relative crystallisation of components and adhesive properties.

Polyurethane hot melts provide more versatile adhesion and higher durability since materials crosslink after moisture curing. Isocyanate-free adhesives are desirable in order to provide a safer way of providing high performance. MicroEmission technology has been developed, based on controlling isocyanate reactivity. New technology comprising different functional prepolymers has also emerged, providing high performing hot melts with zero free isocyanates.

IL20

ENZYME-POLYMER NANOHYBRIDS

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In this presentation, two methods involving synthetic, water-soluble polymers for the stabilization of enzymes, and most generally proteins, will be discussed.

On the one hand, end-functional polymers obtained by RAFT polymerization are assessed as alternative to PEGylation in a biotechnological/pharmaceutical context. Straightforward conjugation experiments are followed by careful chromatographic purification leading to the isolation of semi-discrete protein-polymer species. The latter enable a more precise evaluation of the effect of conjugation on the stabilization of proteins, which is studied in various conditions to produce relevant phase diagrams.

On the other hand, we investigate the coating of enzymes with a thin layer of hydrogel. Particularly, we present a simplified protocol for single-protein encapsulation that maintains the nanoscopic character of the protein, an important feature for bionanotechnology. Through an extensive study with a range of proteins with various functions and sizes, we postulate the universality of the method. The intrinsic reactivity of the hydrogel coating is further exploited for labeling and surface immobilization.

IL21

POLYMER-BASED REDOX FLOW BATTERIES: NEW APPLICATIONS FOR REDOX-ACTIVE FUNCTIONAL MACROMOLECULES

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For renewable energy sources such as solar, wind, and hydroelectric to be effectively used in the grid of the future, flexible and scalable energy-storage solutions are necessary to mitigate output fluctuations. For systems that are intended for both domestic and large-scale use, safety and cost must be taken into account as well as energy density and capacity, particularly regarding long-term access to metal resources, which places limits on the lithium-ion-based and vanadium-based RFB development. Here we describe an affordable, safe, and scalable battery system, which uses organic polymers as the charge-storage material in combination with inexpensive dialysis membranes, which separate the anode and the cathode by the retention of the non-metallic, active (macro-molecular) species, and an aqueous sodium chloride solution as the electrolyte. In parallel, hybrid redox-flow batteries were developed and several types of organic redox flow batteries. In addition, redox flow batteries with a new tubular cell design were discovered.

References

1) Electrochimica Acta 2017, 228, 494; ChemistryOpen 2017, 6, 216; Energy Technology 2017, 5, 225; NPG Asia Mater. 2017, 9, e340; Angew. Chem. Int. Ed. 2017, 56, 686; ACS Energy Lett. 2016, 1, 976; Angew. Chem. Int. Ed. 2016, 55, 14427; J. Power Sources 2016, 335, 155; Chem. Rev. 2016, 116, 9438; Chem. Mater. 2016, 28, 3401; NPG Asia Materials 2016, 8, e283; Polym. Chem. 2016, 7, 1711; Adv. Mater. 2016, 28, 2238; Nature 2015, 527, 78; Polym. Chem. 2015, 6, 7801.

IL22

USING CRYSTALLISATION DRIVEN ASSEMBLY FOR THE FORMATION OF 2D NANOMATERIALS

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Crystallization-driven self-assembly (CDSA) has become a powerful method in accessing a wide range of complex nanostructures. The preparation of 2D structures, however, particularly those aimed towards biomedical applications, is limited, with few boasting biocompatible and biodegradable characteristics. Control over two dimensions still remains a key goal in obtaining ultrathin materials with unique chemical, physical and optical properties. We show that CDSA of a range of block copolymers results in the unprecedented formation of large uniform diamond-shaped platelets, up to several microns in size. Investigation into unexpected self-assembly rules has also allowed the preparation of hierarchical novel structures using block copolymer blending. The methods used provide a simple dissolution protocol for the preparation of 2D nanomaterials, with potential applications in drug delivery, tissue engineering, imaging and in nanocomposites.

IL23

INTRODUCING MECHANICS INTO "CLICK"-CHEMISTRY: FORCE-INDUCED CROSSLINKING AND SELF-HEALING OF POLYMERS

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Sensing stress in materials[1] and subsequent repair by autonomous processes is a major issue in material-science, especially well developed in polymers. We are reporting two different strategies to achieve a stress-dependent triggering of chemical reactions directly inside a polymer, able to visualize and subsequently heal the generated damage. The first concept is based on polymeric bis(*N*-heterocyclic carbene) (NHC) copper(I) mechanocatalysts, activated by external force to generate a monocarbene complex, suitable for a subsequent copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC), which directly enables stress-sensing via a fluorogenic reaction[2]. A second strategy uses a capsule based self-healing system, which – after stress-induced rupture – can trigger fluorescence directly at the site of the damage event[3]. Subsequent autonomous healing is then activating a triggered crosslinking reaction, able to repair damage at temperature close to 0 °C[4-5].

References

1) May, P. A.; Moore, J. S. Polymer mechanochemistry: techniques to generate molecular force via elongational flows. Chem. Soc. Rev. 2013, 42, 7497-7506.
2) Michael, P.; Binder, W. H. A Mechanochemically Triggered “Click” Catalyst. Angew. Chem., Int. Ed. 2015, 54, 13918-13922.
3) Dohler, D.; Rana, S.; Rupp, H.; Bergmann, H.; Behzadi, S.; Crespy, D.; Binder, W. H. Qualitative sensing of mechanical damage by a fluorogenic "click" reaction. Chem. Commun. 2016, 52, 11076-11079.
4) Rana, S.; Döhler, D.; Nia, A. S.; Nasir, M.; Beiner, M.; Binder, W. H. “Click”-Triggered Self-Healing Graphene Nanocomposites. Macromol. Rapid. Commun. 2016, 1715-1722
5) Neumann, S.; Dohler, D.; Strohl, D.; Binder, W. H. Chelation-assisted CuAAC in star-shaped polymers enables fast self-healing at low temperatures. Polym. Chem. 2016, 7, 2342-2351.

IL24

UNIVERSAL CONDITIONS FOR THE CONTROLLED POLYMERIZATION OF ACRYLATES, METHACRYLATES, AND STYRENE VIA Cu(0)-RDRP

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Atom transfer radical polymerization (ATRP) typically requires various parameters to be optimized in order to achieve a high degree of control over molecular weight and dispersity (such as the type of initiator, transition metal, ligand, solvent, temperature, deactivator, added salts, and reducing agents). These components play a major role when switching monomers, e.g., from acrylic to methacrylic and/or styrenic monomers during the synthesis of homo- and block copolymers as the stability and reactivity of the carbon centered propagating radical dramatically changes. This is a challenge for both “experts” and nonexperts as choosing the appropriate conditions for successful polymerization can be time-consuming and overall an arduous task. In this work, we describe one set of universal conditions for the efficacious polymerization of acrylates, methacrylates and styrene (using an identical initiator, ligand, copper salt, and solvent) based on commercially available and inexpensive reagents (PMDETA, IPA, Cu(0) wire). The facile nature of these conditions, combined with readily available reagents, will greatly expand the access and availability of tailored polymeric materials to all researchers.[1]

References

1) J. Am. Chem. Soc., 2017, 139 (2), pp 1003–1010

IL25

RATIONAL DESIGN OF ABC TRIBLOCK TERPOLYMER SOLUTION NANOSTRUCTURES WITH CONTROLLED PATCH MORPHOLOGY

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Compartmentalization is the most important feature in living organisms, best seen in plant or animal cells, where different compartments have different functions. We aim at mimicking nature in synthesizing multicompartment micelles, which simultaneously can host different payloads, such as drugs or magnetic or fluorescent nanoparticles. The self-assembly of ABC triblock terpolymers in solution and in the bulk are ideally suited for such a task.

We present a flexible route for the hierarchical, guided self-assembly of triblock terpolymers into multicompartment micelles of different shapes and sizes, simply by choosing the right solvent conditions and solvent sequences. These MCMs can have spherical shapes, like hamburgers, clovers, or footballs, or they reversibly form worm-like structures with alternating compartments. The different compartments can be loaded with various nanoparticles or drugs.[1] In a systematic approach we combine particle geometries with internal morphology and thereby establish a library of so far unprecedented nanostructures. We designed the block terpolymers to control the geometry of the nanostructure from spheres, cylinders to sheets and vesicles, and the patches on the core as spheres, cylinders, gyroids and lamellae.[2]

References

1) A.H. Gröschel et al. Nat. Commun. 3:710 (2012); Nature 503, 247 (2013).
2) T. I. Löbling et al. Nat. Commun. 7:12097 (2016); ACS Macro Lett. 5, 1044 (2016).

IL26

NANOCELLULOSES AND WELL-DEFINED POLYMERS – HYBRID MATERIALS WITH GREAT POTENTIAL

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Today´s societal challenges, with rapidly increasing environmental concern combined with the ever-increasing need for highly specialized materials, have spurred a reawakened interest for biofibers. Of these, cellulose is the most abundant and holds great promise for use in composite materials. More recently, cellulose nanocrystals and nanofibrils have been specifically explored [1]. To utilize the full potential of these nanosized structures, their surface characteristics have to carefully tailored to control features such as dispersion and adhesion [2].

The surface properties can be modified by attaching polymers, either covalently or non-covalently. For covalent modification, preformed polymers may be utilized, or initiators for reversible-deactivation radical polymerization can be attached, where after grafting-from can be conducted. The non-covalent approach is explored by the adsorption of polyelectrolytes.

This contribution aims at describing some of our recent findings when utilizing controlled radical polymerization to control the surface properties of nanocelluloses; either by the grafting-from approach [3], or by non-covalent approaches, either using diblock copolymers or latex nanoparticles obtained by the polymer induced self-assembly (PISA) process [4].

References

1) Habibi, Y. Chem. Soc. Rev., 2014,43, 1519-1542
2) Missoum, K., Belgacem, M. N., Bras, J. Materials 2013, 6(5), 1745-1766
3) Malmtröm, E.; Carlmark, A., Polym. Chem., 2012,3, 1702-1713
4) Carlmark, A., Lansalot, M., d'Agosto, F. et al. Polym. Chem., 2014, 5, 6076-6086

IL27

GLYCAN INSPIRED BIOMATERIALS; TARGETING BACTERIAL TOXINS

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Glycan (sugars) dicate a huge range of biological processes from infection, to tumor growth to blood types. Synthetic glycomaterials could therefore be used to engage, or disrupt, these processes for healthcare applications. Despite advances in polymerization methodologies, most glycopolymers remain rather simple, static, polymers simply displaying monosaccharides. Whilst these have *avidity* (due to the cluster glycoside effect) glycopolymers with *specificity* are less common - this is a major problem due to the inherent promiscuity of most lectins, which bind many different sugars, and vice versa which limits their application.

We have developed a program to mimic complex glycans, with the aim of improving specificity and selectivity. [1-4]. Here we will show progress in the synthesis of glycopolymers with high selectivity towards pathogenic carbohydrate binding toxins for their sequestration or detection.[5] This is achieved by considering allosteric as well as primary binding sites and matching glycopolymer architecture to these. The role of heterogeneity (mixing) in affinity and selectivity will also be discussed and the use of bilayer interferometry to understand the binding, to generate highly specific inhibitors of the cholera toxin.

References

1) Jones, M. W., Otten, L, Richards, S-J, Lowery, R., Phillips D. J., Haddleton D. M., Gibson MI. Chem. Sci., 2014, 5, 1611
2) Richards, S-J., Jones, MW, Hunaban, M., Haddleton, DM., Gibson, M.I., Angew. Chem. Int. Ed., 2012, 51, 7812
3) Won, S., Richards, S-J., Walker, M., Gibson, MI., Nanoscale Horizons, 2017, 2, 106
4) Deller, R.C., Vatish, M., Mitchell, D.A., Gibson, M.I., Nat. Commun., 2014, 5, 3244
5) Richards, SJ, Otten, LC, Gibson, MI, J. Mater. Chem. B., 2016, 4, 3046

IL28

H-BONDING ACTIVATION FOR ROP: ENZYMATIC VS ORGANIC CATALYSIS

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Many chemical reaction processes are based on transition metal based catalysts, which turn to be impurities for some applications (biomedical and microelectronics for example). As a consequence, it is of high interest to develop alternatives based on non-metallic polymerization processes.

For the Ring Opening Polymerization (ROP), many organometallic catalysts have been developed. A promissing alternative is the use of enzymes. Lipases can indeed catalyze ROP (but also other reactions) when used in non aqueous media, through H-bonding activation. They have the advantage to perform the reactions in mild conditions and could be also selective. Recent results will be presented for the ROP of caprolactone.

An other possible alternative would be to utilize purely organic catalysts instead of organo-metallic compounds. It will then be presented the results we have obtained for the ring-opening polymerization of lactide and lactones with very simple organocatalysts through H-bonding activation. Control and rapid polymerization occured and stars or block copolymers were synthesized.

References

1) S. Koeller, J. Kadota, A. Deffieux, F. Peruch, S. Massip, J.-M. Léger, J.-P. Desvergne, B. Bibal, J. Am. Chem. Soc. 2009, 131, 15088–15089
2) J. Kadota, D. Pavlovic, J.-P. Desvergne, B. Bibal, F. Peruch, A. Deffieux, Macromolecules. 2010, 43, 8874–8879
3) C. Thomas, F. Peruch, A. Deffieux, A. Milet, J.-P. Desvergne, B. Bibal, Adv. Synth. Catal. 2011, 353, 1049–1054
4) D. Jardel, C. Davies, F. Peruch, S. Massip, B. Bibal, Adv. Synth. Catal. 2011, 358, 1110–1118
5) C. Thomas, A. Milet, F. Peruch, B. Bibal, Polym. Chem. 2013, 4, 3491–3498
6) J. Kadota, D. Pavlovic, H. Hirano, A. Okada, Y. Agari, B. Bibal, A. Deffieux, F. Peruch, RSC Adv. 2014, 4, 14725–14732

IL29

MACROMOLECULAR MATERIALS VIA PRECISION PHOTOCHEMISTRY

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Installing chemical functionality at precise locations within complex macromolecules as well as onto three dimensional direct laser written constructs in the mildest possible fashion (visible light) and without any catalyst becomes possible with powerful light driven, quantitative ligation protocols.[1-7] Advanced light induced processes enable the parallel encoding of multiple molecules onto predefined locations on 3D microstructures in one step as well as the wavelength dependent addressing of specific parts of a macromolecule for its highly orthogonal functionalization (λ-orthogonal photochemistry). The lecture will highlight how macromolecular ligations can be directed in their selectivity by the application of photonic fields, how light can be used as an orthogonal trigger in macromolecular chain folding, how the high efficiency of light driven chemistry can be exploited for the synthesis of sequence defined macromolecules[2] or explore – time permitting – how diffraction unlimited laser lithography may become possible based on photo-click chemistry concepts.

References

1) Delaittre, G.; Goldmann, A. S.; Mueller, J. O.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 11388–11403. 2) (a) Mueller, J. O.; Schmidt, F. G.; Blinco, J. P.; Barner-Kowollik, C. Angew. Chem. Int. Ed., 2015, 54, 10284–10288; (b) Lederhose, P.; Wuest, K. N. R.; Barner-Kowollik, C.; Blinco, J. P. Chem. Commun. 2016, 52, 5928-5931. 3) Altintas, O.; Glassner, M.; Rodriguez-Emmenegger, C.; Welle, A.; Trouillet, V.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 5777–5783. 4) Pauloehrl, T.; Welle, A.; Bruns, M.; Linkert, K.; Börner, H. G.; Bastmeyer, M.; Delaittre, G.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2013, 52, 9714–9718. 5) Frick, E.; Anastasaki, A.; Haddleton, D. M.; Barner-Kowollik, C. J. Am. Chem. Soc. 2015, 137, 6889–6896. 6) Pauloehrl, T.; Delaittre, G.; Winkler V.; Welle, A.; Bruns, M.; Börner, H. G.; Greiner, A. M.; Bastmeyer, M.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2012, 51, 1071–1074. 7) Claus, T. K.; Telitel, S.; Welle, A.; Bastmeyer, M.; Vogt, A. P.; Delaittre, G.; Barner-Kowollik, C. Chem. Commun. 2017, in press.
8) (a) Zydziak, N.; Feist, F.; Huber, B.; Mueller, J. O.; Barner Kowollik, C. Chem. Comm. 2015, 51, 1799-1802; (b) Zydziak, N.; Konrad, W.; Feist, F.; Barner-Kowollik, C. 2016, Nat. Comm. 7, 13672

IL30

ENGINEERING OF FATTY ACID METHYL ESTERS TOWARDS BIO-BASED POLYMERS WITH ORIGINAL PROPERTIES

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In this study, vegetable oils were used as a platform for the design of sustainable polyesters exhibiting a hyperbranched architecture. For that purpose, the approach by polycondensation of ABn-type monomers (n>2) was favored. Plant oils and/or fatty acid methyl esters were chemically modified to synthesize multifunctional precursors featuring ester (A) and alcohol moieties (B). Simple, safe and efficient chemical transformations were considered to provide industrial perspectives to this work. Two main platforms of ABn-type monomers were developed by (1) acid hydrolysis of epoxidized vegetable oils and (2) thiol- ene/metathesis coupling reactions. The subsequent polycondensation of these oily-derived monomers, performed in bulk, gave access to novel renewable hyperbranched polyesters. The branching density as well as the thermo-mechanical properties of these materials were adjusted by designing and selecting the chemical structure of the fatty acid-based monomers. Finally, the post-functionalization of these hyperbranched polyesters with the aim at tuning their properties opened the scope of their applications, from commodity plastics to advanced materials.

References

1) Testud B., Grau E., Pintori D., Taton D., Cramail H., Green Chem, 2017, 19, 259-269.

IL31

COMPLEX GLYCOPOLYMER STRUCTURES AND THEIR INTERACTIONS WITH LECTINS

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Glycopolymers have been attracting more and more attention due to their multivalent binding property towards selected lectins. Combination of controlled polymerization techniques with click reactions ensure the synthesis of complex glycopolymer structures with desired binding properties.[1]

Understanding the specific multivalent carbohydrate-protein interactions is crucial to determine the structure-property relationships and to design accordingly the next generation of functional glycomaterials. Therefore, we investigate the structure-property relationships between the mammalian lectins and multivalent carbohydrate polymers, which may have applications for anti-adhesion therapy. Moreover, we have investigated the affinity of poly(mannose-methacrylate), helical glycocopolypeptides, gp120, start shaped glycopolymers, and cyclodextrin centered glycopolymers with a selected mannose binding lectin (DC-SIGN) that exists on dendritic cells, using SPR technique.[2-5] Selected members of a glycopolymer library were used to demonstrate the interactions between DC-SIGN and mannose rich polymers. We extend this study to a broader set of polymers to examine the effect of chain length, end group, architecture, thermoresponsive block, and number of arms in the star shaped polymers on the lectin binding.

References

1) C. R. Becer, R. Hoogenboom and U. S. Schubert, Angew. Chem. Int. Ed., 2009, 48, 4900-4908.
2) C. R. Becer, Macromol. Rapid Commun. 2012, 33, 742-752.
3) C. R. Becer, M. I. Gibson, J. Geng, R. Ilyas, R. Wallis, D. A. Mitchell and D. M. Haddleton, J. Am. Chem. Soc., 2010, 132, 15130-15132.
4) Q. Zhang, J. Collins, A. Anastasaki, R. Wallis, D. Mitchell, C. R. Becer, and D. M. Haddleton, Angew. Chem. Int. Ed. 2013, 52, 4435-4439.
5) Q. Zhang, L. Su, J. Collins, G. Chen, R. Wallis, D. Mitchell, D. M. Haddleton, C. R. Becer J. am. Chem. Soc. 2014, 136, 4325-4332.

IL32

POLYPEPTIDES BY LIGHT: PHOTO-POLYMERISATION OF N-CARBOXYANYDRIDES (NCA)

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Light is a convenient trigger for polymerisations as it is spatially defined and digital in nature offering spatiotemporal control. Consequently, photoinitiation has been efficiently employed in various polymerisations, most notably in free radical and cationic processes. Most recently, photoinitiation has also been added to the techniques of controlled radical polymerisation.[1] An approach that has not been explored to date is light-induced ROP of amino acid N-carboxyanhydrates (NCA). The last decade has seen a significantly increased interest in this polymerization since synthetic polypeptides are amongst the most simple and accessible peptidomimetic biomaterials

We have recently report the first example of UV-initiated synthesis of polypeptides from NCAs.[2] The particular emphasis was the proof of concept and the demonstration that the initiation process is selective and the polymers are structurally well-defined. Moreover, we have expanded the concept to the light-triggered grafting of synthetic polypeptides from nanoparticles and planar surfaces.

References

1) S. Dadashi-Silab, S. Doran and Y. Yagci, Chem. Rev., 2016, 116, 10212.
2) T. Stukenkemper, J. F. G. A. Jansen, C. Lavilla, A. A. Dias, D. F. Brougham, A. Heise, Polym. Chem. 2017, 8, 828.

IL33

BENZODIOXINONE PHOTOCHEMISTRY. A VERSATILE ROOT TO MACROMOLECULAR SYNTHESIS

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Benzodioxinones undergo photoinduced decomposition generating ketenes and benzophenone. In this presentation, photoinduced reactions of benzodioxinones and their use in polymer synthesis will be presented. Mechanistic details for the production ketene and benzophenone from the photolysis of benzodioxinone indicates that under certain conditions each intermediate may undergo further reactions useful for the formation of various polymeric structures. While ketenes are efficient to participate in step-growth polymerization via through the reaction with the compounds possessing hydroxyl or amine groups, benzophenone released during the photolysis can be used as photoinitiator for free radical polymerization and cationic polymerization. It was demonstrated that photolysis of heterobifunctional monomers equipped with benzodioxinone and aliphatic hydroxyl groups leads to the formation of oligoesters with narrow molecular weight distribution. Benzodioxinone photochemistry is also useful to induce cross-linking of monofunctional vinyl monomers in the absence of conventional photoinitiator and crosslinker. Several other applications such as *in situ* formation of hyper-branched polymers and self-healing will also be discussed.

References

1) Yilmaz G, Kumbaraci V, Talinli N, Tatar P, Demirel AL, Yagci Y, J. Polym.Sci., Polym. Chem., 2012, 50, 2517
2) Kumbaraci V, Aydogan B, Talinli N, Yagci Y, J. Polym.Sci., Polym. Chem., 2012, 50, 2612
3) Durmaz YY, Kumbaraci V, Demirel AL, Talinli N, Yagci Y. Macromolecules, 2009, 42, 3743
4) Tasdelen MA, Kumbaraci V, Jockusch S, Turro NJ, Talinli N, Yagci Y. Macromolecules, 2008, 41, 295
5) Tasdelen MA, Kumbaraci V, Talinli N, Yagci Y. Macromolecules, 2007, 40, 4406
6) Kumbaraci V, Talinli N, Yagci Y. Macromol. Rapid Commun., 2007, 28, 72
7) Tasdelen MA, Kumbaraci V, Talinli N, Yagci Y. Polymer, 2006, 47, 7611
8) Kumbaraci V, Talinli N, Yagci Y. Macromolecules, 2006, 39, 6031

IL34

CONTROLLING POLYMERSOME SHAPE AND FUNCTION

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Polymersomes are vesicular structures, of which the membrane is composed of amphiphilic block copolymers. Traditionally polymersomes have a spherical morphology. For many nanomedicine related applications, however, the controlled construction of differently shapes particles is of great interest. We have recently developed dialysis procedures which allow us to shape change spherical vesicles in a range of different morphologies. Using polystyrene-poly(ethylene glycol) block copolymers as building blocks, vesicles prepared in a mixture of organic solvent and water were reshaped into discs and bowl-shaped vesicles named stomatocytes. By encapsulation of catalytic particles in the newly formed cavity of these stomatocytes, devices were obtained which showed motion when exposed to chemical fuel. The behavior of these nanomotors could be directed by employing fuel gradients and by using self-regulating enzymatic networks, which made the motors move with constant speed in changing fuel concentrations. Employing poly(ethylene glycol)-poly-DL-lactide polymers, dialysis in different concentrations of electrolyte led to prolate shaped deformation, resulting in tubular polymersomes. The aspect ratio could be controlled by a change in electrolyte concentration. These biodegradable particles show much promise in the area of nanomedicine.

References

1) Wilson D.A.; Nolte, R.J.M.; van Hest, J.C.M., Autonomous movement of platinum-loaded stomatocytes. Nature Chemistry 2012, 4, 268
2) L. K. E. A. Abdelmohsen., D.S. Williams, J. Pille, S.G. Ozel, RS.M. .Rikken, D.A. Wilson, J.C.M. van Hest Formation of Well-Defined, Functional Nanotubes via Osmotically Induced Shape Transformation of Biodegradable Polymersomes. Journal of the American Chemical Society 2016 138, 9353-9356.

IL35

METATHESIS POLYMERIZATION OF AMINO ACID DERIVATIVES

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The BOC-protected amino acid cystine can be converted into unsaturated, disulfide containing macrocycles and polymerized through either olefin or disulfide ring-opening metathesis polymerization (ED-ROMP) to yield hetero-multifunctional polymers with molar masses of >20 kDa.[1,2] The polymers can be degraded by a mild reducing agent, e.g. DTE, or by alcoholysis. Deprotection of pendant amino groups can be achieved under acetic conditions, leading to water soluble polymers that can be functionalized for instance with anhydrides. Furthermore, the main-chain alkene units can be used for (photo-)crosslinking reactions for the production of hydrogels.

References

1) F. N. Behrendt, H. Schlaad, Polym. Chem. 2017, 8 (2), 366-369.
2) Manuscript in preparation.

IL36

SYNTHESIS OF POLYAMIDE 6 WITH ARAMIDE UNITS

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Lightweight materials with structural properties are expected to replace heavy metal components in order to reduce the consumption of energy and therefore the release of CO_2 in some cases. In composite materials, some polyamides are considered nowadays as an alternative to epoxy or polyester thermosets as far as their properties and processing can be adapted for the production of parts at low price.

Polyamide 6 is one of the most common polyamide and is synthesized by hydrolytic or activated anionic ring-opening polymerization, but there is still a need to find new synthesis methodologies to prepare new materials in order to vary its properties.

This work presents a strategy based on the combination of anionic ring-opening polymerization of ε-caprolactam and condensation polymerization of aminobenzoate derivatives for the synthesis of aliphatic-aromatic copolyamides. Thermal characteristics of some polyamides will be discussed. More generally, this approach intends to demonstrate the possibility of marrying two chemistries and to synthesize new materials.

IL37

MECHANISMS OF SOLUBILITY ENHANCEMENT FOR HYDROPHOBIC DRUGS IN POLYMERIC SPRAY-DRIED DISPERSIONS

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Blending with a polymer excipient represents a promising strategy for oral delivery of hydrophobic active pharmaceutical ingredients (APIs). After ingestion, the excipient must release the API at a concentration significantly higher than the equilibrium solubility of its crystalline form, and maintain this supersaturation over the course of hours. It remains a largely empirical process to design an effective excipient for a given API, and especially to understand what factors contribute to supersaturation maintenance. It has been suggested that the excipient and API form some kind of unspecified "nanostructure". We have used cryogenic transmission electron microscopy and synchrotron small-angle X-ray scattering to follow the state of dispersion of various model APIs, such as phenytoin and probucol, during a standard dissolution assay in phosphate buffered saline. Both commercially available excipients, such as hydroxypropyl methylcellulose acetate succinate, and custom-synthesized polymers, are compared. Nanostructures are indeed directly observed, and shown to correlate with the concentration of API in solution. Furthermore, we disclose a new mechanism of supersaturation maintenance, by storing APIs in micelle corona, rather than the traditional sequestration in the micelle core.

IL38

LIVING RADICAL RING-OPENING REDOX POLYMERIZATION (R3P) OF DITHIOLS

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We have recently discovered an efficient and "greener" method for the oxidative polymerization of 2-[2-(2-sulfanylethoxy)ethoxy]ethanethiol (DODT). Our method produces the desired polymers at ambient temperature and pressure, does not require protection of the thiol groups and uses no chlorinated reagents or solvents. High molecular weight disulfide polymers (up to M_n = 233,000 g/mol with M_w/M_n as low as = 1.15 were obtained. The M_n – conversion plot showed exponential growth, and 90% monomer conversion was reached in 5 minutes. SEC showed the coexistence of oligomers with high MW polymers. We found that the oligomers were rings. The structure of the high MW polymers was investigated by ^{1}H and ^{13}C NMR. Under highly oxidative conditions 750 MHz NMR did not detect the presence of thiol end groups. SEC conformational analysis also showed compact structures, providing indirect evidence that even the high MW fractions contain rings. We extended the same concept to thiol-functionalized polyisobutylene (HS-PIB-SH) and produced biodegradable PIB-disulfides. There is evidence that ring structures are involved in this polymerization as well. Detailed structural analysis of the PIB-based polydisulfides are in progress.

References

1) Rosenthal-Kim, E.Q.; Puskas, J.E.: Molecules, 2015, 20, 6504-6519.
2) Rosenthal, E.Q.; Puskas, J.E.: Pure & Applied Chem. 2012, 84(10), 2121-2133.
3) Rosenthal, E.Q.; Puskas, J.E.; Wesdemiotis, C.: Biomacromolecules, 2012, 13(1), 154-164.

IL39

SYNTHETIC ROUTES TO SIMPLIFYING MOLECULAR COMPLEXITY

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Incredible progress has been made in synthetic polymer chemistry to control the polymer chain length, structure and architecture via controlled/living polymerization reactions as well as their functionalization via efficient post-modification chemistries. The development in this field is still very intense and dynamic, leading to an ever-increasing molecular complexity.

However, this increasing complexity on the molecular level demands for highly advanced specialists possessing the skillset to synthesize such chemical structures. This clearly limits or slows down the advancement to new scientific areas. Hence, we have addressed this challenge over the years by developing *simple* synthetic routes, while maintaining a molecular complexity, thereby providing the synthetic tools for many scientists to prepare highly functional polymer materials with unprecedented molecular precision.

Synthetic routes, possibilities, remaining challenges and opportunities for next generation polymers will be discussed with the aim to development and study of structure-property relationships of polymeric materials. As such, novel syntheses of polymer materials for smart materials and battery related materials will be presented as examples.

IL40

FROM FUNCTIONALIZED POLYMERS TO NON-ISOCYANATE POLYURETHANES (NIPUS)

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Conventional polyurethanes (PUs) are being synthesized from isocyanates, which require hazardous and toxic phosgene for their manufacture. Current academic and industrial research thus aims at establishing safer and “greener” alternative routes to more environmentally friendly PUs. Among these, the isocyanate-free aminolysis of a dicyclic carbonate to form non-isocyanate PUs (NIPUs) is nowadays the most investigated and promising strategy.

In this context, we have been investigating the post-polymerization chemical modification of telechelic precursors, such as α,ω-dihydroxy telechelic polycarbonates, polyesters, polyethers or polyolefins, into their corresponding five-membered cyclic carbonate end-functionalized polymers, which upon aminolysis eventually afford high molar mass polyhydroxyurethanes (PHUs)/NIPUs ($M_{n,SEC} \leq$ 68 000 g.mol^{-1}).[1-3]

Another more straightforward route we have been exploring towards the desired telechelic precursors of NIPUs relies on the direct synthesis of suitably end-functionalized polymers through the ring-opening metathesis polymerization (ROMP) of a cyclic olefin using functionalized chain transfer agents (CTAs). The metathesis pathway thus enables, via different bifunctional symmetric alkene CTAs, to access to well-defined ditelechelic polyolefins, such as α,ω-dithiocarbonate functionalized PCOEs, precursors of NIPUs.[4,5] Our most significant results will be presented.

References

1) M. Helou, O. Miserque, J.M. Brusson, J.F. Carpentier, S. M. Guillaume Green Chem. 2011, 13, 266-271.
2) L. Annunziata, A. K. Diallo, S. Fouquay, G. Michaud, F. Simon, J.-F Carpentier, S. M. Guillaume Green Chem. 2014, 16, 1947-1956.
3) E. Vanbiervliet, S. Fouquay, G. Michaud, F. Simon, J.-F. Carpentier and S. M. Guillaume, Macromolecules, 2017, 50, 69-82.
4) L. Annunziata, S. Fouquay, G. Michaud, F. Simon, S. M. Guillaume, J.-F. Carpentier Polym. Chem. 2013, 4, 1313-1316.
5) A. K. Diallo, L. Annunziata, S. Fouquay, G. Michaud, F. Simon, J.-M. Brusson, S. M. Guillaume, J.-F Carpentier Polym. Chem. 2014, 5, 2583-2591.

IL41

TOPOLOGICAL POLYMER CHEMISTRY TOWARD MACROMOLECULAR GRAPH CONSTRUCTIONS

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Topologically intriguing polymer chain architectures have continuously been an attractive research subject [1]. A class of *multicyclic* polymer topologies, including three subclasses of *spiro*-, *bridged*- and *fused*-forms, are particularly unique not only from the topological geometry viewpoint but also from their programmed folding structures of biopolymer relevance. We have developed an *electrostatic self-assembly and covalent fixation* (ESA-CF) protocol, in which ion-paired polymer self-assemblies are employed as key intermediates. A variety of multicyclic polymer constructions of the three subclasses and their hybrid-forms, including a triply-*fused* tetracyclic and a quadruply-*fused* pentacyclic forms (unfolded tetrahedron-graph, and "shippo"-form, respectively) have been synthesized through the ESA-CF process in conjunction with a tandem alkyne-azide addition, i.e., *click*, and olefin metathesis, i.e., *clip*, reactions [2,3]. Moreover, a topologically significant *fused*-tetracyclic $K_{3,3}$ graph polymer construction, known as a prototypical non-planar graph in topological geometry, and remarkably identified in cyclic polypeptides (cyclotides) of diverse biofunctions, has been synthesized through the ESA-CF by using a uniform-size dendritic polymer precursor having six cyclic ammonium salt end groups carrying two units of a trifunctional carboxylate counteranions [4].

References

1) Topological Polymer Chemistry: Progress of cyclic polymers in synthesis, properties and functions, Y. Tezuka ed., World Scientific, Singapore, 2013.
2) H, Heguri, T. Yamamoto, Y. Tezuka, Angwew. Chem. Int. Ed., 54, 8688 (2015).
3) Y. Tominaga, T. Yamamoto, Y. Tezuka, Macromolecules, 49, 4076 (2016).
4) T. Suzuki, T. Yamamoto, Y. Tezuka, J. Am. Chem. Soc., 136, 10148 (2014).

IL42

STEREOCHEMICAL CONTROL OF MATERIALS PROPERTIES THROUGH NUCLEOPHILIC THIOL-YNE ADDITIONS

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Nature has evolved the ability to create large and complex molecules in which the precise control over the stereochemistry within the molcules is critical to their function. Most likely as a consequence of the difficulty in achieving hundreds of consecutive additions with high enantioselectivity, this area has recieved relatively little study in polymer science. This presentaion will focus on the advances that have been made to create materials with precisely defined stereochemistry in the backbone of the polymer, primarily through the use of the oganocatalysed nucleophilic addition of thiols to activated alkynes.

References

1) Angew. Chem. Int. Ed. (2016) 55, 13076 - 13080

IL43

LINEAR GRADIENT MULTI-BLOCK COPOLYMERS WITH UP TO 14 BLOCKS: A RAPID AND GENERAL STRATEGY FOR AN INTERESTING CLASS OF MATERIALS WITH EXCELLENT MECHANICAL PROPERTIES

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We present a one-pot strategy for living AB gradient diblock and multiblock copolymers with low dispersity (< 1.10). The approach relies on the *in-situ* monitoring of the statistical carbanionic copolymerization, which permits direct observation of the monomer consumption. Copolymerization of isoprene and styrene (I/S) in cyclohexane is known to lead to a strong gradient, with isoprene reacting considerably faster than styrene. The subtle change from styrene to *p*-methylstyrene (I/*p*-MS) as a comonomer leads to a surprising result. Extremely divergent copolymerization parameters are obtained (r_I =33.9 r_{pMS}=0.026), enabling the one-step synthesis of gradient structures with narrow gradient between both blocks. Repeated addition of isoprene/p-MS mixtures leads to multi-gradient copolymers with up to 14 blocks and elevated molecular weights of up to 500,000 g/mol in a one-pot procedure, using several addition steps (M_w/M_n = 1,05-1,08). The multi-block copolymers form ordered phase-segregated nanostructures and exhibit sequence-dependent mechanical properties.

IL44

NEW POLYMERS AND STRATEGIES FOR DRUG DELIVERY APPLICATIONS

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This lecture will present our recent achievements in the field of macromolecular engineering for biomedical applications, and especially the use of controlled radical polymerization as a tool for the design of:

(i) Degradable vinyl materials[1] by radical ring-opening polymerization (rROP) using cyclic ketene acetal (CKA) monomers.[2] In particular, 2-methylene-4-phenyl-1,3-dioxolane (MPDL) was copolymerized with oligo(ethylene glycol) methyl ether methacrylate (OEGMA) by NMP to produce well-defined and degradable PEG-based copolymers.[3]

(ii) Polymer prodrug nanoparticles. We developed of new class of polymer prodrug nanoparticles by using the "*drug-initiated*" method,[4] which consisted in the controlled growth of hydrophobic polymers from anticancer drug-bearing alkoxyamines or chain transfer agents to prepare, by NMP or RAFT, well-defined and high drug content polymer prodrug nanoparticles with in vitro and in vivo anticancer activity.[5,6]

References

1) Delplace, V.; Nicolas, J. Nature Chem. 2015, 7, 771
2) Tardy, A.; Nicolas, J.; Gigmes, D.; Lefay, C.; Guillaneuf, Y. Chem. Rev. 2017, 117, 1319
3) Delplace, V.; Guégain, E.; Harrisson, S.; Gigmes, D.; Guillaneuf, Y.; Nicolas, J. Chem. Commun. 2015, 51, 12847
4) Nicolas, J. Chem. Mater. 2016, 28, 1591
5) Harrisson, S.; Nicolas, J.; Maksimenko, A.; Bui, D. T.; Mougin, J.; Couvreur, P. Angew. Chem., Int. Ed. 2013, 52, 1678
6) Bao, Y.; Boissenot, T.; Guégain, E.; Desmaële, D.; Mura, S.; Couvreur, P.; Nicolas, J. Chem. Mater. 2016, 28, 6266

IL45

HIGHLY AROMATIC POLYMER ARCHITECTURES DESIGNED FOR OPTOELECTRONIC APPLICATIONS

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The organic/flexible electronics industry demands new innovative polymeric materials. Besides conducting and semiconducting polymers, also the insulating materials in between, the dielectrics, as well as materials with special optoelectronic properties are highly important since they determine significantly the final performance of the device. High performance hyperbranched (hb) polymers (e.g. hb polyphenylenes, hb-PPh) offer significant potential in the application as gate dielectric material which can be adopted for high performance OFETs by design-matching with the respective semiconducting material. The branching provides the highly needed solubility and allows solution processing or even processing by printing techniques. For multilayer device preparation, we also developed suitable crosslinking strategies which can be thermally or photochemically induced.[1] Furthermore, hyper-branched polyvinylsulfides through thiol-yne addition of B3+A2 monomers [2] proved to be excellent candidates for high refractive index (HRI) materials well suited for 1D planar all-polymer photonic crystals and efficient light out-coupling from OLEDs [2,3]. Polymers with RI as high as 1.79 have been achieved. Furthermore, crosslinkable linear polycarbazoles with benzophenone substituents show excellent Thermally Activated Delayed Fluorescent (TADF) properties.

References

1) R. Pötzsch, B. Voit, Macromol. Rapid Commun. 2012, 33, 635.
2) Q. Wei, R. Pötzsch, X. Liu, H. Komber, A. Kiriy, B. Voit, P.-A. Will, S. Lenk, S. Reineke, Adv. Funct. Materials 2016, 26, 2545.
3) Q. Wei, P. Kleine, Y. Karpov, X. Qiu, H. Komber, K. Sahre, A. Kiriy, R. Lygaitis, S. Lenk, S. Reineke, B. Voit, Adv. Funct. Materials, on-line, January 2017

IL46

EMULSION TEMPLATED HYDROGELS: SUPERABSORBENTS, STIMULUS-RESPONSE, ION-EXCHANGE, AND SELF-CROSSLINKING

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PolyHIPEs are porous emulsion-templated polymers that are usually synthesized within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs) [1,2]. Several different systems of highly porous hydrogel polyHIPEs (HG-PHs), containing both ionic monomers (methacrylic acid (MAA) or acrylic acid (AA)) and non-ionic monomers (hydroxyethyl methacrylate (HEMA) or *N*,*N* -dimethylacrylamide (DMAA)), were synthesized within oil-in-water HIPEs and proved to be highly water absorbent [3-6]. The extraordinary high water uptakes were ascribed to a hydrogel-swelling-driven void expansion mechanism. PDMAA which was self-crosslinked through the formation of methylene radicals exhibited superior water uptake compared to PDMAA crosslinked using a crosslinking comonomer. The water uptakes in HG-PHs containing ionic monomers were pH-responsive, while those in HG-PHs containing *N*-isopropylacrylamide (NiPAAm) were temperature-responsive. Superabsorbent, mechanically robust, high-porosity hydrogels based on 2-acrylamido-2-methyl-propansulfonic acid (AMPS) exhibited unusually high uptakes of water and artificial urine. The highly accessible sulfonic acid groups produced a high ion exchange capacity and resulted in rapid dye absorption. These highly swollen HG-PHs did not fail at compressive strains of up to 60%, they retained the absorbed water, and they recovered their shapes upon the removal of stress.

References

1) Silverstein MS. Prog Polym Sci 2014;39:199-234.
2) Silverstein MS. Polymer 2014;55:304-320.
3) Kulygin O, Silverstein MS. Soft Matter 2007;3:1525-1529.
4) Cohen N, Silverstein MS. Macromolecules 2012;45:1612-1621.
5) Ovadia M, Silverstein MS. Polym Intl 2016;65:280-289.
6) Kovacic S, Silverstein MS, Macromol Rapid Commun 2016;37:1814-1819.

IL47

NEW SPIN ON OLD POLYMERS: VERSATILE MATERIALS USING SIMPLE CHEMISTRY AND ELECTROSPINNING

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Functional electrospun polymeric nanofibers are rapidly evolving as indispensable platforms for various biomedical applications such as sensing, drug delivery and tissue engineering.[1] Among crucial requirements for nanofibers toward such applications are properties such as their facile multi-functionalization, anti-biofouling nature and robustness in the biological milieu. Over the past few years, our research efforts have focused upon fabrication of such reactive hydrophilic nanofibers. Toward this end, two different approaches have been explored: (a) electrospinning of amphiphilic polymers,[2] and (b) crosslinking of hydrophilic polymers.[3] The first approach utilizes reactive amphiphilic polymers which allows formation of nanofibers with hydrophobic interiors and hydrophilic exteriors. In the latter approach, crosslinking can be carried out *in situ* during electrospinning or post-electrospinning. Various 'clickable' polymers synthesized over the past decades were utilized to obtain nanofibers. Design of such nanofibers and their application towards sensing of biomolecules will be disclosed in this presentation.

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References

1) Kalaoglu Altan, O. I.; Sanyal, R. and Sanyal, A. Polymer Chemistry 2015, 6, 3372-3381.
2) Kalaoglu Altan, O. I.; Sanyal, R. and Sanyal, A. Biomacromolecules, 2015, 16, 1590-1597.
3) Kalaoglu Altan, O.I. ; Verbraeken, B. ; Lava, K. ; Gevrek, T.N. ; Sanyal, R. ; Dargaville, T. ; De Clerck, K. ; Hoogenboom, R. and Sanyal, A. ACS Macro Letters, 2016, 5, 676-681.

IL48

IMPROVEMENT OF NITINOL CORROSION RESISTANCE BY SIATRP : THE KEY ROLE OF ELECTROGRAFTING PROCESS

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The coating of Nitinol (NiTi) surface by a polymer layer has become very appealing this last decade owing to its increased attractiveness in the biomedical field. While its intrinsic properties helped ensure its popularity [1,2], its worldwide implementation is still hampered by nickel inclusions, leading to the release of carcinogenic Ni^{2+} ions.

Among all the recent ways to modify Nitinol surfaces, the elaboration of self-assembled monolayers (SAM) that can kick off the initiation of a polymer layer is of great interest as their high order confer a reinforcement of the metal surface corrosion resistance, and bring new functionalities to the metal for post-modification purposes.

Herein, we emphasis the benefits of electro-grafting [3] assisted functional monolayer self-assembly onto nitinol alloy compared to the traditional thermally-assisted ones by the preparation of functional monolayers that could initiate the SI-ATRP of a model monomer. It will be demonstrated how electro-grafting process allow fast SAM preparation in mild conditions while preventing degradation of ATRP initiating sites. The proof of concept is validated by initiation of DMAEMA by ATRP and the characterization of properties of the resulting materials.

References

1) Barras C.D., Myers K.A., Eur. J. Vasc. Endovasc. Surg., 2000, 19, 564
2) Duerig T.W., Mater. Sci. Eng. A, 2006, 69, 438
3) Vanhooland, A.; Devillers, S.; Issakova, T.; Michaux, C.; Delhalle, J.; Mekhalif, Z. J. Electrochem. Soc. 2016, 163 (10), G1–G5

IL49

MULTICOMPONENT REACTIONS IN POLYMER SCIENCE: FROM VERSATILE TUNING OF STRUCTURE AND PROPERTIES TO SEQUENCE DEFINED MACROMOLECULES

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Multicomponent reactions are an established tool in organic chemistry. They offer high atom-economy, straightforward practical procedures and most importantly structural diversity can easily be achieved by variation of the used components. Only recently, the benefit of these one-pot reactions was realized for macromolecular engineering. Especially the Passerini three-component and Ugi four-component reactions demonstrate attractive tools for polymer synthesis. Here, two different approaches to form polymers can be followed: either synthesizing the monomer first via an isocyanide-based MCR (IMCR) or forming the polymer directly by the use of IMCR-reactive bifunctional components. Both approaches will be discussed in detail and led to a large variety of different polymer architectures offering a variety of tunable properties. Moreover, multicomponent reactions are an excellent tool for the design of highly defined polymer architectures, including dendrimers and sequence defined polymers.

IL50

MOLECULAR ENGINEERING WITH ANIONIC COPOLYMERISATION

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Anionic polymerisation is well-known for its fine control of molecular structure and has been widely adopted for the synthesis of a variety of molecular architectures. Anionic polymerisation also lends itself well to the synthesis of copolymers with precise sequence distributions.

We present recent highlights of research at Durham University in the field of sequence-controlled anionic copolymerization. Specifically we will describe the synthesis of a series of copolymers prepared using diphenylethylene and derivatives which includes perfect alternating copolymers, sequence-controlled terpolymers and telechelic polymers[1,2]. Moreover, in each case, the resulting sequence is entirely controlled by copolymerization kinetics with all monomers are present from the start on the reaction. As such these copolymerisation reactions are effectively a contrived statistical copolymerisation whereby all monomers undergo polymerisation simultaneously in what we (and others) have described as a “fire and forget” approach.

We will also present some previously unreported results for the copolymerization of 2,3-dimethyl butadiene (DMB) by anionic polymerisation. DMB is an interesting yet largely forgotten member of the diene family which behaves with significantly different copolymerization kinetics to the more familiar butadiene and isoprene.

References

1) 1. Hutchings, L. R.; Brooks, P. P.; Parker, D.; Mosely, J. A.; Sevinc, S., Monomer Sequence Control via Living Anionic Copolymerization: Synthesis of Alternating, Statistical, and Telechelic Copolymers and Sequence Analysis by MALDI ToF Mass Spectrometry. Macromolecules 2015, 48, 610.
2) 2. Natalello, A.; Hall, J. N.; Eccles, E. A. L.; Kimani, S. M.; Hutchings, L. R., Kinetic Control of Monomer Sequence Distribution in Living Anionic Copolymerisation. Macromolecular Rapid Communications 2011, 32, 233.

IL51

INNOVATIVE POLYMERS FOR ENERGY AND BIOELECTRONICS

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New redox polymers and ion conducting polymer electrolytes are actively searched for improving the performance of several emerging technologies in energy and bioelectronics. Examples include the development of polymer electrolytes for all solid batteries with increase security or organic battery electrode materials obtained from natural sources for green energy. Interestingly similar materials are of interest for bioelectronics such as new biocompatible materials for electrodes in contact with the skin or the brain. In this presentation we will share our latest results on the design of innovative polymes which include new poly(ionic liquid)s, iongels, polycarbonate polymer electrolytes, PEDOT biofunctional materials or single ion-conducting block copolymers. The use of macromolecular engineering tools for designing the polymer properties for the needs of the different devices will be highlighted.

References

1) N. Casado, G. Hernandez, H. Sardon, D. Mecerreyes "Current trends in redox polymers for energy and medicine" Progress in Polyme Science 2016, 52, 107-135
2) L. Porcarelli, AS. Shaplov, M. Salsamendi, JR. Nair, YS. Vygodskii, D. Mecerreyes, C. Gerbaldi, " Single-ion block copoly(ionic liquid)s as electrolytes for all-solid state lithium batteries" ACS Applied Materials&Interfaces 2016, 8,16, 10350-10359
3) M. Isik, T. Lonjaret, H. Sardon, R. Marcilla, T. Herve, G.G. Malliaras, E. Ismailova, D. Mecerreyes "Cholinium-based iongels as solid electrolytes for long-term cutaneous electrophysiology" Journal of Materials Chemistry C 2015, 3, 34, 8942-8948

IL52

ENGINEERING THE IMMUNE SYTEM WITH POLYMERIC NANOMATERIALS

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The field of immuno-engineering has vastly expanded the last decade and offers new avenues for the treatment of infectious diseases and cancer. My research group works at the interface between life sciences and materials chemistry with a special interest in polymer chemistry, nanotechnology and immunology. In my talk I will give an overview of our recent findings in how we can engineer the adaptive and innate immune system using synthetic nanomaterials to fight cancer and infectious diseases. In this regard we are developing strategies that allow for (1) efficient targeting of dendritic cells in lymphatic tissue for engineering adaptive immunity, (2) decorating cancer cells and infected cells with motifs that activate innate immunity and (3) engineering the tumor stroma.

IL53

PRECISION POLYMER CHEMISTRY FOR BIONANO APPLICATIONS

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Chemists are remarkably proficient at directing the synthesis of small molecules, but fine-tuning the structures of large molecules, such as those found in polymers, is far more taxing. Despite many years of research, the field of macromolecular engineering i.e. the preparation of large molecules with strict control over their size and chemical groups has many mountainous challenges yet to overcome. Nature provides endless examples of precisely engineered macromolecules; proteins, for instance, which contain amino-acid side-chains that are accurately positioned, often in a way that determines the proteins' roles. Synthetic chemists have tried to recreate nature's exceptional control over macromolecules, and in so doing they have designed new materials with precisely defined structures, for use in applications ranging from materials to medicine. The lecture will describe our use of complex polymeric architectures designed by controlled polymerisation techniques to probe cellular mechanisms. In particular, we are interested in the design of drug delivery vectors to optimise their uptake by cells.

References

1) Danial, M.; My-Nhi Tran, C.; Young, P.G.; Perrier, S.; Jolliffe, K.A. Nat. Commun., 2013, 4:2780 DOI: 10.1038/ncomms3780
2) Cobo, I.; Li, M.; Sumerlin, B. S.; Perrier, S. Nature Mat. 2015, 14 (2), 143-159
3) Boyer, C.; Bulmus, V.; Davis, T.P.; Ladmiral, V.; Liu, J.; Perrier, S. Chem. Rev., 2009, 109 (11), 5402-5436.
4) Gody, G.; Maschmeyer, T.; Zetterlund, P.B.; Perrier, S. Nat. Commun., 2013, DOI: 10.1038/ncomms3505

IL54

POLYPHOSPHOESTERS: NEW TRENDS IN SYNTHESIS AND DRUG DELIVERY APPLICATIONS

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Thanks to their biocompatibility and degradability properties, polyphosphoesters are appealing polymers for biomedical applications. In contrast to aliphatic polyesters, such as poly(lactide), the pentavalency of the phosphorus atom allows the easy modification of the polyphosphoester properties by simply adjusting the nature, the length and the functionality of the polyphosphate pendant group. Therefore, macromolecular engineering of polyphosphoesters [1] was applied to design well-defined architectures and functionalities adapted to drug nanocarriers.

Amphiphilic block copolymers with a crosslinkable lipophilic polyphosphoester block have been synthesized. In water, their micelles have shown efficiency for the encapsulation of poorly soluble drugs [2]. Double hydrophilic diblock copolymers with one block able to complex calcium have been achieved. Some of them were found efficient templates for the growth of calcium carbonate, leading to porous and small-sized carriers by aqueous or supercritical CO_2 processes [3]. These degradable materials offer thus a versatile platform for the design of drug delivery vehicles.

References

1) Ergul Z., Jérôme C., Macromolecular Bioscience (2016), 16(12), 1745
2) Clement, B., Grignard, B., Koole, L., Jérôme, C., Lecomte, P., Macromolecules, 2012, 45(11), 4476
3) Ergül, Z., Debuigne, A., Calvignac, B., Boury, F., Jérôme, C., Journal of Materials Chemistry B, 2015, 3, 7227-7236

IL55

REDOX POLYMERS: THE FUTURE FOR LI-ION BATTERIES?

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This presentation is centered on the development of novel energy storage systems with enhanced performances through original organic electroactive material chemistry and engineering approaches. Deciphering the fundamental flaws and building better organic batteries is our primary target, the long-term goal of this research being the development of sustainable all-carbon-based batteries. Based on this, we focus on three complementary yet, distinct directions with specific goals: improve and develop new organic radical materials for pseudo-capacitive energy storage by engineering high energy density nitroxide radical containing block copolymer architectures; develop novel block copolymer architectures for high performance solid polymer electrolytes and develop either hybrid organic-inorganic electrochemical energy storage materials or hybrid supercapacitor redox polymer gels that combine best-of-both worlds characteristics. Accordingly, this research aims the design and development of novel electroactive organic materials and architectures and, by doing so, develop faster, safer & longer-lasting organic batteries, capacitors and their hybrids.

IL56

DESIGNER MOLECULES IN PRECISION POLYMERIZATIONS TOWARD ADVANCED MACROMOLECULAR ENGINEERING

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Biopolymers such as DNA and proteins are expressing their functions based on sequence and position of functional groups in the pendant groups as well as shape (topology) of the main chain. For synthetic polymers, control of the chain length and terminal groups is now possible using living polymerizations, but that of topology and sequence is still extremely difficult.

Our recent efforts have been directed to creative design of molecules (i.e., initiators and monomers) in polymerizations with cleavable and/or renewable bonds to control for control of side-chain sequence and main-chain topology for vinyl polymers via to lead to construction of new type of “well-defined polymers” as well as development of functions derived from the controlled structure.

References

1) Ouchi, M.; Nakano, M.; Nakanishi, T.; Sawamoto, M.: Alternating Sequence Control for Carboxylic Acid and Hydroxyl Pendant Groups via Controlled Radical Cyclopolymerization of Divinyl Monomer Carrying Cleavable Spacer. Angew. Chem. Int. Ed., 2016, 128, 14804-14809.
2) Oh, D. Y.; Ouchi, M.; Nakanishi, T.; Ono, H.; Sawamoto, M.: Iterative Radical Addition with a Special Monomer Carrying Bulky and Convertible Pendant: A New Concept toward Controlling the Sequence for Vinyl Polymers. Acs Macro Lett. 2016, 5, 745-749.
3) Hibi, Y.; Ouchi, M.; Sawamoto, M.: A strategy for sequence control in vinyl polymers via iterative controlled radical cyclization. Nature Commun. 2016, 7.
4) Kammiyada, H.; Ouchi, M.; Sawamoto, M.; A Study on Physical Properties of Cyclic Poly(vinyl ether)s Synthesized via Ring-Expansion Cationic Polymerization. Macromolecules 2017, 50, 841–847.

IL57

DESIGN AND APPLICATIONS OF DIGITAL POLYMERS

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Digital polymers are synthetic macromolecules that allow molecular storage of information. For instance, a binary sequence can be inputted in a polymer chain using two monomers that are intentionally defined as 0 and 1 bits. Typically, a readable sequence is synthesized using multistep-growth protocols that allow exact placement of the coded monomer units in the chains. Using such strategies, our group has recently described the synthesis of different class of digital polymers, including polyphosphodiesters, poly(alkoxyamine phosphodiester)s, poly(alkoxyamine amide)s, poly(triazole amide)s and polyurethanes. In all cases, the digital information stored in the polymer can be efficiently read using tandem mass spectrometry. In addition, dynamic polymers (e.g. alkoxyamine-based structures) allow erasing of information. The relevance of these different macromolecules for applications in the field of data storage, long-term storage and product identification will be discussed in this presentation.

References

1) Lutz, J.-F.; Ouchi, M.; Liu, D. R.; Sawamoto, M., Science 2013, 341, 1238149.
2) Colquhoun, H.; Lutz, J.-F., Nat. Chem. 2014, 6, 455.
3) Lutz, J.-F.; Lehn, J.-M.; Meijer, E. W.; Matyjaszewski, K., Nat. Rev. Mater. 2016, 1, 16024
4) R. K.; Meszynska, A.; Laure, C.; Charles, L.; Verchin, C.; Lutz, J.-F., Nat. Commun. 2015, 6, 7237.

IL58

SPECIFICALLY INTERACTING POLYMERS: CAN POLYMER CHEMISTS STILL LEARN ANYTHING FROM MUSSELS?

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Bio-inspiration has become one of the key stratregies to develop advanced materials.1 For instance, the byssal adhesion system of marine mussels offeres rich sources of inspiration for decades.2 Mussels adhesives outperform in several aspects technical glues and lead toward bioinspired materials e.g. water based adhesives, coatings or hydrogels. The identification of l-dihydroxyphenylalanine (Dopa) as a key moiety for adhesion, triggered a class of Dopa carrying polymers with remarkable properties.

Here we summarize work going bejond those instant adhesives, as Dopa can be enzymatically generated on demand via tyrosinase processing of tyrosine-bearing precursors. Enzymatically activable adhesives were specifically selected to bind to certain surfaces, leading to antifouling coatings, which bind under salt water.3 Moreover, Dopa has an important role in providing cohesion. Exploiting the underlying processes offers opportunities to realize a novel enzyme-mediated polyaddition route, which enabled polymerization of oligopeptides to segmented precision polymers.4 Those have sequential similarities to mussel foot proteins and show ideal functionalities for adhesives. The resulting polymers exhibit irreversible adsorption toward different surfaces under ultra-hostile conditions, highlighting the potentials for next generation under water glues.

References

1) Dujardin E, Mann S. Adv. Mater. 14, 775-788 (2002).
2) Lee H, Lee BP, Messersmith PB. Nature 448, 338-341 (2007)
3) Wilke P, Helfricht N, Mark A, Papastavrou G, Faivre D, Börner HG. A J. Am. Chem. Soc. 136, 12667-12674 (2014).
4) Horsch, J. Wilke P, Andreas, F., Rompel A., Börner HG. (2017), submitted.

IL59

MULTIFUNCTIONAL POLY(IONIC LIQUID)S: FROM SYNTHESIS TO APPLICATIONS IN ENERGY AND ENVIRONMENT

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Poly(ionic liquid)s (PILs) are a subclass of polyelectrolytes that gained an enabling role in many fields of polymer chemistry and material science. PILs combine the unique properties of ionic liquids with the flexibility and properties of macromolecules, and provide novel attractive functions. Recently, the precision design of novel PILs by controlled/living polymerization (CLP) techniques was intensively searched for developing emerging applications.

This talk will first discuss recent routes for the precision synthesis of all vinyl-imidazolium based (co)polymers in water or in organic media under non-demanding experimental conditions. We will then describe the preparation of innovative redox and surface active PILs, and show the potential of these PILs in battery applications and for multifunctional coatings. More specifically, we will show how macromolecular engineering can be exploited for designing innovative polymer cathodes for ultra-high performance Li storage with unprecedented performances (high capacities and ultra-long life-span over more than 3000 cycles at an extreme current-rate). This innovative and effective molecular design for polymer cathodes opens up new horizons in developing an economical and environmentally benign platform for large-scalable fabrication of high performance batteries.

IL60

CONTROLLING THE FUNCTIONALITY AND TOPOLOGY OF POLYMERS PREPARED BY RADICAL POLYMERIZATION THANKS TO THIOL CHEMISTRY

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A methodology that allows controlling the functionality and topology of copolymers prepared by radical polymerization using a single molecule will be presented. This approach relies on a monomer carrying a xanthate moiety[1] that can be used to introduce both branching points and pending functional groups. The rational design of the xanthate monomer, as well as the synthesis and characterization of functional linear, branched and bottlebrush copolymers will be presented.[2,3] Parameters allowing to control the degree of branching and functionality will be discussed. The synthesis of branched polymers carrying pending polymerizable units as well as amphiphilic molecular bottlebrushes will be presented as example of functional branched architectures accessible through this methodology.

References

1) Nicolaÿ, R. Macromolecules 2012, 45, 821
2) Le Neindre, M., Magny B., Nicolaÿ R. Polym. Chem. 2013, 4, 5577
3) Le Neindre, M., Nicolaÿ R. Polym. Inter., 2014, 63, 887

IL61

POLYBENZOXAZINE-BASED NANOCOMPOSITES: FROM SYNTHESIS TO HIGH PERFORMANCE MATERIALS

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Polybenzoxazines are currently drawing lot of interest in the field of materials science and more particularly as thermosetting materials. Based on a remarkable balance of material properties, combining both the specific advantages of traditional epoxy and phenolic resins, polybenzoxazines appear as unique candidates for the production of high-performance materials, particularly when they are filled with nanoparticles like carbon nanotubes for instance.

One of the most relevant characteristic features of benzoxazines relies on the great versatility of the monomer molecular design with a special appeal for bio-based or renewable organic compounds in order to prepare a novel family of sustainable biopolymers.

The design of the monomer stucture is thus of prime interest, not only to control the polymerization but also to promote the development of special interactions with selected nanofillers in order to take full advantage of their excellent intrinsic properties and to pave the way to the preparation of nanohybrids with remarkable properties.

IL62

CONJUGATED POLYMERS: VERSATILE ORGANIC SEMICONDUCTORS WITH A PLETHORA OF APPLICATIONS.

Dirk Vanderzande

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Conjugated polymers or organic semiconductors are in the focus of research since 1977. In these 40 years they have been integrated in different types of electronic devices of which solar cells form the most recent development. At the moment an efficiency has been achieved of about 12%. Still further improvements can be expected. This progress is the result of a combination of introducing new materials, develop insights in the fundamental working principles and the introduction of new device architectures.

For said devices efficiency is critical dependent on achieving a specific nano-morphology in the active layer. The variety of materials used has increased substantially. Recently different interlayers materials have been identified which can lead to improvements of more than 15% of the achieved efficiency . It is still under discussion what the exact phenomenon is behind this efficiency improvement. Furthermore recent work has shown that details of the chemistry and structure of the polymers has mayor impact on the performance. An overview of the state-of-the-art will be presented. Finally the issue of scalability will be addressed.

IL63

POLY(1,2,3-TRIAZOLIUM)S: FUNCTIONAL AND DYNAMIC POLYMER ELECTROLYTES

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Poly(ionic liquid)s (PILs) are peculiar polyelectrolytes that ideally combine the unique properties of ionic liquids (high ionic conductivity, thermal, chemical and electrochemical stabilities) with those of polymers (mechanical stability, processing and tunable macromolecular design). We have pioneered in 2013 a new class of PILs having 1,2,3-triazolium cationic groups in the repeating unit as innovative functional and dynamic ion conducting polymer materials. Their synthesis merges the robust and orthogonal nature of the copper(I)-catalyzed azide-alkyne cycloaddition, the quantitative nature of the *N*-alkylation of 1,2,3-triazoles and anion metathesis reactions, together with different chain growth or step growth polymerization techniques. Establishment of precise structure/properties relationships allowed the development of several ion conducting materials having high thermal, chemical and electrochemical stabilities as well as high ionic conductivity. In addition, we have shown that polymer networks having 1,2,3-triazolium cross-links possess the appealing attributes of vitrimers where dynamic exchange through trans-*N*-alkylation reactions afford materials that can be reprocessed, reshaped and recycled. The latest developments in poly(1,2,3-triazolium) materials and their potential applications as solid electrolytes and dynamic materials will be presented.

IL64

URETHANE-CONTAINING MACROMONOMERS AS NOVEL HYDROGEL BUILDING BLOCKS FOR SOLVENT- AND INITIATOR FREE 3D PRINTING APPLICATIONS: THE ULTIMATE SOLUTION?

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3D printing was introduced as one of the latest novelties in the biomaterials field. The theory is straightforward and the possibilities and applications practically endless. Indeed, starting from a scan obtained using a medical imaging technique, a 3D reconstruction of a (part of a) tissue or organ is realized using a carefully selected material (polymer, ceramic, metal or a combination). Using the plethora of commercially available and/or in-house developed 3D printers, this discipline has gained a huge interest in the biomaterials community. In addition to research into the capabilities and challenges of 3D printing devices, a focus on the materials constituting the printed scaffolds has been witnessed.

In the presentation, an overview will be given on previously applied polymers within Ghent University in collaboration with various national and international (industrial) collaborators with the aim to develop scaffolds for hard or soft tissue engineering applications. The pro’s and cons of the various applied materials and printing technologies will be highlighted. On the material level, a recent development covering urethane-containing cross-linkable macromonomers for 3D printing will be highlighted.

IL65

NEW FRONTIERS FOR CONTROLLED NETWORKS IN THE NANO- AND MICROSCALE

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The Harth group is invested in the interface between polymeric material design and biomedical engineering. Areas of research include the preparation and investigation of materials for targeted drug delivery in cancer, glaucoma and Type 1 diabetes. Two synthetic strategies have been developed to prepare semibranched polylgycidols for applications as injectable materials in orthopedic applications, working as delivery matrices or materials that are developed as tissues with advanced mechanical properties. The strengthening of porous biological materials such as bone via polymerization techniques is a topic that has been recently started. An ink-jet printing technology has been invented for the preparation of particles in micron size that are capable of crosslinking under light-initiated conditions to confine a multitude of drug molecules or catalysts. The goal in all of the projects is to create materials with a translational outlook that are based on novel synthetic approaches and techniques to advance the field of polymeric and macromolecular materials.

IL66

DEEPER INSIGHT INTO THE RDRP POLYMERIZATION OF VINYLIDENE FLUORIDE

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Two strategies of RDRP of vinylidene fluoride (VDF) are presented. First, in contrast to the MADIX copolymerization of VDF with other comonomers (TFP, PMVE, and MAF),[1] that of VDF has been very rarely reported.[2-3] The synthesis of PVDF using MADIX solution polymerization was thus investigated in details.

More efficient protocols of solution polymerization were developed and afforded relatively well-defined PVDF.[2-3] The careful polymer chain-end monitoring using MALDI-TOF as well as ^{1}H, ^{19}F, and HETCOR ^{1}H-^{19}F NMR nonetheless revealed that VDF reverse additions and transfer to solvent reactions affect the control of the polymerization.[2,4] Indeed, these undesired reactions are responsible for a non-negligible loss of CTA and for the accumulation of non-reactive polymer chains in the reaction medium. However, the synthesis of PVDF with high chain-end functionality was achieved, and attempts to reinitiate further chains were explored to lead to original macromonomers, block copolymers,[5] and dendrimers. This work is the first comprehensive study of the MADIX solution polymerization of VDF and further trends on the limits.

References

1) B. Ameduri, Macromolecules 2010, 43, 10163.
2) M. Guerre, B. Ameduri, V. Ladmiral, Macromolecules 2015, 48, 7810.
3) M. Guerre et al. Macromolecules, 2016, 49, 5386.
4) M. Guerre et al., Macromol. Chem. Phys., 2016, 217, 2275.
5) M. Guerre et al. Polym. Chem., 2016, 7, 6918.

IL67

AMINE-BASED AND AMINE-REACTIVE POLYMERS: A VERSATILE TOOLBOX FOR POLYMER CONJUGATION

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Reversible-deactivation radical polymerizations, including reversible addition-fragmentation chain transfer (RAFT) polymerization, have shown a high tolerance towards functional groups allowing the synthesis of functional polymers with a high degree of control over topology, composition, and functionality.

In this context, our contribution is based on the development of original heterofunctional monomers and their use in RAFT polymerization to access to amine-based polymers and amine-reactive polymers.

This presentation aims to highlight the utility of amine-based polymers with a “charge-shifting” behaviour for gene delivery and the interest of amine-reactive polymers as a platform for the design of useful materials for bioconjugation.

IL68

THERMODYNAMICS OF THE INTERACTION OF NATURAL POLYMERS WITH NANOCELLULOSE

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Isothermal titration calorimetry is a powerful technique to investigate the thermodynamic interaction between nanoparticles and biological polymers. We have started to use this technique to look at the interactions between cellulose nanocrystals and proteins as well as hemicelluloses to be able to better understand their potential interaction in materials, in biological systems and as drug carriers. From this work, we have found that most lasting interactions are driven by entropy, rather than enthalpy, as adsorption releases part of the surface bound water on the nanocellulose and part of the hydration shell around dissolved molecules. As a result, single aminoacids do not bind to nanocellulose, even when both have an opposite charge. The structure of the adsorbed polymers can also be controlled by the amount of surface functionalities on the nanoparticles, making it possible to tailor how proteins and polymers shape themselves on the nanoparticulate surface.

In this presentation I will present how we carried out our work, what we found and where we will be going form here.

IL69

BUILDING DYNAMIC AND FUNCTIONAL NANOSTRUCTURES IN WATER: TADPOLES TO TOROIDAL NANORATTLES

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Our group developed the second method which utilizes the reversible addition-fragmentation chain transfer (RAFT) emulsion polymerization of styrene with a thermoresponsive (poly(N-isopropylacrylamide), PNIPAM) MacroCTA in water. Upon cooling, a temperature directed morphology transformation (TDMT) results in the formation of a wide range of nanostructures, ranging from spheres, worms, rods, vesicles, donuts, and lamellae; with the additional feature of controlled surface chemical functionality derived from the R-group on the MacroCTA.

1. **Tadpoles**: Multicompartment tadpole nano-objects are a rare and intriguing class of structures with potential in a wide range of applications. Here, we demonstrate the synthesis of chemically multifunctional tadpoles made at high weight fraction of polymer (> 10 wt. %). The tadpoles can be dried, rehydrated, and stored in water for 5 months without a change in shape

2. **Nanorattles** are complex structures consisting of an outer shell and a detached inner core. We report a method to produce chemically multifunctional toroidal nanorattles directly in water that can then be triggered to individual toroidal micelles.

References

1) Kessel, S.; Urbani, C. N.; Monteiro, M. J. Angew Chem Int Edit 2011, 50, (35), 8082-8085.
2) Jia, Z. F.; Bobrin, V. A.; Truong, N. P.; Gillard, M.; Monteiro, M. J. J Am Chem Soc 2014, 136, (16), 5824-5827
3) Bobrin, V. A.; Monteiro, M. J. J Am Chem Soc 2015, 137, (50), 15652-15655

IL70

MICROFLOW REACTIONS: FROM CONTROLLED POLYMERIZATION TO SEQUENCE-DEFINED OLIGOMERS

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Macromolecular chemistry has matured to a point where virtually any polymer structure can be synthesized via combinations of controlled polymerization approaches, postpolymerization modification and efficient ligation strategies. Still, large hurdles have to be overcome to take the next step in research, that is being able to provide such complex materials reliably on significant scale for use in advanced applications. A solution to this problem is to use continuous flow synthesis techniques. Flow reactors are associated with high reproducibility, intrinsically simple reaction scale-up and improved product qualities due to reduction of side reactions.

The potential of flow chemistry for preparative macromolecular chemistry will be discussed mainly for the synthesis of sequence-defined and sequence-controlled polymers. Sequence-controlled macromolecules are associated with unique properties, and their synthesis marks a turning point in macromolecular chemistry, by reaching a level of precision otherwise only known from certain biomacromolecules. Challenges in the synthesis of such materials will be addressed, as well as emerging applications, giving emphasis to monodisperse sequence-defined oligomers that can be accessed from single monomer insertions in combination with advanced chromatography separation.

IL71

MULTI-STIMULI RESPONSIVE SELF-ASSEMBLED BLOCK COPOLYMERS VIA A CATECHOL/BORONIC ACID LIGATION

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A wide range of well-defined **boronic acid** and **nitrocatechol** end-functionalized homopolymers were synthesized via the Reversible Addition-Fragmentation chain Transfer (RAFT) process from the corresponding chain transfer agents[1]. The coupling reaction between complementary end-functionalized homopolymers led to **amphiphilic block copolymers (BCP)** featuring a multistimuli-responsive covalente **boronate ester junction**. The efficiency of the coupling reaction, the self-assembly of these BCPs in aqueous medium into nano-aggregates and their ability to encapsulate hydrophobic molecules were assessed and characterized by NMR (^{1}H, DOSY), fluorescence, DLS, Cryo-TEM and SEC.

The **multi-responsiveness of the covalent junction** was then investigated upon applying various stimuli such as pH, addition of sugar and UV light, resulting in the dissassembly of BCP based nano-objects and the release of the fluorescent probe[2]. Interestingly, the release profile of model molecules was found to be readily and finely modulated through the nature of stimuli and also by successively applying different stimuli.

References

1) F. Coumes, A. Malfait, M. Bria, J. Lyskawa, P. Woisel, D. Fournier, Catechol/boronic acid chemistry for the creation of block copolymers with a multi-stimuli responsive junction, Polymer Chemistry 7 4682 - 4692 (2016), doi: 10.1039/C6PY00738D
2) F. Coumes, P. Woisel, D. Fournier, Facile Access to Multistimuli-Responsive Self-Assembled Block Copolymers via a Catechol/Boronic Acid Ligation, Macromolecules 49 8925 (2016), doi: 10.1021/acs.macromol.6b01889

IL72

H-BONDING DRIVEN SELF-ASSEMBLY OF AMPHIPHILIC POLYMERS

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We have studied supramolecularly engineered amphiphilic macromolecules (SEAM) consisting of a supramolecular structure directing unit (SSDU) at the junction of the hydrophobic and hydrophilic segment of the polymer. The SSDU is made of a H-bonding group (hydrazide or amide) and a naphthalene-diimide (NDI) chromophore. By synergistic H-bonding and aromatic interaction, the SSDU pre-assembles and thus the subsequent step, involving hydrophobic association of the wedge, becomes a function of the first step (dictated by molecular interaction). Therefore the ultimate morphology of the self-assembled structure is determined by the distinct nature of the molecular interaction involved in the first step by ignoring the packing parameters. Consequently, two amphiphilic copolymers having identical chemical structure and same hydrophobic/ hydrophilic balance produce distinctly different polymersome or cylindrical micelle depending on the nature of the single H-bonding functional group of the SSDU. So prominent is the motivation for self-selection, that in a mixture of two such polymers, self-sorted assembly was noticed although these two polymers differ merely by a *SINGLE* H-bonding functional group. The presentation will highlight our recent results in this area.

NOTES

ORAL COMMUNICATION'S ABSTRACTS

OC01

RAFT/MADIX EMULSION COPOLYMERIZATION OF VINYL ACETATE AND N-VINYLCAPROLACTAM: TOWARDS WATERBORNE PHYSICALLY CROSSLINKED THERMORESPONSIVE PARTICLES

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Waterborne latex produced by emulsion polymerization and stimuli-responsive polymers are two classes of interesting polymers with myriad of applications. It is thus relevant to produce stimuli-responsive polymers as particles by emulsion polymerization process. Poly(*N*-vinylcaprolactam) (PVCL) is a biocompatible thermoresponsive polymer of interest (1). Few studies have investigated the controlled radical (CRP) emulsion polymerization of less activated monomers such as vinyl esters or vinylamides and none of them dealt with CRP of VCL by polymerization in aqueous dispersed media. In the present work, thermoresponsive particles physically crosslinked by means of supramolecular non-covalent hydrophobic interactions between the poly(*N*-vinylcaprolactam-*co*-vinyl acetate) statistical copolymers were synthesized by RAFT/MADIX emulsion polymerization mediated using a xanthate functionalized poly(ethylene glycol). The reversible swelling-to-collapse transition, analogue to chemically crosslinked microgels, was monitored according to the initial feed of hydrophobic VAc. In a preliminary study, careful investigation of the reactivity ratios of VAc/VCL provided valuable information on copolymer microstructure (2). The copolymers of this study were hydrolyzed into promising thermoresponsive biocompatible statistical copolymers based on vinyl alcohol and *N*-vinylcaprolactam co-monomer units.

References

1) J. Ramos, A. Imaz, J. Forcada, Polymer Chemistry 2012, 3, 852-856
2) L. Etchenausia, A. Malho Rodrigues, S. Harrisson, E. Deniau-Lejeune, M. Save Macromolecules 2016, 49, 6799–6809

OC02

AN INJECTABLE, ANISOTROPIC HYDROGEL FOR DIRECTED CELL AND NERVE GROWTH

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Spinal cord injury affects approximately two million people worldwide and leads to a permanent loss of motor and sensory function below the point of injury. Repair is impeded due to the lack of stimulating growth factors, the presence of inhibiting molecules, and the formation of a cavity and scar tissue. Multiple channel spinal cord bridges, pre-made of natural or synthetic polymers, have demonstrated the importance of physical guidance to direct growing nerves across the injury site. In the case of acute spinal cord injury, however, a low invasive therapy is required to avoid further damage and impairment. Therefore, injectable hydrogels offer an alternative to implants as they are formed in situ. Unfortunately, these types of hydrogels currently lack unidirectional orientation to guide the regenerating nerves and rebuild the highly organized nerve pathways that were damaged. Therefore, we developed a new type of biomaterial, called an Anisogel, which combines low invasiveness with physical guidance. After injection, the material forms an anisotropic structure and induces aligned nerve growth, even in the presence of minimal guidance cues.

OC03

POLYMERIZATION-INDUCED SELF-ASSEMBLY FOR REINFORCED ACRYLIC COATINGS

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Polymerization-induced self-assembly (PISA) is nowadays recognized as an efficient and valuable approach to synthesize core-shell nanoparticle dispersions, constituted of amphiphilic block copolymer assemblies, in water. It has further been demonstrated that the morphology of the particles can be tuned by the careful choice of the monomers, the respective block length and the solvent of polymerization.[1,2,3]

Using two different strategies, we demonstrate here how one can take advantage of the current developments in PISA to prepare waterborne acrylic coatings exhibiting enhanced mechanical properties. In the first strategy, the materials are entirely constituted of *spherical* soft-core/ hard-shell particles made of highly asymmetric poly(acrylic acid)-*b*-poly(*n*-butyl acrylate) block copolymers prepared by RAFT-mediated emulsion polymerization.[4,5] The second one relies on the use of *highly anisotropic,* high T_g particles added in limited quantities as reinforcing fillers to conventional acrylic latex coatings. In both approaches, films could be formed at room temperature. Mechanical tests on the resulting films showed that they exhibit high stiffness and high extensibility, seemingly contradictory properties, which could be reached thanks to the specific organisation of the materials.

References

1) J. Rieger, Macromol. Rapid Commun. 2015, 36, 1458.
2) M. Lansalot, J. Rieger, F. D'Agosto. In Macromolecular Self-assembly, John Wiley & Sons, Inc, 2016, pp 33-82.
3) S. L. Canning, G.N. Smith, S.P. Armes, Macromolecules 2016, 49, 1985.
4) M. Chenal, J. Rieger, C. Vechambre, J.M. Chenal, L. Chazeau, C. Creton, L. Bouteiller, Macromol. Rapid Commun. 2013, 34, 1524.
5) M. Chenal, C. Vechambre, J. M. Chenal, L. Chazeau, V. Humblot, L. Bouteiller, C. Creton, J. Rieger, Polymer, 2017, 109, 187.

OC04

SYNTHESIS OF POLY(BUTYLENE SUCCINATE) AND POLY(BUTYLENE ADIPATE) COPOLYMERS USING ENZYME CATALYSIS

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Enzymes have become attractive alternative in polymer and organic syntheses due to their inherent biocompatibility and high selectivity. They are of great interest for tissue engineering applications, including cardiovascular diseases, where three-dimensional fibrous scaffolds that mimic the cardiac extracellular matrix (ECM) properties are needed. Therefore, we studied in detail the synthesis of novel elastomeric multiblock copolyesters using *Candida antarctica* Lipase B (CALB). The copolymers consist of different hard and soft segments, where hard segments are build up from either diethyl succinate or divinyl adipate reacted with butanediol while soft segment blocks are based either on dilinoleic diol or on dihydroxy polyisobutylene. The main advantage of using the proposed non-toxic catalyst is that bio-catalysed functionalization and polymerization at mild temperatures can be achieved.[1,2] We demonstrate that the properties of these new materials can be controlled by varying the hard and soft segments blocks composition and ratios thus allowing the preparation of materials matching the target application.

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References

1) S. Sen and J. E. Puskas, Molecules, 2015, 20, 9358–79.
2) Y. Jiang, A. J. J. Woortman, G. O. R. A. van Ekenstein and K. Loos, Biomolecules, 2013, 3, 461–80.

OC05

NEW APPROACHES TO CONTROLLED SYNTHESIS OF POLYMERS VIA “LIVING” RADICAL POLYMERIZATION

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In this report a few examples of new approaches to controlled synthesis of polymers using living radical polymerizations are presented. Low temperature nitroxide-mediated polymerization was used for controlled synthesis of PMMA and MMA-styrene copolymers. New two-stage method of synthesis of graft PS-g-polydiene copolymers by macronitroxide-mediated polymerization was developed.[1] A new approach to the synthesis of graft PMMA-g-polydiene copolymers using low-temperature polymerization with boroxyl radicals was suggested.[2] Living nitrone-mediated polymerization was used for the preparation of styrene – vinyl acetateABAblock-gradient copolymers. Also new high-active catalytic forms of Cu(0) – different copper mirrors – were used for fast SET-polymerization[3,4].

The products were characterized by GPC, NMR, IR Spectriscopy, TGA and AFM.

This work was supported by the Russian Science Foundation (grant 14-13-00683).

References

1) M. Yu. Zaremski, O.V. Borisova. Patent 2478656 (Russia) 2011
2) Yu. N. Bubnov, M.Yu. Zaremski, M.E. Gurskii. patent 2461580 (Russia) 2011
3) M.Yu. Zaremski, B.A. Zagribelny, A.P. Orlova, S.B. Zezin, A.V. Olenin. Patent 2566302 (Russia) 2014
4) M.Yu. Zaremski, B.A. Zagribelny, A.P. Orlova, S.B. Zezin, A.V. Olenin. Patent 2566303 (Russia) 2014

OC06

FUNCTIONAL THIN HYDROGEL LAYERS

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The volume phase transition in stimuli sensitive hydrogels is important for many applications, e. g. as (micro-) actuator and sensors materials, or in controlled cell attachment-detachment and controlled drug delivery. Most investigations focus on temperature or pH-sensitive polymers, however, a variety of other parameters (e. g. host-guest interactions) has been studied. The majority of these applications require the use of hydrogels as thin layers at surfaces and interfaces. Therefore, the behavior of bulk hydrogel may not be necessarily extended to these types of geometries. Responsive polymers networks are interesting materials for a variety of different applications due to the fact that they can perform a large volume transition. However, the swelling transition is a diffusion limited process. Thus, the decrease of the feature size is an appropriate way to create structures with reasonable response time. The possibility to pattern responsive polymer networks makes them useful for application in micro-system technology as well as in biomedicine. The ability to optimize the integration of these polymers is critical for the development of platforms that harness the unique abilities of responsive polymer networks.[1-3]

References

1) A. Döring, W. Birnbaum, D. Kuckling, Chem. Soc. Rev. 2013, 42, 7391-7420.
2) W. Birnbaum, D. Kuckling, Polym. Chem. 2012, 3, 2039–2049.
3) W. Birnbaum, C. Weinberger, V. Schill, S. Haffer, M. Tiemann, D. Kuckling, Colloid Polym. Sci. 2014, 292, 3055–3060.

OC07

SINGLE CHAIN FOLDING ENGINEERING TOWARD NANOMEDICINE AND CATALYSIS APPLICATIONS

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Linear polymer chains can be folded to individual single-chain nanoparticles (SCNPs) by means of different intra-chain crosslinking techniques. SCNP formation is reminiscent of protein folding to functional bioentities although current synthetic methods lack the perfection of protein folding to highly-efficient enzymes. Two limiting SCNP molecular architectures can be obtained depending on the synthesis route and the amphiphilic nature of the SCNP precursor employed: sparse morphology, or type I, resembling that of intrinsically disordered proteins and globular morphology, or type II, mimicking the typical conformation of enzymes.[1] SCNPs of type I show the presence of multiple locally compact, but accessible, sites / cavities / zones, so-called "local pockets", whereas SCNPs of type II display, on average, a single pocket of larger size. The possibility to anchor, either temporally or permanently, active species like drugs or catalysts onto these local pockets paves the way to the use of SCNPs in a variety of nanomedicine and catalysis applications.[1]

References

1) Gonzalez-Burgos, M., Latorre-Sanchez, A., and Pomposo, J. A. (2015) Advances in single chain technology. Chem. Soc. Rev., 44, 6122-6142.

OC08

BIODEGRADABLE PROTEIN-POLYMER SUPRAMOLECULAR ASSEMBLIES: SYNTHETIC APPROACHES AND PROPERTIES

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Amphiphilic protein-polymer chimeras -the so-called *Giant Amphiphiles*- have been designed to mimic the hierarchical assembly displayed in biological and synthetic material systems over a wide range of lengths. During the last years we synthesized several such protein-polymer amphiphilic bioconjugates using different synthetic approaches varying from the direct coupling of end-functionalized polymers to proteins, to the grafting of polymers from protein macroinitiators. Interestingly, these protein-polymer conjugates have shown to assemble into well-defined, functional superstructures suitable for a variety of materials applications.

In the present work, our latest synthetic approaches, involving the Atom Transfer Radical Polymerization (ATRP), the enzyme catalyzed ATRP (eATRP) and the Ring Opening Polymerization (ROP) grafting *of* a series of monomers *from* protein biomacroinitiators will be comparatively presented. The development of chimeric enzyme supramolecular assemblies (proteinosomes) which are designed to merge the catalytic and structural/functional properties of biomolecules with those of responsive polymers will be discussed and their potential application in biomedicine and nanotechnology evaluated.[1,2]

References

1) K. Velonia, A. E. Rowan, R. J. M. Nolte, R. J. M. J. Am. Chem. Soc. 124, 4224 (2002); B. Le Droumaguet, G. Mantovani, D. M. Haddleton, K. Velonia, K. J. Mater. Chem., 17, 1916 (2007).
2) B. Le Droumaguet, K. Velonia, Angew. Chem., Int. Ed. 47, 6263-6266 (2008); E. Daskalaki, B. Le Droumaguet, D. Gérard, K. Velonia, Chem. Commun. 48, 1586 (2012).

OC09

SUPRAMOLECULAR BIOMATERIALS: FROM FUNDAMENTALS TO ADVANCED HEALTHCARE SOLUTIONS

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Supramolecular hydrogels are dynamically cross-linked materials exhibiting properties similar to traditional hydrogels, but which are capable of viscous flow under shear stress (shear-thinning) and rapid recovery of mechanical properties when the stress is relaxed (self-healing). These properties afford minimally invasive implantation in vivo through direct injection or catheter delivery to tissues, contributing to a rapid gain in interest in their application for drug delivery and tissue engineering. Herein, we discuss the preparation and application of shear-thinning, injectable hydrogels driven by non-covalent interactions between modified biopolymers (BPs) and biodegradable nanoparticles (NPs). The hierarchical construction of these biphasic hydrogels allows for multiple therapeutic compounds to be entrapped simultaneously and delivered with differential release profiles in vitro and in vivo. Moreover, delivery of loaded therapeutics can be tuned over several months, enabling novel long-term treatment strategies for a variety of chronic diseases. Overall, this presentation will demonstrate the facile synthesis and in-depth characterization of the properties of an injectable hydrogel affording minimally invasive application in vivo and controlled release of therapeutics.

References

1) Webber, M.J.†; Appel, E.A.†; Meijer, E.W.; Langer, R.* “Supramolecular Biomaterials,” Nature Mater., 2016, 15, 13-26.
2) Appel, E.A.†; Tibbitt, M.W.†; Webber, M.J.; Mattix, B.A.; Veiseh, O.; Langer, R.* “Self-Assembled Hydrogels Utilising Polymer-Nanoparticle Interactions,” Nature Commun., 2015, 6, No. 6295.
3) Yu, A.C.; Chen, H.; Chan, D.; Agmon, G.; Stapleton, L.M.; Sevit, A.M.; Tibbitt, M.W.; Acosta, J.D.; Zhang, T.; Franzia, P.W.; Langer, R.; Appel, E.A.* “Scalable Manufacturing of Biomimetic Moldable Hydrogels for Industrial Applications,” Proc. Nat. Acad. Sci. USA, 2016, 113, 14255-14260.

OC10

NEW POLYMERIZATION METHODOLOGY OF AMINO-ACID MONOMERS

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Poly(amino acid) is an important biomimetic materials due to their unique biocompatibility, and potential application in gene transfection, drug delivery, and prevention of viral infections.[1-3] For example, ε-Poly-lysine (ε-PL) is an uncommon cationic homopolymer produced by the fermentation process. Due to its significant antimicrobial activity and nontoxicity to humans, ε-PL is now industrially produced as an additive, *e.g.* for food and cosmetics. However, due to the lack of appropriate polymerization method, ε-PL is now produced mainly by a fermentation process.

Here, we report a new chemical strategy, based on ring-opening polymerization (ROP) of lactam, to obtain ε-PL with diverse molecular weight from renewable lysine monomer. Compared with ROP of lysine *via* the *N*-carboxyanhydride (NCA) intermediate, this new strategy for ε-PL, through ROP and without phosgene, allows for new opportunities in biomaterials applications.[4]

References

1) Chen, X. Y.; Lai, H. W.; Xiao, C. S.; Tian, H. Y., Chen, X. S.; Tao, Y. H.; Wang, X. H. Polymer Chemistry 2014, 5, 6495-6502.
2) Lai, H. W.; Chen, X. Y.; Lu, Q.; Bian, Z., Tao, Y. H.; Wang, X. H. Chemical Communications 2014, 50, 14183-14186.
3) Jia, F.; Chen, X. Y.; Zheng, Y.; Qin, Y. S.; Tao, Y. H.; Wang, X. H. Chemical Communications 2015, 51, 8504-8507.
4) Tao, Y. H.; Chen, X. Y.; Jia, F.; Wang, S. X.; Xiao, C. S.; Cui, F. C., Li, Y. Q., Bian, Z., Chen, X. S.; Wang, X. H. Chemical Science 2015, 6, 6385-6391.

OC11

ISOSORBIDE AS A BUILDING BLOCK FOR POLYESTERS AND POLYCARBONATE, CHALLENGES AND APPLICATIONS

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Isosorbide or 1,4-3,6 dianhydrohexitol, derivated from starch and more precisely from sorbitol, is one of the chemical intermediates of interest in the field of thermoplastic materials and for curable resins application. Hence, isosorbide found its place as a monomer suitable for polycondensates synthesis [1] like polyesters, polycarbonates and thermoplastic polyurethanes. Concerning aliphatic [2] or semi-aromatic polyesters [3], the addition of isosorbide increases glass transition temperature, opening to this new polymer several usual applications of amorphous polymers.The properties of other thermoplastics like polycarbonates [4] or TPU can as well be improved by the incorporation of isosorbide.

The preparation of poly (ethylene-co-isosorbide) terephthalate with different ratios of isosorbide will be particularly detailed. The structure – properties relationship will permit a focus on the synthesis of polyesters with semi-crystalline or amorphous structures. The influence of isosorbide on the polymerization, on the processing of the resulting polyester as well as the modification of the final properties will be enlightened.

The same works in polycarbonate field will be described as well and industrial applications enlightened.

References

1) F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J.-P. Pascault, Prog. Polym. Sci. 2010, 35, 578–622,
2) B. Noordover , V. van Staalduinen , R. Duchateau , C. Koning , A. Rolf, M. Mak , A. Heise , A. Frissen, J. van Haveren, Biomacromolecules, 2006, 7, 3406,
3) R. Storbeck, M. Ballauff, J. Applied Polym. Sci., 1996, 59, 1199,
4) European Patent 2 033 981 A1 (2009) M. Fuji, M., Akita, T. Tanaka (Mitsubishi Chem.)

OC12

POLYMERSOMES AND MULTICOMPARTMENT SYSTEMS FOR SYNTHETIC BIOLOGY

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Next-generation synthetic biology approaches are expected to rely on the engineering of multifunctional vesicular compartments for mimicking specific cellular functions. The key characteristics of such vesicular compartments are their permeable and non-permeable nature of outer membrane to communicate with the external environment for controllable bio-inspired functions and actions [1].

Here, we report on the design and fabrication of stimuli-responsive polymersomes [2, 3], hollow capsules [4] and polymersomes-based multicompartments. With the control over their membrane permeability and functionality it is possible to switch off/on multienzymatic reactions by enzyme-enclosed polymersomes [5] and polymersomes-based multicompartments. Thus, the common use of isolated polymersomes and polymersomes-based multicompartments enabled us to carry out parallel enzymatic reactions, also providing the substrate-channeling effect of enzymes adjacent. Moreover, these vesicular systems are also able to trigger post-encapsulation and controllable release processes using protein mimics [4], enzymes or Au nanoparticles as well docking and undocking processes of low- and high-molecular weight (bio)molecules outside and inside of polymersomes´ membrane. Selected examples will be shown to highlight the potential of those vesicular systems in synthetic biology.

References

1) P. Schwille, Science 2011, 33,1252.
2) J. Gaitzsch et al., Angew. Chem. Int. Ed. 2012, 51, 4448.
3) B. Iyisan et al., Chem. Mater. 2016, 28, 1513
4) X. Liu et al. Adv. Sci. 2016, http://dx.doi.org/10.1002/advs.201600308
5) D. Gräfe et al., Nanoscale 2014, 6, 10752.

OC13

"COLORED" MULTI-STIMULI RESPONSIVE HYDROGELS

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Controlled deformation processes are ubiquitous both in biological systems and materials science. For example, muscles may undergo expansion or contraction as a result of an external physiological stimuli. Similarly, synthetic smart polymer gels, capable of swelling or deswelling in response to various physical and/or chemical stimuli, have been developed during the last decades. Complexes fabricated from the electron deficient cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and electron-rich guests have become one of the most important building blocks for the synthesis of colored self-assembled architectures.[1,2] Here, we report on the successful engineering of new multi-stimuli responsive macromolecular hydrogels featuring $CBPQT^{4+}$ based complexes. More particularly, we have exploited these colored $CBPQT^{4+}$ based interactions to i) control the swelling/shrinking processes of materials by applying different stimuli (T, V, competitive macromolecules)[3] i) to impart both thermal and temporary memory function to hydrogels and iii) to develop polymeric hydrogel systems capable of swelling *via* a supramolecular transmission. An important practical aspect of these new functional materials is that all relevant phenomena (swelling/shrinking processes, memory function) have an associated visible readout.

References

1) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J., Cyclobis(paraquat-p-phenylene). A Tetracationic Multipurpose Receptor. Angew. Chem. 1988, 27 (11), 1547-1550.
2) Sambe, L.; de La Rosa, V. R.; Belal, K.; Stoffelbach, F.; Lyskawa, J.; Delattre, F.; Bria, M.; Cooke, G.; Hoogenboom, R.; Woisel, P., Programmable Polymer- Based Supramolecular Temperature Sensor with a Memory Function. Angewandte Chemie-International Edition 2014, 53 , 5044-5048
3) K. Belal, F. Stoffelbach, J. Lyskawa, M. Fumagalli, D. Hourdet, A. Marcellan, L. D. Smet, L. De smet, V. R. De la rosa, G. Cooke, R. Hoogenboom, P. Woisel, Recognition-Mediated Hydrogel Swelling Controlled by Interaction with a Negative Thermoresponsive LCST Polymer, Angewandte Chemie International Edition, 2016, 55, 13974–13978.

OC14

RECYCLABLE CROSSLINKED POLYMER NETWORKS WITH FULL PROPERTY RECOVERY VIA ONE-STEP CONTROLLED RADICAL POLYMERIZATION

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Conventional polymer networks cannot be recycled into high-value products because of permanent, covalent crosslinks. Rubber tires illustrate the problems ranging from economic loss to sustainability issues associated with spent, crosslinked polymers. A nitroxide-mediated polymerization strategy has been developed for one-step synthesis of recyclable crosslinked polymers from monomers or polymers that contain carbon-carbon double bonds amenable to radical polymerization.[1] Resulting materials possess dynamic alkoxyamine crosslinks that undergo reversible decrosslinking as a function of temperature. As demonstrated with polybutadiene as starting material, and styrene, a nitroxide molecule and bifunctional initiator for initial crosslinking, a model for tire rubber is produced at temperatures comparable to those for tire molding. Upon cooling, crosslinks are made permanent due to the strong temperature dependence of the reverisible nitroxide capping/uncapping reaction. From thermomechanical characterization, when the original model rubber is chopped into bits and later remolded in the melt state, the properties of the resulting material at temperature below 373 K indicate full recovery of crosslink density after multiple reprocessing steps. Other strategies for reprocessing of crosslinked polymers with (nearly) complete property recovery will be discussed.

References

1.) K. Jin, L. Li, and J.M. Torkelson, Adv. Mater. 2016, 28, 6746-6750.

OC15

THE SYNTHESIS AND CHARACTERIZATION OF FARNESENE-BASED INDUSTRIAL POLYMERS

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A bio-based route to the production of *trans* -β-farnesene has recently been commercialized. *Trans* -β-farnesene is capable of being polymerized by both anionic and cationic pathways, creating low molecular weight polymers with structure-property relationships unique within the diene class of monomers.

Trans-β-farnesene is produced through fermentation of sugar feedstocks. The pathway offers an alternative to petroleum-based feedstocks derived as by-products of naptha or ethane cracking. Anionic polymerization of the monomer produces a highly branched "bottle-brush" structure, with rheological properties that are markedly different than those of linear diene polymers. Specifically, a lack of entanglements is observed even at relatively high molar masses. For hydroxyl-terminated oligomers, Tg as a function of molar mass follows a trend opposite non-functional materials.

The synthesis and characterization of *trans* -β-farnesene-based polymers will be presented, including anionically prepared low molecular weight diols and monols.

OC16

SYNTHESIS AND SOLUTION PROPERTIES OF PHPMA BASED COPOLYMERS CONTAINING STABLE NITROXYL RADICALS

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This work focused on the synthesis and the aqueous solution properties of a novel amphiphilic PCL-b-PHPMA diblock copolymers possessing 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) stable radical covalently conjugated in the hydrophobic poly(ε-caprolactone) (PCL) block. A new synthetic approach (a four-step pathway) that combines ring-opening polymerization (ROP), carbodiimide chemistry (DCC method), a RAFT polymerization technique and followed by chemical oxidation was employed to successfully produce for the first time a series of corresponding TEMPO-containing PCL-b-PHPMA diblock copolymers. EPR spectroscopy was applied to verify successful oxidation of the synthesized series of PCL-b-PHPMA diblock copolymers and to investigate the dynamics of polymer chains before and after micellization process. The diblock copolymers self-assembled in PBS into spherical nanoparticles[1]. It was proven that PCL-b-PHPMA designed nanoparticles have excellent sensitivity and could be used as detectable probes in EPR imaging at extreme dilution conditions. PCL-b-PHPMA nanoparticles interact in blood plasma with different blood plasma proteins such as HSA, ImG, and and various apolipoproteins.

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References

1) Svetlana Petrova, Damir Klepac, Rafal Konefał, Sami Kereïche, Lubomir Kováčik, Sergey K. Filippov, Synthesis and Solution Properties of PCL-b-pHPMA Diblock Copolymers Containing Stable Free Nitroxyl Radicals, Macromolecules, 2016, 49, 5407-5417.

OC17

POLYAMPHOLYTE MICROGELS: FROM MOLECULAR DESIGN TO IONIC TRAPS AND SWITCHES

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This paper is focused on tailored synthesis, characterization and functionalization of responsive polyampholyte microgels able to switch their surface charge at different pH. In particular, different synthesis methods (precipitation polymerization, polymerization in W/O emulsion) were developed that allow application of different molecular reactive building blocks (monomers, macromonomers, crosslinkers) and control the amount and distribution of ionisable groups and charges in microgels. Using controlled synthesis methods microgels with controlled size, narrow size distribution and statistical, [1] core-shell [2,3] and Janus-like distribution of ionisable groups were synthesized. The behavior of polyampholyte microgels in aqueous solutions was investigated to understand their properties like swelling/deswelling, charge modulation and colloidal stability. The experimental data combined with theoretical calculations and simulations indicate that amount, distribution and balance between ionisable groups in microgels govern their properties in aqueous solutions. Ampholyte microgels were used as cargo for the uptake/release of polyelectrolytes and proteins, colloidal templates for the biomineralisation and controlled growth of the CaCO3 nanocrystals as well as building blocks for design of functional coatings.

References

1) R. Schroeder, A. Rudov, L. A. Lyon, W. Richtering, A. Pich, I. I. Potemkin, Macromolecules 2015, 48, 5914-5927.
2) S. Schachschal, A. Balaceanu, C. Melian, D. Demco, T. Eckert, W. Richtering, A. Pich, Macromolecules 2010, 43, 4331- 4339.
3) W. Richtering, A. Pich, Soft Matter 2012, 8(45), 11423-11430.

OC18

ALTERNATIVES TO CONVENTIONAL POLYMERIZATION INITIATORS

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Radical initiators are belonging to a class of chemical species finding a broad range of applications in organic chemistry and material science. Among various possibilities the generation of these species is mainly obtained from the thermolysis or photolysis of peroxy compounds including alkyperoxides, dialkyperesters, hyroperoxides, alkyl peracid, diacylperoxides, percarbonates or azo derivatives. In material science these compounds are particularly useful as polymerization initiators, crosslinking agents or chemical modification of the polymer backbone. Despite peroxy and azo derivatives are routinely applied in radical polymerization, it has to be mentioned that some drawbacks are associated to their use. Indeed due to their inherent reactivity, their preparation, storage, handling and shipping is often challenging and raise severe safety issues. In this lecture, we will present our latest results on the use of organic electron donors[1] and alkoxyamines as efficient alternative to peroxy and azo compounds used in material science.

References

1) Broggi, J.; Rollet, M.; Clément, J.-L.; Canard, G.; Terme, T.; Gigmes, D.; Vanelle, P. Angew. Chem. Int. Ed. 2016, 55 (20) 5994-5999.

OC19

SHAPE RECORDING MATERIALS

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Clothing and footwear industries have a general problem with mail order and internet business: more than 50% of all orders are being returned by the customers because of problems with the size or the general fit. Thus, a solution to this problem could provide a tremendous potential for cost reduction.

This problem can be solved with textiles that have the ability to store a three dimensional shape. Polymaterials has developed a suitable material under a contract from atways AG. For demonstration of the function, shape recording „socks“ were produced to record the shape of the foot of a potential customer („shoe profile“). The material and the demonstrators had to fulfill several properties, such as:

- simple use: „unpack – pull on – remove – mail back“
- high elasticity before and after performing the shape recording function for simple handling
- „one size fits all“: shoe size 36-50 (German system)
- textile haptics
- less than 3 min. for shape recording
- > 99.5% accuracy
- no requirement for hazard symbols
- material costs < 30ct per „shoe profile“

These requirements can be met by a material based on a polyurethane elastomer. A series of demonstrators was produced.

OC20

RING OPENING OF SUSTAINABLE DIOXOLANONE MONOMERS AS A NEW ROUTE TO FUNCTIONAL, DEGRADABLE POLYESTERS

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Biodegradable aliphatic polyesters built from sustainable feedstocks are one of the most promising solutions to address the pollution and oil-dependence challenges of modern plastics but remain limited in monomer scope and the resultant polymer properties. We report a family of monomers that are built from renewable resources and use the elimination of small molecules to access aliphatic polyesters, circumventing challenging monomer syntheses to make these functionalized polymers. The driving force for ring opening polymerization is the elimination of formaldehyde or acetone from easy-to-synthesize 1,3-dioxolan-4-ones to produce an array of structurally divergent polyesters. The polymers are prepared with high retention of stereochemistry, meaning isotactic polymers are easily prepared from natural enantiopure feedstocks. Reaction kinetics, structure/property relationships, copolymers of traditional cyclic esters, and direct recycling of waste paraformaldehyde showcase the scope of this new reaction in polymer chemistry.

OC21

STRAIGHTFORWARD SYNTHESIS OF SUBSTITUTED THIOLACTONES AND THEIR APPLICATION TO POLYMER SYNTHESIS AND MODIFICATION

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There is an increasing need for simple synthetic procedures that allow catalyst-free polymer synthesis and modification under stoichiometric conditions at mild temperatures, without the need for tedious and costly purification steps. In this regard, Du Prez et *al.* have recently shed a new light on the use of thiolactones, especially 5-membered ring γ-thiolactones, in the field of polymer chemistry (1). We here report a new modular platform for thiolactone synthesis that enables various substituents (alkyl, phenyl, perfluoroalkyl, phosphonate) to be easily bonded to the thiolactone ring. A series of original mono- and disubstituted thiolactones is presented. An amine-thiol-ene conjugation strategy involving these new thiolactone building blocks resulted in successful end-functionalization of amino-terminated polymers and step-growth polymerizations. Due to the many possibilities of functionalization offered by this new method for making thiolactones, a novel generation of polymers with tailor-made chemical and physical properties can be envisioned.

References

1) Espeel, P.; Du Prez, F. E. European Polymer Journal 2015, 62, 247-272.

OC22

ENGINEERING MICROBIAL RESPONSES WITH SYNTHETIC POLYMERS

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Here, our efforts towards the understanding of how synthetic polymeric materials can interfere with bacteria microbiology, adhesion and virulence will be described. We will report our efforts using polymers that can either sequester signalling molecules, to interfere with microbial communication; or that can sequester the bacteria into clusters, thus stopping adhesion to host. Using a combination of computational methods, in vitro assays and animal models, we demonstrate that the response of the bacteria to these interactions with polymers is complex and it can often result in the upregulation of (unwanted) phenotypes. However, this response is bacteria specific, and can also result in the downregulation of important virulence factors, including the production of toxins. Finally, we demonstrate that these polymers can minimise the pathogenic burden and reduce the ability of bacterial pathogens to colonise in-vitro and in-vivo models.

References

1) Xue, X., Pasparakis, G., Halliday, N., Winzer, K., Howdle, S. M., Cramphorn, C. J., Cameron, N. R., Gardner, P. M., Davis, B. G., Fernandez-Trillo, F., and Alexander, C. (2011) Synthetic Polymers for Simultaneous Bacterial Sequestration and Quorum Sense Interference. Angew. Chem., Int. Ed. 50, 9852–9856.
2) Lui, L. T., Xue, X., Sui, C., Brown, A., Pritchard, D. I., Halliday, N., Winzer, K., Howdle, S. M., Fernandez-Trillo, F., Krasnogor, N., and Alexander, C. (2013) Bacteria clustering by polymers induces the expression of quorum-sensing-controlled phenotypes. Nat. Chem. 5, 1058–1065.
3) Perez-Soto, N., Moule, L., Crisan, D. N., Insua, I., Taylor-Smith, L. M., Voelz, K., Fernandez-Trillo, F., and Krachler, A. M. (2016) Capture of Vibrio cholerae by charged polymers inhibits pathogeniciy by inducing a sessile lifestyle. bioRxiv 066563.

OC23

SYNTHESIS OF pH-RESPONSIVE GLYCOPOLYPEPTIDES AND THEIR INTERACTIONS WITH LECTINS

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Many biological processes depend on specific interactions between glycoproteins and lectins, including cell-cell communication, binding of toxins and pathogenic infection. Synthetic glycopolypeptides are a useful tool to investigate those processes, since they can mimic properties of glycoproteins and are relatively easy of access. Glycopolypeptides can be prepared by polymerization of glycosylated monomers or by post-polymerization glycosylation in organic solvents.[1,2] These methods are often restricted to monosaccharides but in most biological interactions more complex sugars are involved. We developed a post-polymerization glycosylation method for poly(α,L-glutamic acid) with 1-deoxy-1-amino sugars using amide coupling in aqueous media.[3] The sugar density on the PGA scaffold is well adjustable and can reach up 80% depending on the chemical nature of the sugar. Using this approach different sugars like mono-, disaccharides and sugars with linkers can be coupled and well-defined glycopolypeptides are obtained.[3,4] They show pH- and sugar dependent helix-coil transitions. Precipitation of the lectin ConA as well as isothermal calorimetry measurements demonstrate biological activity.

This work was supported by the IUPAC Transnational Call in Polymer Chemistry and the German Research Foundation (DFG).

References

1) Kramer J.R. et al., J. Am. Chem. Soc., 132:15068-15071, 2010
2) Sun J. et al., Macromolecules, 43:4445-4448, 2010
3) Mildner R. et al., J. Polym. Sci. Pol. Chem., 51:3925-3931, 2013
4) Mildner, R. et al. Biomacromolecules 15, 4528-4533, 2014

OC24

EMPOWERING INERT POLYETHERS WITH FUNCTIONAL EPOXIDES: SYNTHESIS AND BIOLOGICAL APPLICATIONS

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Poly(ethylene glycol) (PEG) is by far the most well-known synthetic biocompatible polymer for its widespread use in the food, cosmetics, and biomedical applications. However, its limited functionality combined with its challenging synthetic nature often poses challenges for advanced material design and synthesis. Recently, new functional monomers based polyglycerols and their derivatives are emerging as alternatives for next-generation biocompatible polymers with controlled functionalities and architectures. The present talk will cover the design and the synthesis of well-defined stimuli-responsive polyethers such as pH-, and redox-stimuli for biocompatible and biodegradable smart drug delivery systems. Furthermore, our recent effort in the development of novel functional epoxide monomers with multifunctionality will be highlighted.

OC25

POLYMER SYNTHESIS BY TANDEM REACTION OF α-(HALOMETHYL)ACRYLATE VIA ADDITION-FRAGMENTATION AND CLICK REACTIONS

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α-(Halomethyl)acrylate undergoes nucleophilic addition-elimination (S_N2') reaction to afford an α-substituted acrylate that can accept the Michael addition of nucleophiles. These nucleophilic reactions were applied to step-growth polymerization of mono- and bifunctional monomers, *i.e.* the tandem reaction of α-(halomethyl)acrylate and various dithiols.[1] Because the second step was slow prevented by the hydrobromic acid generated in the first step, a base that does not afford an acidic salt, *e.g.*, K_2CO_3, and a phosphine catalyst were necessary to achieve a high degree of polymerization. Similar polymerization of α-(halomethyl)acrylate was also achieved with primary diamines via S_N2' and aza-Michael addition reactions.

Importantly, the S_N2' reaction proceeds much faster than the subsequent Michael addition, and selective S_N2' reaction was achieved in the optimized condition. Bis[α-(halomethyl)acrylate], therefore, afforded the liner polyesters through the polymerization with dithiols, bisphenols, and primary monoamines. The resulting polymers bearing acryloyl groups can be applied to further nucleophilic or radical reactions.

These polymerizations proceed at ambient temperature in air and have the advantages, tolerance to functional groups and good atom economy.

References

1) Y. Kohsaka, K. Hagiwara, K. Ito Polym. Chem., in press (DOI: 10.1039/C6PY02145J).

OC26

FABRICATION OF POLYMER-PROTEIN HYBRIDS BASED ON THIOL-DISULFIDE EXCHANGE REACTIONS

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In recent years, fabrications of polymer-protein hybrids with multiresponsiveness have been attracting increasing attention.[1] In our group, we designed triple-responsive polymer-protein networks based on molecular recognition.[2] Reduced bovine serum albumin (BSA) was modified with multiple β-cyclodextrin (βCD) by thiol-disulfide exchange reaction. The βCD-modified BSA was added into the aqueous solution of acrylamide copolymer with pendant adamantyl groups, resulting in the formation of polymer-protein network structures. The assembled polymer networks show triple-responsive behaviors upon treatment with trypsin, reduced glutathione or native βCD.

We also synthesized virus-mimicking protein nanogels with temperature-induced reversible structures and redox responsiveness by crosslinking a thermally responsive polymer poly(di(ethyleneglycol) methyl ether methacrylate-co-2-(2-pyridyldisulfide) ethylmethacrylate) with reduced BSA molecules through thiol-disulfide exchange reaction.[3] The lower critical solution temperature (LCST) and sizes of the nanogels can be controlled by controlling the reaction conditions. The nanogels are able to change their structures responding to the temperature change, and will be used as a new platform for protein delivery.

References

1) Wang, H.; Shi, Y.; Wang, L.; Yang, Z. Chem. Soc. Rev. 2013, 42, 891–901.
2) Chen, D.; Hou, W.; Wu, D.; Wu, Y.; Cheng, G.; Zhao, H. ACS Macro Lett. 2016, 5, 1222–1226.
3) Zhang, Y.; Zhang, J.; Xing, C.; Zhang, M.; Wang, L.; Zhao, H. ACS Biomater. Sci. Eng. 2016, 2, 2266–2275.

OC27

TRIAZOLINEDIONE-BASED CLICK AND TRANSCLICK REACTIONS: A MACROMOLECULAR RELAY

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The reaction of triazolinediones (TADs) and indoles is of particular interest for polymer chemistry applications,[1] as it is a very fast and irreversible additive-free process at room temperature, but can be turned into a dynamic covalent bond forming process at elevated temperatures, giving a reliable bond exchange or 'transclick' reaction.[2] In this paper, we report an in-depth study aimed at controlling the TAD-indole reversible click reactions through rational design of modified indole reaction partners. This has resulted in the identification of a novel class of easily accessible indole derivatives that give dynamic TAD-adduct formation at significantly lower temperatures. We further demonstrate that these new substrates can be used to design a directed cascade of click reactions of a functionalized TAD moiety from an initial indole reaction partner to a second indole, and finally to an irreversible reaction partner. This controlled sequence of click and transclick reactions has been demonstrated both on small molecule and macromolecular level, and the factors that control the reversibility profiles have been rationalized and guided by mechanistic considerations supported by theoretical calculations.

References

1) K. De Bruycker, S. Billiet, H. A. Houck, et.al., Chem. Rev. 2016, 116, 3919-3974.
2) S. Billiet, K. De Bruycker, F. Driessen, et.al., Nat. Chem. 2014, 6, 815-821.
3) H. A. Houck, K. De Bruycker, S. Billiet, et.al., 2017, in press.

OC28

LASSOS AND LOOPS: TOPOLOGICAL CONTROL OVER THE INTERFACIAL PHYSICO-CHEMICAL PROPERTIES OF POLYMER ASSEMBLIES

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The application of distinctive polymer topologies, beyond linearity, to yield cyclic and loops-forming surface-grafted assemblies, enables a broad modulation of highly relevant, interfacial physico-chemical properties. This is especially valid on flat surfaces, where the ultra-dense and highly compact character of cyclic polymer "brushes" provide an enhanced steric stabilization of the interface and a superlubricious behavior.[1] Alternatively, when cyclic brushes form shells on inorganic nanoparticles (NPs), their extraordinary structural properties make them impenetrable and long-lasting shields, which extend the stability of NP dispersions and hinder any interaction with serum proteins.

Polymer topological effects, typically observed in bulk or in solution are amplified by adding an additional boundary such as a grafting surface. Their precise tuning translates into materials with unprecedented properties and extremely high applicability.

References

[1]) G. Morgese, L. Trachsel, M. Romio, M. Divandari, S.N. Ramakrishna, E.M. Benetti, Angewandte Chemie, Int. Ed. 2016, 55, 15583

OC29

PHOSPHORUS CHEMISTRY AS A TOOL FOR THE PRODUCTION OF METAL-CONTAINING POLYMERS AND POLYELECTROLYTES

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Metal-containing polymers (MCPs) are processable materials that offer many unique properties originating from the transition metals that they incorporate. Depending on the type of metal and the polymer structure, MCPs have been successfully used, for example, as magnetic, catalytic, emissive, antimicrobial, redox-active, and preceramic materials.[1] The continued need for new functional materials has motivated us to take advantage of the unique chemistry of phosphorus (*i.e.*, hydrophosphination) to synthesize polymers containing different combinations of iron, ruthenium, and tungsten. Starting from phosphine gas, we prepared phosphines containing one, two, or three metallocene units which were subsequently converted into polymerizable phosphines and phosphonium salts.[2] Free-radical polymerization of the monomers produced polyelectrolytes with unusual redox properties,[3] heterobimetallic polyelectrolytes with utility as precursors to nanostructured, alloyed metal phosphides,[4] and the first example of a polymer containing three different transition metals per repeating unit.[5] This presentation will detail our recent progress surrounding the design, synthesis, characterization, and applications of phosphorus-based metal-containing polymers and polyelectrolytes.

References

1) Whittell, G. R.; Hager, M. D.; Schubert U. S.; Manners, I. Nat. Mater. 2011, 10, 176-188.
2) Rabiee Kenaree, A.; Cuthbert, T.J.; Barbon, S.M.; Boyle, P.D.; Gillies, E.R.; Ragogna, P.J.; Gilroy, J.B. Organometallics 2015, 34, 4272-4280.
3) Rabiee Kenaree, A.; Berven, B.M.; Ragogna, P.J.; Gilroy, J.B. Chem. Commun. 2014, 50, 10714-10717
4) Rabiee Kenaree, A.; Gilroy, J.B. Dalton Trans. 2016, 45, 18229-18240.
5) Rabiee Kenaree, A.; Gilroy, J.B. Submitted.

OC30

(AB)n-MULTIBLOCK COPOLYMERS VIA SIMPLE ONE-STEP MELT CONDENSATION CHEMISTRY

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We have prepared $(AB)_n$-multiblock copoly(esterimide)s via a simple one-pot melt condensation method.[1] The blocky nature is the result of phase separation taking place in the early stages of the melt polymerization process. The liquid crystal fraction phase separates from the isotropic fraction and this phase separation effectively shuts down transesterification reactions, preventing randomization of the polymer backbone. The $(AB)_n$ -multiblock copoly(esterimide)s exhibit two distinct glass transition temperatures at 120 °C (A-block) and at 220 °C (B-block). When introducing phenylethynyl end-groups, these reactive functionalities end-up exclusively at the termini of the high Tg B-blocks, effectively forming a phenylethynyl-terminated $B(AB)_n$-reactive oligomer. Upon thermal treatment, crosslinking via the phenylethynyl end-groups results in a thermoset where the T_g of the B-block increases by as much as 106 °C. The T_g of the A-block remains unchanged. Atomic force microscopy images confirm the presence of two distinct domains. The ‘hard’ imide rich B-blocks form domains of ~100–200 nm that are embedded in the imide poor or ‘soft’ A-blocks. Crosslinked $(AB)_n$-multiblock copolymer films exhibit excellent high temperature shape-memory characteristics.

References

1) Guan, Q.; Norder, B.; Chu, L.; Besseling, N.A.M.; Picken, S.J.; Dingemans, T.J. Macromolecules 2016, 49(22), 8549–8562.

OC31

MULTI-RESPONSIVE COORDINATION POLYMERS UTILISING METAL-STABILISED, DYNAMIC COVALENT IMINE BONDS

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We report the use of dynamic-covalent imine bonds for the construction of hydrolytically stable, multi-responsive coordination polymers. To this aim we combine imine bonds and tailored M–L bonds to obtain *smart*, dynamic-covalent polymer materials[1] that are responsive via their imine and M–L bonds, and through both types of bonds in concert.[2]

As key binding motif we rely on a tridentate pincer ligand bearing a 2,6-diiminopyridine moiety, known to coordinate to octahedral metal ions in 2:1 fashion. As such, this pincer can be considered as the dynamic-covalent structural analogue of the classic terpyridine ligand.

We show by various techniques (including NMR, DOSY, UV/vis and viscometry) that selective end-functionalisation of macromonomers with this motif yields stable polymers that are sensitive to a range of stimuli, effectively yielding a multi-responsive main-chain coordination polymer, giving access to five different macromolecular states with distinct material properties.

By appending the pincer moiety with a clickable azide group, straightforward extension of our approach is possible by introduction of the pincer into other polymers, thus offering a promising approach to generate new *smart* polymers with tailored functionalities.

References

1) F. García, M. M. J. Smulders, J. Polym. Sci., Part A: Polym. Chem. 2016, 54, 3551-3577
2) F. García, J. Pelss, H. Zuilhof, M. M. J. Smulders, Chem. Commun. 2016, 52, 9059-9062

OC32

ALBUMIN-POLYMER-DRUG CONJUGATES - A FINAL END TO THE MOLECULAR WEIGHT RACE

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The main advantage of polymers as carriers of therapeutic agents is the increased circulation time and stability of the conjugated drug. The downside of increased molecular weight is the accumulation in organs and associated toxicity for polymers exceeding then renal excretion limit. This decades-long struggle can now be put to a final stop. By synthesizing short polymers (< 10 kDa) and attaching these to albumin (a highly abundant uniquely recycled protein) we obtained the desired long circulation without the usual toxicity, still retaining other celebrated properties of macromolecular prodrugs such as high drug loading [1].

Keys to our success were a) a novel RAFT agent which facilitates simple albumin conjugation, and b) self-immolative chemistry coupled to a disulfide trigger for intracellular drug release [1],[2]. Therapeutic effect of these albumin-polymer-drug conjugates was validated *in vitro* for several drugs (antiviral and anticancer), whereas extended circulation has been validated *in vivo* in mice. We believe that this methodology offers game changing opportunities for chemotherapy.

References

1) Smith, A. A., Zuwala, K., Pilgram, O., Johansen, K. S., Tolstrup, M., Dagnæs-Hansen, F., & Zelikin, A. N. (2016). Albumin–Polymer–Drug Conjugates: Long Circulating, High Payload Drug Delivery Vehicles. Acs Macro Letters, 5(10), 1089-1094. doi:10.1021/acsmacrolett.6b00544
2) Riber, C. F., Smith, A. A. A. and Zelikin, A. N. (2015), Self-Immolative Linkers Literally Bridge Disulfide Chemistry and the Realm of Thiol-Free Drugs. Adv. Healthcare Mater., 4: 1887–1890. doi:10.1002/adhm.201500344

OC33

DANCING IN THE DARK WITH SULFUR AND SELENIUM: NEXT GENERATION IR OPTICAL POLYMERS FOR IR THERMAL IMAGING

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We will discuss our recent develops on the synthesis of a new class of chalcogenide containing macromolecules containing a very high content of sulfur and selenium units in the copolymer backbone to afford a new class of optical polymers for use in mid-IR thermal imaging. The inclusion of these chalcogenide units into polymeric materials imparts both very high refractice indices (n » 2.0) and high optical transparency in the near and mid-IR spectrum. Infrared (IR) optical technology are widely used in optical communication as well as in, military and defense applications that require high resolution imaging under conditions of pure darkness. Currently, synthetic polymers CANNOT be used as transmitting materials for mid-IR imaging applications, as lenses, or other device components fabricated from these materials strongly absorb IR irradiation in the spectral window (3-5 mm) required for thermal imaging. We will discuss the novel synthetic polymerization approaches employed to prepare these new copolymers, along with optical characterization of these materials.

OC34

TWOFOLD HELICAL POLYMERIZATION: THERMAL SOLID-STATE POLYMERIZATION OF 7-CYANO-7-ALKOXYCARBONYL-p-BENZOQUINONE METHIDES

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A helix is well known as a motif that exhibits chirality with right- and left-handedness. The handedness of the 2_1 helical molecular assemblies can be briefly discriminated and defined by the supramolecular-tilt-chirality method. Such a finding directed us toward twofold (2_1) helical polymerization, which may produce the corresponding a right- or a left-handed polymer, respectively.

7-Cyano-7-alkoxycarbonyl-1,4-benzoquinone methides bearing alkoxy group such as 2’-fluoroethoxy (**1a**), 2’-chloroethoxy (**1b**), 2’-bromoethoxy (**1c**) and pentafluorobenzyl (**1d**) were synthesized. The halogen atoms of the alkoxy group in the quinone methide skeleton greatly affected their crystal structures, which belong to space group $P2_1/c$ for **1a**, $P2_1/a$ for **1b**, P-1 for **1c** and $P2_1/n$ for **1d**, respectively. The thermal solid-state polymerizations in vacuo at 60 °C or 100 °C gave amorphous polymers with regular head-to-tail configuration, and proceeded with retention of the crystal shapes in appearance. Relations between the molecular assembly modes and the polymerization modes indicated that twofold assemblies (2_1) of **1b** and **1d** are able to undergo 2_1 helical polymerization with handedness.

OC35

POLYMERIC ARSENICALS AS FUNCTIONAL POLYMER SCAFFOLDS

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Post-polymerization modification is a well-established method of tuning polymer properties and installing desirable functionality into polymer compositions. Traditionally, in chain-growth polymerization, monomers with reactive pendent groups such as epoxides, thiolactones, azlactones, activated esters, aldehydes/ketones, protected alkynes, *etc*., capable of undergoing 'click'-type reactions have been used.

Recently, polymers synthesised with an organic arsenical at the α-chain end have been shown to undergo efficient, highly selective, modification of disulfide bond containing proteins and peptides. Arsenic can exist in two biologically relevant oxidation states, trivalent arsenous acid (As(III)) and pentavalent arsenic acid (As(V)) which are chemically distinct. For example, As(V) undergoes electron transfer reactions with thiols whereas As(III) exhibits a strong preference to form covalent bonds with thiols which is enhanced for chelating dithiol groups and was exploited for the reported disulfide bond modification.

Herein, As(V)-functional (co)polymers have been prepared by reversible deactivation radical polymerization (RDRP) using a novel arsenic monomer. The pendent As(V) groups are readily reduced to As(III) which subsequently undergoes dynamic modification with a range of thiol reagents.

OC36

POLY(METHYL VINYL ETHER-ALT-MALEIC ACID)-BASED HYDROGELS AND THEIR BIOMEDICAL APPLICATIONS

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As a biocompatible polymer, poly(methyl vinyl ether-altmaleic acid) (P(MVE-alt-MA)) and its derivatives have many important applications in biotechnology, pharmacology and health care. Through using P(MVE-alt-MA) as a starting material, a series of hydrogels, P(MVE-alt-MA)-crosslinked egg white (EW) and chondroitin sulfate, and PEG-crosslinked P(MVE-alt-MA) were prepared. On the other hand, two supramolecular hydrogels were constructed from azobenzene (or adamantane) grafted P(MVE-alt-MA) (P(MVE-alt-MA)-g-Azo (or Ad)) (guest polymer) and β -cyclodextrin grafted P(MVE-alt-MA) (P(MVE-alt-MA)-g-β-CD) (host polymer) respectively. Using these P(MVE-alt-MA)-based hydrogels as 3D cell scaffold, we tried to culture ovarian cancer cells, which indicates these hydrogels can provide an ideal platform to study the behavior of ovarian cancer cells.

References

1) K. Hu, N. Z. Zhou, Y. Li, S.Y. Ma, Z. B. Guo, M. Cao, Q. Y. Zhang, J. F. Sun, T. Z. Zhang, N. Gu, ACS Appl. Mater. Interfaces 8(2016)15113–15119.
2) Z. B. Guo, K. Hu, J. F. Sun, T.Z. Zhang, Q.Y. Zhang, L.N. Song, X. Z. Zhang, N. Gu, ACS Appl. Mater. Interfaces 6(2014) 10963–10968.
3) N. Z. Zhou, X. E. Ma, T. Z. Zhang, X. X. Chen, Z. C. Guo, D. D. Ma, N. Gu, J. Nanosci. Nanotechnol. 16(2016)12134–12144.
4) Z. C. Guo, T. Z. Zhang, K. Fang, J. Dou, N. Z. Zhou, X. E. Ma, N. Gu, RSC Adv. 6(2016) 43892–43900.
5) X. E. Ma, N. Z. Zhou, T. Z. Zhang, Z. C. Guo, W. J. Hu, C. H. Zhu, D.D. Ma, N. Gu, RSC Adv. 6(2016) 13129–13136.

OC37

THIN FILMS OF AMPHIPHILIC BLOCK COPOLYMERS DESIGNED FOR OPTICAL SENSOR APPLICATION

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Synthesis of multi-block copolymers of varied composition and structure and their potential application as thin film optical sensors for vapor analytes will be discussed. Amphiphilic as well as double hydrophilic block copolymers comprising polyether (PEO, PPO) and polyamide (DMAA, DEAA) blocks were obtained via redox polymerization in aqueous media. The chemical structure and composition were investigated by NMR, FTIR and SEC. Block copolymer properties in solution and especially structuring/aggregation in aqueous media were followed by DLS and ζ-potential measurements.

In order to evaluate the application of the developed copolymers as self-consistent optical indicators, thin films were spin coated on silicon substrates by using copolymer solutions of appropriate composition and concentration. Reflectance spectra of the deposited films were recorded and refractive indexes, extinction coefficients and thickness were determined using non-linear curve fitting. Sensing properties were tested by *in-situ* monitoring of the changes in optical properties of the films when exposed to different analytes (e.g. humidity, methanol and acetone vapor). The influence of the copolymer composition, structure and postdeposition annealing on the optical and sensing properties of the films was demonstrated.

OC38

ELECTROGENERATED THIN FILMS OF MICROPOROUS POLYMER NETWORKS WITH REMARKABLY INCREASED ELECTROCHEMICAL RESPONSE TO NITROAROMATIC ANALYTES

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Microporous Polymer Networks (MPNs) represent a rapidly growing area of materials science. Thin films of microporous polymer networks (MPN) have been generated by electrochemical polymerization of a series of multifunctional carbazole- or thiophene-based monomers. The microporous films show high S_{BET} surface areas up to 2200 m^2/g as directly measured by krypton sorption experiments. A correlation between the number of polymerizable carbazole or thiophene units of the monomer and the resulting surface area is observed. For thiophene-based monomers electrochemical polymerization in boron trifluoride diethyletherate (BFEE)/dichloromethane (DCM) mixtures allows for the generation of MPN films with optimized porosity.

Electrochemical sensing experiments with 1,3,5-trinitrobenzene as prototypical nitroaromatic analyte demonstrate an up to 180 times increased current response of MPN-modified glassy carbon electrodes in relation to the non-modified electrode (see Figure). We expect a high application potential of such MPN-modified electrodes for boosting the sensitivity of electrochemical sensor devices. [1-2]

References

1) A. Palma-Cando, U. Scherf, "Electrogenerated thin films of microporous polymer networks with remarkably increased electrochemical response to nitroaromatic analytes", ACS Appl. Mater. & Interfaces 2015, 7, 11127-11133.
2) A. Palma-Cando, G. Brunklaus, U. Scherf, "Thiophene-Based Microporous Polymer Networks via Chemical or Electrochemical Oxidative Coupling", Macromolecules 2015, 48, 6816–6824.

OC39

TEACHING AN OLD DOG NEW TRICKS - THE WONDERFUL WORLD OF AZOBENZENES

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The current drive towards sustainable processes in macromolecular science requires alternative polymers with on demand degradability.[1] Importantly, degradation is not dependent on the origin of the building blocks but on the chemical linkages present in the polymer.[2] The variety of degradation units in such materials remains limited. Increasing the diversity of degradable polymers might allow for better matching soft matter materials to specific applications. In many cases, azo polymers are synonymous with photoresponsive polymers.[3] While minimal efforts have been devoted to designing degradable polymers incorporating azo moieties, indeed, the azo unit can be cleaved by chemical and/or biochemical stimuli, accelerate the rate of reduction and in turn the degradation of the polymer.[4] Herein we introduce a strategy for the synthesis of ADMET polymers which possess self-immolative degradable enzyme-triggered azobenzene units, thus establishing a new class of chain-shattering polymers.[5] Specifically, the introduced system is a prime example of a stimuli responsive biodegradable polymer and additional studies have shown the applicability of the new polymeric material for single chain nanoparticle synthesis for applications in imaging and delivery.[6]

References

1) K. Yao and C. Tang, Macromolecules, 2013, 46, 1689
2) K. E. Uhrich, S. M. Cannizaro, R. S. Langer and K. M. Shakesheff, Chem. Rev., 1999, 99, 3181
3) L. Ding, M. Xu, J. Wang, Y. Liao and J. Qiu, Polymer, 2014, 55, 1681
4) K. Golka, S. Kopps and Z. W. Myslak, Toxicol. Lett., 2004, 151, 203
5) H. Mutlu and C. Barner-Kowollik, Polym. Chem., 2016, 7, 2272
6) J. T. Offenloch, J. Willenbacher, P. Tzvetkova, C. Heiler, H. Mutlu and C. Barner-Kowollik, Chem. Commun., 2017, 53, 775

OC40

INCREASING THE SOLUBILITY RANGE OF POLYESTERS BY TUNING THEIR MICROSTRUCTURE WITH COMONOMERS

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ω-Pentadecalactone (PDL) is a biobased 16-membered macrolactone that can be derived from renewable resources [1]. Its regular structure makes it highly crystalline and thus interesting as a biobased replacement for linear low density polyethylene [2]. However, its solubility is very limited (chloroform) which hinders the use of PDL polymers in other applications requiring a large solubility range. Copolymerization with a branched lactone was investigated as a way to reduce the crystallinity because it is expected to disrupt the copolyesters' microstructure [3].

It was attempted to break the crystallinity of PDL-based copolyesters by copolymerization with the branched and biobased lactone δ-undecalactone (UDL), whose homopolymer is amorphous. In order to assess the influence of the branched comonomer on the microstructure (random or block-like) of the copolymer, the monomer distribution was analyzed with ^{13}C NMR. The crystallinity and the solubility of the copolymers were investigated via DSC resp. Hansen solubility parameter studies.

References

1) Romero-Guido, C., et al., Appl Microbiol Biotechnol 2011, 89 (3), 535-547.
2) van der Meulen, I., et al., Macromolecules 2011, 44 (11), 4301-4305.
3) (a) Wilson, J. A., et al., ACS Macro Letters 2016, 5 (3), 346-350; (b) Wilson, J. A., et al., Biomacromolecules 2015, 16 (10), 3191-3200; (c) Wilson, J. A., et al., Macromolecules 2015, 48 (4), 950-958.
4) "The research for this work has received funding from the European Union (EU) project ROBOX (grant agreement n° 635734) under EU's Horizon 2020 Programme Research and Innovation actions H2020-LEIT BIO-2014-1. Any statement made herein reflects only the author's views. The European Union is not liable for any use that may be made of the information contained herein."

OC41

DESIGN OF MULTIBLOCK POLYMERS BY CHAIN SHUTTLING POLYMERIZATION

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Multiblock polymers possess spectacular self-assembling abilities, leading to a wide range of morphologies and applications in many different fields such as biomedicine and microelectronics, but also for making advanced plastics such as thermoplastic elastomers. They were usually synthetized by sequential multistep procedures. The development of chain shuttling polymerization has given rise to new multiblock microstructures.[1-2] This procedure allows indeed a one-step access to multiblock polymers with notably the possibility to finely control the composition of the blocks, by allowing the shuttle of a growing copolymeric chain between two catalysts showing different reactivity ratio *vs.* the comonomers. After a brief state of the art where the main achievements of the field will be discussed, we will present a new catalytic combination allowing chain shuttling polymerization, together with the microstructural characterization of the resulting, not yet described, multiblock microstructure.[3]

References

1) D. J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, Science, 2006, 312, 714–719.
2) A. Valente, G. Stoclet, F. Bonnet, A. Mortreux, M. Visseaux, P. Zinck, Angew. Chem. Int. Ed., 2014, 53, 4638–4641.
3) Y. Phuphuak, F. Bonnet, G. Stoclet, M. Bria, P. Zinck, submitted

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OC42

CONJUGATED SURFACE-GRAFTED POLYMER BRUSHES

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Surface grafted polymer brushes refer to an assembly of macromolecules attached with one end to a surface at sufficiently high density. The stretched conformation of such tethered chains and their conformational freedom lead to unique properties of the brushes. Conductive polymer brushes grafted from surfaces, as examples of such structures, are very desirable for e.g. organic photovoltaics and molecular electronics since they would form directional nanoscale pathway for charge transport. However, direct surface-initiated polymerization of conjugated polymer brushes is still challenging since there are hardly any controlled polymerization techniques easily applicable for that purpose.

Thus, we have introduced and developed self-templating surface-initiated polymerization (ST-SIP) leading to synthesis of ladder-like brushes with one chain in a pair being conjugated.[1] Controlled radical polymerization of a bifunctional monomer is applied first to obtain the macromonomer brushes. The prealigned side groups are subsequently polymerized forming conjugated chains. Such ladder-like brushes after doping were shown to exhibited high and stable in time conductivity in the direction perpendicular to the surface. The proposed route may be easily applied for obtaining other polymer architectures comprising conjugated polymers.

References

1) M. Szuwarzyński, J. Kowal, S. Zapotoczny, J. Mat. Chem. 2012, 22, 20179.
2) K. Wolski, A. Gruszkiewicz, S. Zapotoczny, Polym. Chem., 2015, 6, 7505.
3) K. Wolski, M. Szuwarzyński, S. Zapotoczny, Chem. Sci., 2015, 6, 1754
4) M. Szuwarzyński, K.Wolski, S. Zapotoczny, Polym. Chem., 2016, 7, 5664

OC43

SYNTHESIS OF POLYCARBOSILANES HAVING 5-MEMBERED CYCLIC CARBONATE GROUPS AND THEIR PROPERTIES AS SOLID POLYMER ELECTROLYTES

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Polycarbosilanes, which contains silicon-carbon bonds in the polymer backbone, are very soft polymers, and chemically as well as electrically stable materials. We expect that polycarbosilanes having 5-membered cyclic carbonate groups can be good candidates for solid polymer electrolytes. Polycarbosilane having one 5-membered cyclic carbonate group (polySBMC) or two 5-membered cyclic carbonate groups (polySBDC) in a repeating unit were synthesized by Pt-catalyzed ring-opening polymerization of the corresponding silacyclobutane monomers. Ionic conductivities were examined by addition of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium trifluoromethanesulfonate (LiOTf). The ionic conductivity of both polySBMC and polySBDC increased with the increase in the amount of LiTFSI added. The ionic conductivity of polySBMC decreased with the increase in the amount of LiTOf, and that of polySBDC decreased after an increase. PolySBMC and polySBDC showed ionic conductivity of 6.1×10^{-5} and 1.5×10^{-4} S/cm at 30 ^{o}C, respectively, after the addition of four mole equivalent LiTFSI per cyclic carbonate.

References

1) K. Matsumoto, M. Kakehashi, H. Ouchi, M. Yuasa, and T. Endo, Macromolecules, 49 (24), 9441-9448 (2016).

OC44

CHAIN AND STEP GROWTH POLYMERISATIONS OF CYCLIC IMINO ETHERS – FROM POLY(2-OXAZOLINE)S TO POLY(ESTER AMIDE)S –

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Five- and six-membered cyclic imino ethers (CIEs), also better known as oxazolines and oxazines are highly functional monomers which undergo a cationic ring-opening polymerisation (CROP) to yield poly(2-oxazoline)s and poly(2-oxazine)s, respectively.[1] In particular poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) have attracted significant attention owing to their excellent biocompatibility and antifouling and stealth properties,[2] which has made them a potent alternative for the ‘gold standard’ poly(ethylene glycol).

An alternative approach to prepare 2-oxazoline based polymers is the spontaneous zwitterionic copolymerisation (SZWIP). It is believed to occur via a zwitterionic intermediate which is formed upon the reaction of an electrophilic (M_E) and nucleophilic monomer (M_N) without a catalyst or initiator. CIEs act as M_N and when combined with a M_E containing acidic hydrogens they form poly(ester amide)s or more specific N-acylated poly(aminoester)s (NPAE).[3-5]

In this presentation the potential of CIEs for the preparation of functional biocompatible and biodegradable materials will be discussed. Particular focus will lie on the modularity of NPAE based macromonomers and the combination of CROP/SZWIP and reversible-deactivation radical polymerization techniques for the design of responsive comb polymers.

References

1) R. Hoogenboom, Angew. Chem. Int. Ed. 2009, 48, 7978-7994.
2) L. Tauhardt, K. Kempe, M. Gottschaldt, U. S. Schubert, Chem. Soc. Rev. 2013, 42, 7998-8011.
3) K. Kempe, P. A. J. M. de Jongh, A. Anastasaki, P. Wilson, D. M. Haddleton, Chem. Commun. 2015, 51, 16213-16216.
4) P. A. J. M. de Jongh, A. Mortiboy, G. S. Sulley, M. R. Bennett, A. Anastasaki, P. Wilson, D. M. Haddleton, K. Kempe, ACS Macro Lett. 2016, 5, 321-325.
5) P. A. J. M. de Jongh, M. R. Bennett, G. S. Sulley, P. Wilson, T. P. Davis, D. M. Haddleton, K. Kempe, Polym. Chem. 2016, 7, 6703-6707.

OC45

SELF-ASSEMBLY AND RESPONSIVENESS OF POLYPEPTIDE-BASED STAR AND TRIBLOCK COPOLYMERS

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

OC46

SEMI-CRYSTALLINE VITRIMERS VIA SOLID-STATE POLYMERIZATION

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Vitrimers are a relatively new class of materials which form a "bridge" between classical thermosets and thermoplastics.[1,2] These materials are covalently crosslinked, but rather than being permanent, the crosslinks are dynamic and may rearrange upon heating above the so-called vitrimer transition temperature. This leads to a greater dimensional stability and creep resistance at lower temperatures and (re)processability of the materials at higher temperatures. Here, we present our recent results[3] on the development of a new type of semi-crystalline vitrimer based on poly(butylene terephthalate) (PBT). Glycerol was incorporated as a crosslinker into the amorphous phase of PBT via solid-state polymerization using Zn^{2+} as a transesterification catalyst. It was found that the crystallization characteristics of PBT were not significantly affected by the incorporation of glycerol, leading to similar thermo-mechanical properties below the melting point. Above the melting point, however, a rubbery plateau was observed (consistent with a crosslinked material). The dynamic nature of the crosslinks was confirmed via stress relaxation experiments, revealing a full relaxation at temperatures above the melting point.

References

1) D. Montarnal; M. Capelot; F. Tournilhac; L. Leibler Science 2011, 334, 965.
2) W. Denissen; J.M. Winne; F.E. Du Prez Chem. Sci. 2016, 7, 30.
3) Y. Zhou; J.G.P. Goossens; R.P. Sijbesma; J.P.A. Heuts, Submitted for publication.

OC47

THE APPLICATION OF SELENOLACTONE IN POLYMER SYNTHESIS

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Diselenide containing polymers recently attracted much interest in a wide range of applications as a result of their rapid response to external triggers, such as light or a reductive environment. These multi-responsive diselenide containing polymers have been developed in the last decade for their use in artificial enzymes,[1] controlled drug delivery[2] and self-healing materials.[3] However, the synthetic routes towards diselenide-containing polymers are very limited.[4,5] Herein, a new, quite versatile and powerful protocol for the synthesis of diselenide containing polymers with various architectures was investigated. It consists of a one-pot, two-step process with the generation of a selenol by *in situ* nucleophilic ring-opening of selenolactone with a broad range of amine-containing structures, followed by the transformation of the obtained compounds to the corresponding diselenide through a spontaneous oxidation coupling reaction.

References

1) Huang, X.; Liu, X.; Luo, Q.; Liu, J.; Shen, J. Chem. Soc. Rev. 2011, 40, 1171
2) Tian, Y.; Zheng, J.; Tang, X.; Ren, Q.; Wang, Y.; Yang, W. Part. Part. Syst. Charact. 2015, 32, 547
3) Ji, S. B.; Cao, W.; Yu, Y.; Xu, H. P. Adv. Mater. 2015, 27, 7740
4) Gao, F.; Pan, X. Q.; Zhu, J.; Zhang, Z. B.; Zhang, W.; Zhu, X. L. Polym. Chem. 2015, 6, 1367
5) Cai, Z.; Lu, W.; Gao, F.; Pan, X.; Zhu, J.; Zhang, Z.; Zhu, X. Macromol. Rapid Commun. 2016, 37, 865.

OC48

POLY(2-OXAZOLINE)S: FROM FUNDAMENTAL RESEARCH TO BIOMEDICAL APPLICATIONS

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After celebrating the 50th anniversary since the first report on poly(2-oxazoline)s, we are now experiencing a turning point of this biocompatible polymer towards applications in biomedicine.

The progressive exhaustion of the currently widespread polymers in the field, most notably impacting polyethylene glycol, has triggered a great deal of research on the poly(2-oxazoline) platform. This polymer class allows the chemist to engineer the polymer properties and introduce multiple functionality, adapting the material to a wide variety of applications.

Our research group has targeted two main areas to develop the poly(2-oxazoline) platform that will be discussed in this lecture. First, investigation of the polymerization mechanism to obtain high molar mass, highly defined polymers, milestone that was believed to be unattainable. Second, different strategies to obtain side-chain functional poly(2-oxazoline)s, including functional monomer synthesis and post-polymerization functionalization chemistries.

Finally, specific examples that will be shown include the use of poly(2-oxazoline)s as pharmaceutical excipients, evaluation of degradation and toxicity, including pharmacokinetic behavior, as well as the use of various side-chain functionalized polymers for the preparation of hydrogel cell scaffolds and advanced drug-delivery vehicles and depots.

OC49

DEVELOPMENT OF HIGH PERFORMANCE POLYMERS FROM NATURALLY OCCURRING MYO-INOSITOL

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The focus of this presentation is our recent progress in the development of high performance polymers from *myo*-inositol, a naturally occurring cyclic hexaol. Functionalization of *myo*-inositol via chemo- and regioselective reactions such as ketalization and orthoesterification gives several derivatives bearing rigid polycyclic core structures and reactive groups such as hydroxyl, amino, methacrylate, and epoxy groups. These derivatives were found to be useful monomers for synthesizing polymers such as polyurethanes,[1,2] polyamides,[3] polymethacrylates,[4] and polyspiroketals,[5] whose main chains consisted of the conformationally constrained structures inherited from the monomers. Due to the rigidity of the main chains, the polymers exhibited excellent heat resistance, proving the feasibility of our concept of the utilization of *myo*-inositol as a starting material for high performance polymers.

References

1) Sudo, A.; Shibata, Y.; Miyamoto, A. J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 3956-3963.
2) Okamoto, S.; Onoue, S.; Kobayashi, M.; Sudo, A. J. Polym. Sci. Part A: Polym. Chem. 2014, 52, 3498-3505.
3) Sudo, A.; Sugita, S. J. Polym. Sci., Part A: Polym. Chem. 2016, 54, 3436-3443.
4) Okamoto, S.; Onoue, S.; Muramatsu, M.; Yoshikawa, S.; Sudo, A. J. Polym. Sci. Part A: Polym. Chem. 2015, 53, 2411-2420.
5) Sudo, A.; Sano, T.; Harada, M.; Ishida, D. ACS Macro Lett. 2014, 3, 808-812.

OC50

VITRIMERS BASED ON TRANSALKYLATION OF SULFONIUM SALTS

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Vitrimers[1-2] are a new class of polymeric materials with attractive properties. While being permanently cross-linked, these materials are able to change network topology via thermally triggered, associative exchange reactions. The incorporated exchangeable groups or bonds enable the material to be reshaped and remolded without any loss of network integrity. As an alternative to the use of transesterification chemistry, we explored the catalyst-free transalkylation of sulfonium salts as an exchange reaction for the production of covalent adaptable networks. First, a kinetic study on model compounds confirmed the transalkylation of sulfonium salts in a broad temperature window. Next, networks containing exchangeable bonds were prepared by bulk thiol-ene photopolymerization and subsequent thermal alkylation. The vitrimer-like properties of the poly(thioether – sulfonium salt) cross-linked materials were screened by solubility and stress-relaxation experiments. In addition, the recyclable nature of these covalent adaptable networks was evaluated by multiple grinding – remolding cycles and subsequent thermomechanical analysis.

References

1) M. Capelot, M. M. Unterlass, F. Tournilhac, L. Leibler, Acs Macro Letters 2012, 1, 789-792.
2) W. Denissen, J. M. Winne, F. E. Du Prez, Chemical Science 2016, 7, 30-38.

OC51

SYNTHESIS AND THERMORESPONSIVE PROPERTIES OF MULTI-SENSITIVE LINEAR AND CYCLIC GRAFT COPOLYMERS

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Multifunctional polymers have attracted much attention due to their interesting properties and multipurpose applications. Thus far, examples of multi-sensitive cyclic graft polymers are very scarce. This study aims at synthesis and properties of pH, thermo and oxidation-sensitive graft copolymers. Based on RAFT process and ring-closure reaction, tandem reactions were further used to generate linear and cyclic graft copolymers via reacting thiolactone-bearing copolymers with *N,N* -diethylethylenediamine and poly(ethylene glycol) methyl ether acrylate. Dependence of cloud point on different factors was investigated. Under same conditions, cyclic graft copolymer exhibited higher cloud point due to topology effect. Moreover, an LCST was observed only if the solution pH was suitable. Our study can not only afford a versatile method to prepare multi-responsive graft copolymers but also gain deep insight into the topology-property correlations. Owing to their good biocompatibility and tunable phase transition, the graft copolymers may have a great potential in smart biomedical and interfacial materials.

OC52

THERMORESPONSIVE PNIPAM COATED GOLD NANOPARTICLES FOR SENSORS, COATINGS AND CATALYTIC APPLICATIONS

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Gold nanoparticles (AuNPs) have received significant research attention in the recent years owing to their facile synthesis and unique optical properties, resulting in wide application ranging from, e.g., optoelectronics to biology.[1] Upon agglomeration of the AuNPs in solution, a red-shift of surface plasmon resonance (SPR) can be observed due to the change of interparticle distance. AuNPs can be surface functionalized with different functionalizing agents, such as polymers, surfactants, proteins, peptides etc. to tune the SPR wavelength.[2] Among these functionalizing agents, polymers and in particular stimuli responsive polymers are appealing for the coating of AuNPs, which opened up a new area of intensive research due to their response to external stimuli, such as temperature, pH, light, electrical or magnetic field, salt etc. and also for their potential application as an active delivery vehicle in biomedical science, catalysis and sensors.[3]

Here we will discuss the preparation of thermoresponsive PNIPAM coated AuNPs and their temperature and salt induced association behavior. Next we will demonstrate how these smart NPs can be used for the development of tunable colourimetric temperature and salt-sensors, coatings and catalytic applications.[4-6]

References

1) M. C. Daniel and D. Astruc, Chem. Rev., 2004, 104, 293–346.
2) M. Das, K. H. Shim, S. S. A. An and D. K. Yi, Toxicol. Environ. Health. Sci., 2011, 3, 193-205.
3) S. I. Yusa, K. Fukuda, T. Yamamoto, Y. Iwasaki, A. Watanabe, K. Akiyoshi and Y. Morishima, Langmuir, 2007, 23, 12842–12848.
4) S. Maji, B Cesur, Z. Zhang, B. G. D. Geest and R. Hoogenboom, Polym. Chem., 2016, 7, 1705-1710.
5) Z. Zhang, S. Maji, A. B. da F. Antunes, R. De Rycke, Q. Zhang, R. Hoogenboom and B. G. De Geest, Chem. Mater., 2013, 25, 4297-4303.
6) Z. Zhang, S. Maji, A. B. da F. Antunes, R. De Rycke, R. Hoogenboom and B. G. De Geest, Angew. Chem. Int. Ed., 2016, 55, 7086-7090.

OC53

FLOURIDE CATALYZED CHEMISTRY OF IMIDAZOLYL MONOMERS: A ROBUST POLYMERIZATION STRATEGY TOWARD DENDRIMERS AND POLYCARBONATES

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Advanced polymers with increased structural control and functional group representation is a continuous scientific subject that is addressed by polymer chemists. In this presentation we will revisit 1,1'-carbonyldiimidazole (CDI) as a imidazolyl generating agent of monomers bearing carboxylic groups and alcohols. A library of bench-stable imidazolyl activated monomers of 1,3-diols and higher diol configuration as well as AB_2 dendritic monomers were isolated in 100 gram scales and then after interconnected with a set of complementary monomers to generate either functional polycarbonates or monodisperse polyester dendrimers.[1] Independent of the polymerization technique, being step-wise alternatively divergent dendritic growth, the strategy capitalize on Cesium Fluoride (CsF) as a mild catalyst that allows the polymerization to proceed with fidelity, under benign and simple reaction conditions, with high yields and simple purifications as an outcome.

References

1) Angewandte Chemie International Edition, 54, 8, 2416-2419, 2015

OC54

INVESTIGATIONS INTO THE MECHANISMS OF PHOTO-ATRP AND PHOTO-RAFT

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The development of light-mediated reversible deactivation radical polymerizations (RDRPs) has become a very active area of research over the last few years. In this context, we have recently developed and investigated two photo-mediated RDRPs using cheap LEDs as light sources. The first one is a photocatalyzed ATRP mechanism involving the oxidative quenching of the catalyst, which was a copper-based complex with phenanthroline ligands, selected for its intense absorption in the blue wavelengths range. The second one consists in coupling the RAFT mechanism with a reversible and partial photolysis of the chain-transfer agent (CTA). A dithiocarbamate CTA with a *N*-carbazole Z group was synthesized, which allowed the use of blue or green LEDs. Both mechanisms lead to efficient controls, with in particular linear relationships between molecular weights and monomer conversions. Interestingly, precise temporal controls can be easily achieved, enabling reversible termination or reinitiation of the chains by simply switching off or on the light source. A kinetic modeling is proposed in the case of the photo-RAFT mechanism, which can account for the experimental observations and suggest ways for further improvements.

References

1) Q. Yang, F. Dumur, F. Morlet-Savary, J. Poly,* and J. Lalevée, Macromolecules 2015, 48, 1972-1980.
2) Q. Yang, S. Balverde, F. Dumur, J. Lalevée, and J. Poly,* Polymer Chemistry 2016, 7, 6084-6093.
3) Q. Yang, J. Lalevée, and J. Poly,* Macromolecules 2016, 49, 7653-7666.
4) B. Cabannes-Boué, Q. Yang, J. Lalevée, F. Morlet-Savary, and J. Poly,*, Polymer Chemistry 2017, DOI: 10.1039/C6PY02220K.

OC55

WELL-DEFINED SEMI-INTERPENETRATING POLYMER NETWORKS: THE BIEE-CROSSLINKING APPROACH

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Semi-interpenetrating polymer networks are 3D structures consisting of secondary linear polymer chains that are interlaced – but not covalently bonded – with a primary polymer network. This presentation focuses on well-defined semi-interpenetrating polymer networks generated by means of the BIEE-crosslinking approach, involving the interconnection of (poly(2-dimethylamino) ethyl methacrylate) (pDMAEMA) linear chains with 1,2-bis-(2-iodoethoxy)-ethane in the presence of hydrophobic or hydrophilic linear polymer chains [1]. The mechanical properties of these materials can be easily tuned by altering the content of the encapsulated hydrophobic/hydrophilic linear chains, whereas their well-defined structural characteristics allow for the prediction of their mechanical response *via* mathematical modelling [2]. Moreover, the encapsulation of linear, methacrylate-based (non-conjugated) hydrophobic chains possessing fluorescent moieties within the BIEE-crosslinked pDMAEMA networks results in 3D emissive amphiphilic semi-IPN that are further explored as sorbents for the uptake and fluorescence monitoring of transition metal ions [3].

References

1) Achilleos, M.; Demetriou, M.; Marinica, O.; Vekas, L.; Krasia-Christoforou, T. Polym. Chem. 2014, 5, 4365.
2) Achilleos, M.; Mpekris, F.; Stylianopoylos, T.; Krasia-Christoforou, T. RSC Adv. 2016, 6, 43278.
3) Christodoulou, K.; Leontidis, E.; Achilleos, M.; Polydorou, C.; Krasia-Christoforou, T. Polymers 2016, 8, 411.

OC56

FABRICATION OF ANISOTROPIC MICROPARTICLES VIA DOUBLE-SPEED SEEDED SWELLING POLYMERIZATION

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Over the past few decades, anisotropic microparticles with controllable morphologies and narrow size distribution have attracted substantial research interest. Scientists have designed and fabricated a wide variety of anisotropic particles through a range of methods, including electrospray, microfluidics, lithography, solvent evaporation induced phase separation, emulsion polymerization and dispersion polymerization. Among these methods, seed polymerization is an attractive technique with advantages including flexibility, controllability, and rigorous experimental conditions.

Recently, we developed a novel swelling technology called the double-speed swelling (DSS) procedure,[1-4] which is an efficient way to fabricate Janus-like MSPs based on non-cross-linked PGMA particles. In DSS technique, unlike the traditional swelling process, both the monomer and swelling agent are added simultaneously to the seed emulsion. According to DSS technique, we obtained a series of fascinating particles with various structures, such as Janus, raspberry-shaped, acorn-shaped, and hollow with open mouth, flower-like, yolk–shell and core-satellite superparticles. We also utilized these particles to construct free-standing superparticle-gel membranes with self-sloughing property, light reflection and enzyme carriers, and other applications.

References

1) Macromolecules, 2015, 48, 7592–7603.
2) Macromolecules 2016, 49, 9626–9636.
3) Polym. Chem., 2016, 7, 7078–7085
4) Macromol. Rapid Commun. 2016, 37, 47–52

OC57

UNIQUE BIOMATERIALS AND NANOCOMPOSITES BASED ON MULTIFUNCTIONAL PEG-HYDROGELS

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Our research focuses on 3 intertwined aspects: I) synthesis of **novel biomaterials**, II) development of **micro- and nano-patterning** methodologies and III) control of **cellular responses** to engineered biointerfaces and scaffolds.

With regard to the first aspect, poly(ethylene glycol) (PEG) hydrogels are well known to be non-toxic, non-fouling, non-immunogenic and are therefore widely used in industry, medicine and biomaterials research. While they effectively prevent interactions with proteins and cells, we and others have discovered that modifications on the surface properties, such as applying nano- or micro-sized topography, changing the elastic property or (bio)chemical surface patterning, do aid cell adhesion on the modified areas. ,[1,2]

We have established a library of PEG-based building blocks, ranging from low-molecular weight linear PEG-diacrylates to high molecular weight, star-shaped PEG-macromolecules.[3]

As far as the crosslinking chemistry is concerned, we have developed amine Michael-type addition reactions to crosslink acrylate- and vinyl sulfone-functionalized macromonomers and have “clicked” azide- and alkyne-appended precursors, besides “UV-curing” photosensitive reaction mixtures. [4] On top of that, further thiolation of pre-formed gel films greatly enhances the potential to bind gold nanoparticles to their surface.[5]

References

1) Lensen, M. C.; Schulte, V.; Diez, M. Biomaterials - Physics and Chemistry; InTech, 2011; pp. 397–414.
2) Kelleher, S.; ...; Lensen, M. C. Adv. Eng. Mater. 2012, 14, 56–66.
3) Susan Kelleher, ... Marga C. Lensen* Biomaterials Science 2014, 2 (3), 410 – 418.
4) Zhang, Z.; ... Lensen, M. C. Chem. Mater. 2014, 26, 3624–3630.
5) Fang Ren, ... Marga C. Lensen* Chemistry of Materials, 10.1021/acs.chemmater.6b03548

OC58

PROPAGATION RATE FOR RADICAL POLYMERIZATION OF WATER-SOLUBLE MONOMERS IN AQUEOUS SOLUTIONS

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The understanding of radical polymerization in aqueous solutions has been significantly enhanced thanks to determining the individual rate coefficients. This development has been made possible by description of solvent effect controlling the dependence of propagation rate coefficients, k_p, on monomer concentration, which is assigned to interactions of the solvent consisting of water and monomer with the transition state structure for propagation.

This contribution gives an update on solvent effect for radical polymerization in aqueous solutions that is based on k_p values determined for non-ionized ((meth)acrylamides, (meth)acrylic acid, *N*-vinylamides) and ionized (sodium methacrylate, methacrylate sulfobetaine) monomers using the pulsed-laser polymerization in conjunction with size-exclusion chromatography [1,2]. For non-ionized monomers, the k_p decreases toward higher monomer concentration in aqueous solution that reflects the fluidizing action of water on the transition state structure. For ionized monomers, the dependence of k_p on monomer concentration is diminished and is influenced by the screening effect of counterions. A strong impact of hydrogen bonding on k_p values is revealed by comparing the k_p values determined for some monomers in aqueous and organic solutions.

References

1) Lacík, I., Chovancová, A., Uhelská, L., Preusser, C., Hutchinson, R.A.H., Buback, M. PLP-SEC studies into the propagation rate coefficient of acrylamide radical polymerization in aqueous solution, Macromolecules 2016, 49, 3244–3253
2) Lacík, I., Sobolčiak, P., Stach, M., Chorvát, D., Kasák P. Propagation rate coefficient for sulfobetaine monomers by PLP–SEC. Polymer, 2016, 87, 38-49

OC59

CONTROLLING THE MICRO-ENVIRONMENT OF CELLS BY EXPLOITATION OF MACROMOLECULAR PHOTOCHEMISTRY

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Multi-photon-processes are nonlinear optical phenomena only occurring at high photon densities in the focus of femtosecond pulsed lasers thus can trigger photochemistry within confined space (< 1 µm) inside materials. We present a toolbox of biocompatible photochemistry enabling the manipulation of the micro-environment of living cells. Employing two-photon-initiators (2PI) with either photo-crosslinking or photo-degrading systems enables cell-photoencapsulation or photo-milling of channels for directed cell growth, respectively, within a two-photon-lithography device. Materials of choice are hydrogels with precursors based on natural (e.g., gelatin, hyaluronan, etc.) or biocompatible synthetic polymers (e.g. poly(vinyl alcohol)). These precursors were modified with enes (e.g., methacrylates, vinylesters, norbornenes) or thiols and combined with other (macromolecular) crosslinkers in thiol-ene coupling reactions to form hydrogel networks with arbitrary shape in high resolution. Incorporation of photo-labile groups into networks enables the photo-cleavage of formed crosslinks by the two-photon-process. Taken together these material platforms accompanied by two-photon-technology allow for a spatial-temporal control of the hydrogel properties in the presence of living cells and are therefore an ideal platform technology to study the behavior of cells in different micro-environments.

OC60

BIODEGRADABLE POLYMER NETWORKS VIA TRIAZOLINEDIONE CROSSLINKING OF OLEYL-FUNCTIONALIZED POLY(EPSILON-CAPROLACTONE)

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The application of 1,2,4-triazoline-3,5-dione (TAD) “click chemistry” for the formation of biodegradable polymer networks based on poly(e-caprolactone) (PCL) has been demonstrated. First, α, ω-oleyl terminated PCLs were prepared by two-step, one-pot syntheses via coordination ring opening polymerization of ε-caprolactone initiated by oleyl alcohol and subsequent coupling of obtained prepolymers bearing both an oleyl and hydroxyl end group using diisocyanate. Next, polymer networks were synthesized via Alder-ene reaction of two different bifunctional triazolinediones (bisTADs) with oleyl groups present in PCL macromolecules. Different crosslinking parameters were studied in order to find the optimal conditions for the preparation of sufficiently strong polymer networks. Thermal and mechanical properties, as well as the susceptibility of obtained networks to hydrolytic degradation were analyzed. The influence of the PCL molecular weight, nature of the TAD crosslinker and crosslinking stoichiometry on networks properties were determined.

References

1) S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne, F. E. Du Prez, Nat. Chem. 2014, 6, 815-821.
2) O. Türünç, S. Billiet, K. De Bruycker, S. Ouardad, J. Winne, F. E. Du Prez, Eur. Polym. J. 2015, 65, 286-297.
3) T. Chen, T. Cai, Q. Jin, J. Ji, e-Polymers 2015, 15, 3-13.
4) S. M. Guillaume, Eur. Polym. J. 2013, 49, 768-779.

NOTES

POSTER'S ABSTRACTS

P001

DETAILED INVESTIGATIONS ON BETA-CYCLODEXTRIN CENTERED STAR GLYCOPOLYMERS

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Glycopolymers are of great interest because of their multivalent interactions with carbohydrate binding proteins (lectins).[1] Over recent years several complex mannose-based glycopolymer architectures have been established, each one of them improving the binding affinity towards an animal lectin called DC-SIGN.[2] In this work the development of a new β-cyclodextrin based star initiator enabled new glycopolymer architectures with a supramolecular binding unit. These hybrid structures not only provide specific binding to mannose binding lectins but also allow complexation with a series of small and large molecules. We believe these systems would be valuable tools for advanced drug delivery applications.

References

1) Kiessling et al. Chem. Soc. Rev. 2013, 42, 4476
2) Haddleton et al. J. Am. Chem. Soc. 2014, 136, 4325

P002

ENZYMATIC SYNTHESIS AND POLYMERIZATION OF GLUCOSYL-VINYL MONOMERS

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Carbohydrates represent about 75% of the 200 billion tons renewable biomass produced annually but only around 4% is used by the chemical industry[1]. One of the ways to further utilize carbohydrates is by designing a polymerizable structure in the form of sugar-vinyl monomers. Previously it was reported that *β-glucosidase* can catalyze the synthesis of glucosyl-(meth)acrylate monomers and the best result was achieved by using a thermodynamic approach[2]. In this work, we present the kinetically-controlled enzymatic synthesis of glucosyl-(meth)acrylamide monomers. Although undesirable hydrolysis products are more favorable in the kinetic approach, its advantage is a shorter reaction time compared to the thermodynamic approach. Nonetheless, the monomer yield was significantly improved from 9% to 63% by changing the glucosyl acceptor and adding ionic liquids. RAFT polymerization of these monomers was successfully performed, resulting in glycopolymers with molecular weights of around 25 kg/mol and narrow PDIs (below 1.30). In addition, novel oligocellulose-vinyl macromonomers were synthesized from these glucosyl-vinyl monomers using c*ellodextrin phosphorylase* as the biocatalyst. Average degrees of polymerization of the oligocellulose sequences were 6 to 9 according to H-NMR, MALDI-ToF, and GPC measurements.

References

1) Lichtenthaler, F. W. & Peters, S., 2004. Comptes Rendus Chim., 7(2), p. 65–90.
2) Kloosterman, W. M. J. et al., 2014. Green Chem., 16(4), pp. 1837-1846.

P003

ENHANCEMENT OF GENE DELIVERY BY USING EFFECTIVE COMBINATION OF FREEZE CONCENTRATION AND POLYAMPHOLYTE NANOPARTICLES

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Recently, gene therapy represents as a promising strategy for treatment of various genetic disorders. For effective delivery of genes, it is required to transport genes into cells. Physical methods such as electroporation have been developed to penetrate cell membrane. However, these methods could damage tissues. Previously, we developed new freeze concentration method for internalization of proteins.[1, 2]

Freeze concentration is a physical phenomenon wherein water crystallizes into ice crystal and this ice-crystal excluded the solute molecules at extreme low temperature which ultimately enhances the concentration of materials. This phenomenon is freeze concentration. Here, we presented the beneficial use of new freeze concentration for *in vitro* gene delivery. Moreover, we developed self assembled polyampholyte nanoparticles as a carrier for safe gene transfection. Results from confocal microscope and luciferase activity revealed that the appropriate amount of polyampholyte: DNA and freeze concentration enhances transfection more efficiently in cells. Based on these results, we found an effective combination that are providing simple and non-toxic approach for enhanced gene delivery.

References

1) Ahmed at al.; Biomaterials, 2014, 35, 6508-18.
2) Ahmed et al.; Nanoscale, 2016,8, 15888-901.

P004

DELIVERY OF GOLD NANOPARTICLES USING FREEZE CONCENTRATION METHOD

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Gold nanoparticles are currently used for biological imaging applications. Physical methods such as electroporation have been developed to penetrate cell membrane. However, these methods causing cell damage. Previously, we developed new freeze concentration method for internalization of proteins.[1,2] During freezing, ice forms in the extracellular space, excluding solute molecules and leading to increased concentrations of electrolytes. This is called freeze concentration. It is featured by nontoxicity and high reliability. The purpose of our study was to delivered gold nanoparticles via freeze concentration. In our experiment, we observed that very little AuNP adsorption on L929 cells without freeze concentration. On the other hand, freeze concentration enhances adsorption of nanoparticles around the cells efficiently. These results are indicated that freezing enhances the protein adsorption around the cells efficiently. We expect that this methodology have a broad application in therapeutic applications.

References

1) Ahmed at al.; Biomaterials, 2014, 35, 6508-18.
2) Ahmed et al.; Nanoscale, 2016,8, 15888-901.

P005

ONE-POT SYNTHESIS OF HYPERBRANCHED POLYAMINES BASED ON NOVEL AMINO GLYCIDYL ETHER

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We report the one-pot synthesis of hyperbranched polyethers possessing amino functionality by using a Boc-protected butanolamine glycidyl ether monomer (BAG). A series of hyperbranched Boc-protected polyamino glycerols (PBAG) was prepared through anionic ring-opening multibranching polymerization to yield PBAG with controlled molecular weights (2300-14700 g/mol) and relatively low molecular weight distributions. Subsequent deprotection of PBAG yielded hyperbranched polyaminoglycerols (PAG) possessing a globular polymeric structure that comprise of ran¬domly branched structure with a large number of amine and hydroxyl groups. ^{1}H- and ^{13}C-NMR, GPC and MALDI-TOF measurements confirmed the successful polymerization of the hyperbranched PAG polymer. With its superior biocompatibility of PAG, we anticipated the prospective potentials in biological and biomedical fields.

P006

PHOSGENE-FREE SYNTHESIS OF POLY(L-CYSTEINE) CONTAINING STYRENE MOIETY AS REACTIVE FUNCTION

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A novel approach for pre-polymerization modification available *N*-carboxyanhydride (NCA) precursor, prepared by phosgene-free method offering a safer and green way to obtain by peptide monomers under exceptionally mild reaction conditions, has been developed. The polypeptide bearing a reactive styrene moiety have been prepared through the polymerization of urethane derivative in varying the feed ratio to the initiator to give the corresponding polypeptides without any degradation of styrene moieties. Additionally, the copolymerization successfully accomplished with urethane derivatives of styrene contained cysteine and N_{ε}-Boc-L-lysine in low polydispersity and well-defined structure. Modification of NCA precursor was achieved with a high efficiency through a typical thiol-ene (photo) reaction using benzyl mercaptan as model compound, offers a breakthrough entry to simple functionalization for NCA precursor and the broad scope of this method as a conjugation tool for vast number of functional polypeptides.

References

1) N. Hadjichristidis, H. Iatrou, M. Pitsikalis, G. Sakellariou, Chemical Reviews 2009, 109, 5528
2) S. Yamada, K. Koga, T. Endo, Journal of Polymer Science Part A: Polymer Chemistry 2012, 50, 2527

P007

WELL-DEFINED STAR-SHAPED POLYMERS VIA SET-LRP IN LESS THAN 90 MINUTES

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Synthesis of well-defined star-shaped polymers have been challenging for decades using CRP techniques. Current synthetic methods mainly consist of homo or multi-block star-polymer synthesis, with reaction times from few hours to up to days.[1,2] In aqueous SET-LRP, the pre-disproportionation of Cu(I)Br in water results in highly active, in situ generated Cu(0)-particles. The synthesis of multi-block star-shaped copolymers via aqueous SET-LRP will be discussed in this presentation, which allows rapid and direct access to acrylamide based star-shaped polymers, without any purification steps.[3] Star-shaped homopolymers (DP=60-240) and diblock copolymers of NIPAM with DMA or HEAm were prepared in different ratios with full conversions in <30 minutes. In addition, a sequence-controlled penta-block star polymer was also obtained, with excellent control over MWD (PDI<1.14). In an attempt to investigate the catalytic system, we have employed a British 1 penny coin to polymerize a selection of acrylate monomers using linear and star shaped initiators to obtain polymers even in 50 gram scale (PDI=1.05–1.11).[4] When compared with Cu(0)-wire systems, no induction period was observed, hence demonstrating an economic, easily accessible catalyst for SET-LRP of acrylates.

References

1) A. H. Soeriyadi, C. Boyer, F. Nystrom, P. B. Zetterlund and M. R. Whittaker, J. Am. Chem. Soc., 2011, 133, 11128
2) C. Boyer, A. H. Soeriyadi, P. B. Zetterlund and M. R. Whittaker, Macromolecules, 2011, 44, 8028
3) R. Aksakal, M. Resmini, C. R. Becer, Polym. Chem., 2016, 7, 171
4) R. Aksakal, M. Resmini, C. R. Becer, Polym. Chem., 2016, 7, 6564

P008

POLY(THIOACRYLATE)S: EXPANDING THE MONOMER TOOLBOX OF FUNCTIONAL POLYMERS

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Radically polymerizable monomers such as acrylates, acrylamides and styrenics have been investigated because of their corresponding polymers for many years. As thiol chemistry proved to be a resourceful and powerful tool for the preparation of functional polymers, it has driven us to find a synthetic route and investigate a long forgotten class, the so called thioacrylates.[1,2] This has been done, not only to extend the toolbox for controlled radical polymerization (CRP) techniques, but also to overcome the necessity of protection and deprotection of thiol groups, as they are prone to undergo side reactions. Additionally, the constant need for fast and efficient polymer functionalization under mild conditions promises the thioacrylates as an ideal candidate. Herein, we present a straightforward synthetic approach to prepare various thioacrylate monomers as well as demonstrate their CRP, i.e. RAFT.[3] A trithiocarbonate chain transfer agent was utilized to control the molar mass and dispersity of thioacrylate polymers and blockcopolymerizations with ethylacrylate were studied. Additionally, a protecting group free, solid-phase, iterative protocol based on thiolactones with before mentioned thioacrylates are discussed to yield sequence-defined polymers.

References

1) N. Hadjichristidis, Macromolecules, 1981, 14, 128.
2) N. Hadjichristidis, Polymer, 1981, 22, 63.
3) S. Aksakal and C. R. Becer, Polym. Chem., 2016, 7, 7011–7018.

P009

DOUBLE HYDROPHILIC LINEAR-BRUSH BLOCK COPOLYMER SELF-ASSEMBLY

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Most recently, it could be shown that the self-assembly process of block copolymer is not only limited to the combination of a hydrophilic with a hydrophobic block copolymer but the self-assembly process can also be achieved by combining two hydrophilic blocks.[1-3] The formation of self-assemblies of the so called double hydrophilic block copolymer (DHBC) is driven by a difference in hydrophilicity of the used hydrophilic blocks. It is expected that DHBC-based self-assemblies show increased permeability compared to traditional self-assemblies.

In the present work, a DHBC based on linear pullulan blocks and poly(oligo(ethylene glycol) methyl ether) methacrylate) (POEGMA)-brush blocks is described that was formed via copper(I) catalyzed azide alkyne cycloaddition. The resulting DHBC shows the formation of particles in aqueous solution under ambient conditions that could be observed even under the optical microscope. To preserve the self-assembled particle structures at lower concentrations a biocompatible and FDA approved crosslinking agent, namely sodium trimetaphosphate, was utilized for crosslinking.

Overall, the novel DHBC with a linear-brush block structure was utilized to form completely hydrophilic crosslinked particle structures.

References

1) S. M. Brosnan, H. Schlaad, M. Antonietti, Angew. Chem., Int. Ed. 2015, 54, 9715
2) J. Willersinn, M. Antonietti, B.V.K.J. Schmidt, Macromolecules, 2016, 49 (15), 5331
3) J. Willersinn, A. Bogomolova, M. Brunet Cabré, B.V.K.J. Schmidt, Polym. Chem., 2017, 8, 1244

P010

CROSSLINKER-TAILORED HYDROGELS WITH BISPHOSPHONIC ACID FUNCTIONALITY

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Tailoring the swelling, degradation and mechanical properties of hydrogels is important in a variety of biomedical applications such as drug delivery and tissue engineering applications. In this project, two novel bisphosphonate-functionalized crosslinker monomers were synthesized by the reaction of two bisphosphonate-functionalized diamines (prepared by Michael addition of butane-1,4-diamine or 4,9-dioxa-1,12-dodecanediamine to tetraethyl vinylidene bisphosphonate) with 2-isocyanatoethyl methacrylate, followed by cleavage of bisphosphonate groups using trimethylsilyl bromide. These crosslinkers were incorporated into hydrogels by copolymerization with poly(ethylene glycol) methacrylate (PEGMA) and 2-hydroxyethyl methacrylate (HEMA) at different ratios to control degradability and swelling properties of hydrogels as well as their ability to support mineralization process for biomedical applications.

This work was supported by a grant from Bogazici University Research Fund (11820).

P011

PHOSPHONATE-FUNCTIONALIZED POLY(β-AMINO ESTER) CROSSLINKED HYDROGELS FOR BIOMEDICAL APPLICATIONS

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The controllability of degradation is vital for applications of hydrogels such as drug delivery systems, cell encapsulation and tissue engineering scaffolds. Poly(β-amino ester) (PBAE) macromers can be used as crosslinkers to tailor degradability and mechanical properties of the hydrogels. The structure (e.g. hydrophilicity, steric effect), amount and molecular weight of PBAE macromers affects the porosity and the crosslink density of degradable groups of the hydrogels. In this study, three phosphonate-functionalized PBAE macromers were synthesized via aza-Michael addition of a phosphonate-functionalized amine (prepared from the reaction of 4,9-dioxa-1,12-dodecanediamine with diethyl vinyl phosphonate) and poly(ethylene glycol) diacrylate (PEGDA), 1,6-hexanedioldiacrylate or 1,6-hexanediol ethoxylate diacrylate. The macromers were incorporated into hydrogels by copolymerization with PEGDA to enhance cell adhesion properties and biocompatibility of networks, adding also pH sensitivity to PEGDA hydrogels. The physical (degradation, swelling, porosity and mechanical) and biological (toxicity and cell interaction) properties of the resulting hydrogels were evaluated. The results showed that desired properties can be customized by altering the chemistry and ratio of macromers, leading to potenial new areas of application.

P012

STUDYING THE EFFECTIVE OF CELL ADHESION WITHIN HYPERBRANCHED AND LINEAR POLYMERS

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In this review, synthesis analogue linear and hyperbranched poly(*n*-butyl methacrylate) with acid (COOH) and amine (NH_2) functional group end using free radical polymerisation (FRP) and reversible addition fragmentation chain transfer polymerisation (RAFT) techniques respectively.

After synthesis and characterisation polymers, the biocompatibility of these materials with different alkyl amine end or acid end functionality on epithelial and fibroblast cells were investigated using different methodologies. Tissue culture polystyrene (TCP) was used as a control for comparison purpose. Epithelial and fibroblast cells were cultured in direct polymer films on glass coverslips for 72 hours as intended these materials as surface coating. The experiments results have been observed that the two cell types had different responses to each polymers. Fibroblast cells showed better adhesion and proliferation on acid functionality, while epithelial cells showed greater adhesion on amine functionality.

This work would provide useful information for the synthesis and characterisation a new biomaterials. It has been showed that polymer functionality play an important role in studying the biocompatibility of these materials in *vitro.*

References

1) Rimmer, Stephen, et al. "Highly branched poly-(N-isopropylacrylamide) s with arginine–glycine–aspartic acid (RGD)-or COOH-chain ends that form sub-micron stimulus-responsive particles above the critical solution temperature." Soft Matter 3.8 (2007): 971-973.
2) Carter, Steven, Barry Hunt, and Stephen Rimmer. "Highly branched poly (N-isopropylacrylamide) s with imidazole end groups prepared by radical polymerization in the presence of a styryl monomer containing a dithioester group." Macromolecules 38.11 (2005): 4595-4603.
3) Cox-Nowak, Kayleigh, et al. "Poly (n-butyl Methacrylate) with Primary Amine End Groups for Supporting Cell Adhesion and Proliferation of Renal Epithelial Cells." International Journal of Polymeric Materials and Polymeric Biomaterials just-accepted (2017).

P013

DENDRITIC GLYCOARCHITECTURES FOR DRUG-DELIVERY-SYSTEMS AND POLYMERIC THERAPEUTICS

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Over the last both decades dendritic glycoarchitectures have been successfully investigated as drug-delivery-systems (DDS) and polymeric therapeutics (PT) [1]. Here, we demonstrate the simultaneous use of maltose- and maltotriose-modified glycodendrimers (GD) for the delivery of nucleosides as well as PT for treating chronic lymphocytic leukemia (CLL) [2, 3]. Very shortly, GD with maltotriose decoration is usable as PT to treat CLL without destroying other cells of blood, while GD with maltose as DDS is subsequently addressable to overcome the drug resistance of nucleosides for treating leukemia. Moreover, biological pathways of PT [4] and cellular trafficking of GD as DDS [5] were deeply investigated to further dig out the potential use of GD only possessing different degrees on glucose modification. Moreover, dendritic glycoarchitectures are also used to induce retarding release of proteasome inhibitor bortezomib from DDS/calcium phosphate cement (CPC) for treating multiple myeloma as malignant disease of clonal plasma cells [6]. Structure-property relationship studies for optimizing dendritic glycoarchitectures [7] as DDS in CPC also outlined that CPC possesses a limited loading capacity of drug/DDS complexes.

<u>References</u>

1) D. Appelhans et al., Chemical Society Review 2015, 44, 3968.
2) A. Szulc et al., International Journal of Pharmaceutics 2016, 513 (1-2), 572.
3) I. Franiak-Pietryga et al. Molecular Pharmaceutics 2013, 10, 2490.
4) I. Franiak-Pietryga et al. Macromolecular Bioscience 2017, accepted.
5) M. Studzian et al., Manuscript submitted.
6) C. Striegler et al., Macromolecular Bioscience 2015, 15, 1283.
7) C. Striegler et al. Polymer 2015, 80, 188.

P014

pH SENSITIVE, FUNCTIONAL POLYCARBONATE MICELLES AS HIGHLY SELECTIVE DRUG DELIVERY SYSTEMS

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The use of polymer nanotechnology in the field of drug delivery has gained increased interest as a consequence of its potential to solve issues relating to conventional therapeutic agents, including lack of targeting capability and systemic toxicity.[1] Such intelligent drug delivery systems are exemplified by polymeric micelles, which can encapsulate 'cargoes' within core-shell structures.[2] Polycarbonates are of particular interest in biomedical applications not only as a result of their biocompatibility and tunable degradability, but also of the ease in which functionalities can be incorporated to the polymers.[3] We report the synthesis of a novel pH responsive, functional, and biodegradable polycarbonate *via* ring opening polymerization. The introduction of a norbornene moiety in the monomer structure allows the attachment of multiple functionalities, providing a highly versatile platform for post-polymerization modifications.[4] When poly(ethylene glycol) is attached to the polymer backbone an amphiphilic structure is formed, that self-assembles into spherical micelles. The dual advantage of covalent attachment of a drug alongside a pH sensitive disassembly allows excellent control over drug loading and release, making this polymeric system an excellent candidate for drug delivery applications.

<u>References</u>

1) Clinical Cancer Research, 2008, 14:1310-1316.
2) Nanomedicine, 2012, 7(8):1253-1271.
3) Biomaterials, 2006, 27, 1741-1748.
4) ACS Macro Lett, 2012, 1, 1285-1290.

P015

NOVEL POLYURETHANE BASED HYDROGEL PRECURSORS FOR BIOMEDICAL APPLICATIONS

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Hydrogels are excellent candidates for biomedical applications such as tissue engineering, drug delivery and wound dressings. However, their main drawback is the low mechanical strength and limited processing possibilities.

The present work reports the development of acrylate-terminated, polyurethane-based polyethylene oxide (PEO) hydrogel precursor series (AUP) using a PEO backbone with molecular weights ranging from 2,000 to 10,000 g/mol. The novel precursors combine the favorable mechanical properties of urethane-containing polymers with the well-known biocompatibility of PEO segments. Most interestingly, AUP precursors enable UV crosslinking in the solid state, enabling fabrication of the hydrogels with well defined shapes using several techniques which are not applicable with the current generation hydrogel precursors. Additionally, the physical properties of the hydrogels are strongly affected by the molecular weight of the PEO backbone and the initial water content of the precursor solution. The precursors have been successfully processed via different techniques including film casting, electrospinning and 3D printing. AUP hydrogels exhibited high biocompatibility in cell tests using pre-osteoblasts. Considering their ease of fabrication, favorable mechanical properties and good biocompatibility, AUP hydrogels offer high potential for biomedical applications.

P016

POST-MODIFICATION OF POLYBUTADIENES BY PHOTOINDUCED HYDROGEN ABSTRACTION FROM BENZOXAZINES AND THEIR THERMALLY ACTIVATED CURING

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Polybenzoxazines as a class of polyphenolic thermosets formed by ring-opening polymerization of the 1,3-benzoxazines without using any catalyst progressively substitute resole or novalac type phenolics. These thermosetting materials attract a great interest in diverse scientific and industrial areas due to their superior properties.[1]

Photoinitiator systems that initiate free radicals by a bimolecular process were studied extensively. In these systems, initiation goes through with formation of a triplet excited state of an aromatic carbonyl and then hydrogen abstraction from a donor molecule (co-initiator). Mostly, polymerization of vinyl monomers is started by the radicals generated on the hydrogen donor.[2]

In this regard, as part of our ongoing research interest for developing new photochemical systems for macromolecular synthesis, we now report the use of benzoxazine as both hydrogen donor and aromatic carbonyl photosensitizer to incorporate benzoxazines onto a PB backbone in one simple step.[3]

References

1) Ghosh, N. N.; Kiskan, B.; Yagci, Y. Polybenzoxazines - New high performance thermosetting resins: Synthesis and properties. Prog. Polym. Sci. 2007, 32 (11), 1344–1391.
2) Cook, W. D. Photopolymerization kinetics of dimethacrylates using the camphorquinone amine initiator system. Polymer 1992, 33 (3), 600–609.
3) Arslan, M., B. Kiskan, and Y. Yagci. Post-Modification of Polybutadienes by Photoinduced Hydrogen Abstraction from Benzoxazines and Their Thermally Activated Curing, Macromolecules, 2016, 49 (14), 5026-5032.

P017

PRODUCTION OF pH-STIMULI RESPONSIVE HYDROGEL FOR TREATMENT OF GASTRIC ULCER

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In past decades, polymeric drug carriers have been developed to provide targeted cure in drug delivery applications [1]. Especially, pH-sensitive hydrogels have aroused great interest to use controlled drug release systems due to their hydrophilic structure which support to encapsulate and adjust the release of the drug [2].

In performed study, bone ash-reinforced chitosan-based hydrogels were obtained by encapsulation of bone ash into the hydrogel structure which was fabricated by photopolymerization of chitosan-g-glycidyl methacrylate (CTS-g-GMA) and poly(ethylene glycol) diacrylate (PEGDA) under the UV light. The obtained hydrogel`s structures were characterized by ATR-FTIR, SEM and XRD analyses. Mechanical and swelling tests, TGA, DSC and toxicity analyses were also performed. The obtained hydrogels were loaded with amoxicillin to use for treatment of gastric ulcer. The release of amoxicillin in efficient and controlled manner was provided in media with different pH value (pH:1.2 and pH:7.4). According to all results, it can be visualized that the obtained pH-sensitive chitosan-based hydrogel with this route could be a potential candidate as a drug carrier for treatment of gastric ulcer in the future applications.

References

1) Hatefia, A., Amsdena, B. (2002), Biodegradable injectable in situ forming drug delivery systems. Journal of Controlled Release, 80, 9-28.
2) Narkar, M., Praveen, S., Pawar, A. (2010), Stomach-specific controlled release gellan beads of acid-soluble drug prepared by ionotropic gelation method. AAPS PharmSciTech, 11(1), 267-277.

P018

TAILORED IMIDAZOLIUM-CONTAINING POLYIONENES: POLYMER ADDITIVES FOR ELECTROCHEMICAL DEPOSITION PROCESSES AND COPPER PLATING

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In recent years, polycations and especially imidazolium-containing polycations have gained increasing interest in polymer research as well as materials science. The range of application for cationic imidazolium moieties is diverse. The so-called “Damascene Process” is widely used for manufacturing microelectronic devices, using electrochemical deposition of copper on photolithographically designed multilayer structures. Electrochemical deposition is an important field of research, also with respect to the multifunctional additives employed. Polyionenes are polycations with charges localized in the polymer backbone. This class of polymers shows interesting features in their hybrid-characteristics for copper-plating.

We synthesized novel polyionenes via polyaddition of imidazoles and bis(epoxide)s. This versatile, yet relatively unexplored method can be used for rather well-defined polyionenes. To date, detailed characterization of multiple charged polymers remains challenging and requires special characterization methods. Common methods such as SEC or MALDI-ToF often fail when it comes to polyelectrolytes due to the special nature of multiple charged compounds and the resulting aggregation behavior. We also present a strategy to control the molecular weight by using a chain-stopper and characterization via ^{1}H NMR spectroscopy.[1]

References

1) A. Ziegler, D. Lechner, K. Fischer, P. Broekmann, H. Frey, 2017, submitted.

P019

SYNTHESIS OF HYPERBRANCHED POLYMERS BY METAL FREE PHOTOCHEMICAL APPROACH

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Hyperbranched polymers have received much attention compared to their corresponding linear analogous owing to their inherent characteristics such as higher solubility, reduced solution viscosity and increased level of terminal functionality. Due to these particular characteristics, hyperbranched polymers are commonly employed in different applications such as drug delivery systems, bioimaging agents, gene carriers, viscosity modifiers and catalyst supports.[1] Hyperbranched polymers can be synthesized by applying various polymerization modes. Recently, it has been shown that perylene can be used as sensitizers for photoinduced atom transfer radical polymerization without the requirement of metal catalysis.[2] This work covers the application of perylene for the synthesis of hyperbranched polymers by self-condensing method. For this purpose, tertiary-bromide and benzyl-bromide functional monomers were used as inimers, together with methylmethacrylate and styrene, respectively. Results show that, hyperbranched polymers with narrow molecular weight distributions can be synthesized at mild conditions by metal-free photochemical approaches using this strategy.

References

1) Aydogan C, Ciftci M, Yagci Y, Macromolecular Rapid Communicaiton, 2016, 37 (7), 650-654
2) Miyake GM, Theriot JC, Macromolecules, 2014, 47, 8255–8261

P020

SYNTHESES OF BENZODITHIOPHENE AND THIENOPYRROLEDIONE CONTAINING RANDOM POLYMERS FOR ORGANIC SOLAR CELLS

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In recent years, the organic solar cell (OSC) has attracted considerable attention as promising candidates for renewable energy technology because of their low cost, leight weight and flexibility. In this study, in order to improve the efficiency of the bulk heterojunction solar cell, two conjugated polymers were designed. For this purpose, benzodithiophene and thienopyrroledione containing two random copolymers were synthesized. The effect of varying acceptors such as benzotriazole and benzothiadiazole on optoelectronic properties and the performance of bulk heterojunction polymer solar cells was investigated. Electrochemical and optical studies prove that these copolymers could be candidates for polymer solar cells applications. Both copolymers were n- and p-dopable. Thus, the HOMO and LUMO values were determined by using cyclic voltammetry resulted with the values -5.53 and -3.43 eV for P1 and -5.54 and -3.53 for P2, respectively. The optical band gap of the polymers were calculated by using UV-VIS-NIR spectroscopy as 2.10 and 2.01 eV for P1 and P2, correspondingly. Bulk-heterojunction solar cells were constructed with these polymers as the donor together with $PC_{71}BM$ as the acceptor in the active layer.

P021

MULTIFUNCTIONAL DENDRIMER FORMATION USING THIOLACTONE CHEMISTRY

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Thiolactone chemistry is a powerful tool for the design of complex multifunctional architectures [1-2]. In this study, this versatile click-inspired synthetic strategy is conducted to prepare multifunctional dendrimer-like structures [3]. For this purpose, a thiolactone bearing an isocyanate function, prepared in multigram scale, is utilized for a multiple step functionalization starting from a 4-arm star-shaped poly(ethylene glycol). Amine-thiol-acrylate conjugation is carried out in order to form the aforementioned structures. The efficient aminolysis of the thiolactone ring and the reaction of the generated thiol with the double bond of an acrylate derivative are completed in a one-pot procedure. The choice of the amine and/or acrylate derivatives allow the introduction of different functional groups at each new generation, potentially leading to multivalent dendrimer-like structures.

The present approach allows the independent introduction of 4, 8 and 16 functional groups at the 1st, 2nd and 3rd generation respectively. The presence of 32 hydroxyl groups at the periphery could further permit the introduction of novel functionalities.

References

1) P. Espeel, F.E. Du Prez, Eur. Polym. J., 2015, 62, 247-272.
2) P. Espeel, L.L.G. Carrette, K. Bury, S. Capenberghs, J.C. Martins, F.E. Du Prez, A. Madder, Angew. Chem. Int. Ed., 2013, 52, 13261-13264.
3) N.U. Kaya, F.E. Du Prez, N. Badi, Macromol. Chem. Phys., 2017, DOI: 10.1002/macp.201600575

P022

CONTINUOUS RAFT POLYMERIZATIONS TOWARDS ACRYLATE MULTIBLOCK COPOLYMERS

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Today's polymer manufacturing is under pressure to provide tailor-made properties at low production costs.[1] Continuous production of functional block copolymers might fulfill these demands. Continuous polymerizations, carried out in microfluidic reactors, are associated with high control of reaction parameters, fast heat-exchange and high reaction efficiencies.[2] Combined with the inherent advantages of reversible addition-fragmentation chain transfer (RAFT) polymerizations, microreactors are an ideal engineering tool to develop and synthesize functional multiblock copolymers with high end group fidelity.[3]

Various multiblock copolymers were developed *via* RAFT in a single step, by employing a tubular reactor cascade. Full monomer conversions were targeted to avoid quasi-block copolymer formation and purification steps of macroRAFT agent. In this extent, a theoretic approach was followed to determine required reaction conditions. After verifying these conditions, systematic studies have been carried out on di- and triblock copolymers with well-defined sequences and different monomer/monomer ratios. At a later stage, the employed procedure was extended to synthesize a *n*BuA-*b*-MA-*b*-EA-*b*-*t*BuA tetrablock copolymer in large quantities (± 150 g in 26 h), illustrating the high applicability of multistep flow processes.

References

[1]) Ruzette, A.-V.; Leibler, L. Nat Mater 2005, 4, 19.
[2]) K. Jähnisch, V. Hessel, H. Löwe, M. Baerns, Angew. Chem. Int. Ed. 2004, 43, 406.
[3]) Vandenbergh, J.; de Moraes Ogawa, T.; Junkers, T. Journal of Polymer Science Part A: Polymer Chemistry 2013, 51, 2366.

P023

N-HETEROCYCLIC CARBENE ORGANOCATALYZED RING-OPENING POLYMERIZATION OF N-TOSYL AZIRIDINES WITH FUNCTIONAL AND NON ACTIVATED INITIATORS

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N-Heterocyclic carbenes (NHC) have received increasing attention over the last past 20 years because of their particular steric and electronic properties. They have recently emerged as organocatalysts in the context of polymer chemistry, allowing the precise synthesis of a wide range of macromolecules by chain- or step-growth polymerization processes.[1-2] Generally, aziridines polymerize via a cationic pathway, affording non-controlled hyper-branched poly(ethylene imine). Interestingly, it was recently shown that aziridines could be activated toward anionic ring-opening polymerization (AROP) by *N* -tosylation.[3-4] In this work, the ring-opening polymerization of activated aziridines catalyzed by a NHC, namely 1,3-bis(isopropyl)-4,5(dimethyl) imidazol -2-ylidene, have been investigated in presence of various initiators.[5] In the proposed approach, different activated *N*-sulfonyl amines, non-activated secundary amines as well as trimethylsilyl azide can be used as initiators. Control over molar masses, high chain-end fidelity and low dispersities are observed by size exclusion chromatography, NMR spectroscopy and MALDI-ToF mass spectrometry demonstrating the living/controlled behavior of the organocatalytic ROP of *N*-tosyl aziridines. This methodology provides access to well controlled linear (α-functional) homopoly(aziridines) and aziridine-based block copolymers.

References

1) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, Macromolecules, 2010, 43, 2093–2107.
2) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, Chem. Soc. Rev. 2013, 42 (5), 2142–2172
3) I. C. Stewart, C. C. Lee, R. G. Bergmann, F. D. Toste, J. Am. Chem. Soc., 2005, 127, 17616-17617
4) Rieger, E.; Manhart, A.; Wurm, F. R. ACS Macro. Lett., 2016, 5, 195-198.
5) C. Bakkali-Hassani, E. Rieger, J. Vignolle, F. R. Wurm, S. Carlotti, D. Taton, Chem. Comm., 2016, 52, 9719-9722

P024

CHEMICAL SCAVENGING OF POLYMERIC WASTE USING RENEWABLE MATERIAL AND APPLICATION

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There is growing interest in the development of new materials based on recycled polymers from plastic waste. This is due to the facts of depleting fossil fuels and due to strict environmental laws. In this framework, new technique for the formulation of grease that combines the chemical recycling of poly (ethylene terephthalate) PET with the use of castor oil (CO) has been developed. Comparison to diols used in chemical recycling of PET, castor oil is renewable, easy available, environmental friendly, economically cheaper and hence sustainability indeed. The process parameters like CO concentration and temperature were altered and further the influences of the process parameters has been studied in order to establish technically and commercially viable process. Further thereby formed depolymerized product find an application as base oil in the formulation of grease. A depolymerized product has been characterized by various chemical and instrumental methods, while formulated greases has been evaluated for its tribological properties. The grease formulated using this new environmentally friendly approach presents applicative properties similar, and in some cases superior, compared to those of non-renewable resources based grease.

P025

FUNCTIONALIZATION OF ALIPHATIC POLYCARBONATES BY CLICK CHEMISTRY - A SMART APPROACH FOR BIOMATERIALS DESIGN

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Among the click member family, triazoline dione (TAD) compounds can be used as a dienophile in a Diels-Alder type reaction respecting the features of the click chemistry concept[1,2]. Herein, simple and ultrafast macromolecular functionalization under mild conditions using TAD click chemistry is introduced. Aliphatic polycarbonates (APCs) are chosen as macromolecular platform since this family of polymers present all the prerequisites to be used as biomaterials (biocompatibility and biodegradability)[3,4]. Those “clickable” copolymers are synthetized by ring-opening polymerization (ROP) of cyclocarbonate carrying diene dangling functions. Post-modification with various TAD based compounds were carried out in optimised conditions and the effectiveness of the reaction was assessed with the traditional characterisation tools. Impacts on final thermal properties were evidenced by DSC where shift of the glass transition temperature was observed. A degradability study in different storage conditions also demonstrates the impact of the nature of the lateral function on the shelf-stability of the resulting polymer.

This study provides the proof of concept of the APCs functionalization using TAD click-chemistry and constitutes a key step in the macromolecular design of well-tailored biomaterials.

References

1) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. Angew. Chemie Int. Ed. 2001, 40 (11), 2004–2021
2) Billiet, S.; Bruycker, K. De; Driessen, F. Triazolinediones Enable Ultrafast and Reversible Click Chemistry for the Design of Dynamic Polymer Systems. Nat. Chem. 2014, No. August, 1–7
3) Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A. P. Synthesis and Post-Polymerisation Modifications of Aliphatic Poly(carbonate)s Prepared by Ring-Opening Polymerisation. Chem. Soc. Rev. 2013, 42 (3), 1312–1336
4) Mespouille, L.; Coulembier, O.; Kawalec, M.; Dove, A. P.; Dubois, P. Implementation of Metal-Free Ring-Opening Polymerization in the Preparation of Aliphatic Polycarbonate Materials. Prog. Polym. Sci. 2014, 39 (6), 1144–1164

P026

APPLICATION OF CATIONIC RING-OPENING POLYMERIZATION FOR SYNTHESIS OF FUNCTIONAL POLYMERS

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Synthesis of functional polymers in “metal-free” polymerization systems attracts considerable interest as this methodology enables polymer structure tailoring without contamination of the final products with metallic impurities. The demand for environmentally friendly processes led to the development of variety catalytic systems including also the cationic ring-opening polymerization conducted in the presence of alcohol as the initiator and protic acid as the catalyst. [1] At suitable conditions polymer chain formation proceeds according to Activated Monomer mechanism in which propagation involves reaction between protonated cyclic monomer and hydroxyl terminal group.[2] As the functional group present in the initiator is preserved in the macromolecule, AM polymerization is well suited for the synthesis of macromonomers.[3] When a diol is used as an initiator, a telechelic polymer terminated with hydroxyl groups can obtained.[4] Application of functional, heterocyclic monomer leads to introduction of the pendant reactive groups into the polymer chain.[5]

Presented synthetic method allowed preparation under mild conditions reactive oligoethers/oligoesters (including polylactide) which can be used further as building blocks for complex structures construction.

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References

1) W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle, D. Taton, Prog. Polym. Sci. (2016), 56, 64.
2) S. Penczek, P. Kubisa, Progr. Polym. Sci. (1999), 24, 1409.
3) M. Basko, M. Bednarek, React. Funct. Polym. (2012), 72, 213.
4) M. Basko, P. Kubisa, J. Pol. Sci., Pol. Chem. (2007), 45, 3090.
5) M. Basko, M. Bednarek, L. Billiet, P. Kubisa, E. Goethals, F. Du Prez, J. Pol. Sci, Pol. Chem. (2011), 49, 1597

P027

ACTIVATED ESTER FUNTIONAL CONDENSATION POLYMERS THROUGH LIGHT-INDUCED [4+4] CYCLOADDITION REACTION

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A combination of light-induced condensation polymerization and activated ester substitution reaction is demonstrated as a new method to obtain novel polymeric structures. Bis-anthracene functionalized compound involving pentafluorophenyl ester moiety namely, bisanthracenyl-PFPE, is prepared by an esterification reaction then polymerized under UV light irradiated at 365 nm. Obtained polymer is reacted with a variety of amine compounds namely allylamine, benzylamine, furfurylamine and propargylamine under mild conditions. Quantitative conversions of pentafluorophenyl ester groups into the respective amide groups as well as the thermal behaviors of all polymers are revealed by using various spectroscopic measurements such as FT-IR, GPC, NMR and DSC.

References

1) G. Kaur, P. Johnston, K. Saito, Polym. Chem. 2014, 5, 2171
2) E. Demirel, H. Durmaz, G. Hizal, U. Tunca, J. Polym. Sci. Part A: Polym. Chem. 2015, 54, 480

P028

MICROPARTICLES OF POLYLACTIDE STEREOCOMPLEX CONTAINING METAL IONS FOR PHARMACEUTICAL AGENTS DELIVERY

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Polylactide (PLA) stereocomplex formed from equimolar mixture of PLLA and PDLA stereoisomers precipitates from solution in a form of regular microspheres when medium molecular weight PLAs with terminal ionic groups are used for stereocomplexation. This spontaneous formation of PLA microparticles could be an alternative for emulsion methods of drug carriers preparation.
In the presented work PLAs with terminal carboxyl groups were synthesized by cationic ring-opening polymerization (and additional functionalization) and were used for stereocomplexation performed in the presence of metal ions which induce macromolecules self-organization. By the appropriate choice of stereocomplexation conditions (type of solvent, metal cation, PLA and Mt^{n+} concentrations) as well as PLAs (M_n, number and placement of –COOH groups) the regularity and the size of microparticles (D = 0.6-3.0 μm) can be tuned.

It was demonstrated that stereocoplexation according to described procedure, in the presence of pharmaceutical agent, e.g. vitamins D_3, A, B, led to drug loading of several percent. The susceptibility of microparticles of PLA stereocomplex to hydrolytic degradation was sufficient to release the encapsulated compound.

Acknowledgement: Financial support from National Science Center Poland, grant 2013/11/B/ST5/01618.

References

1) Tsuji H.: Poly(lactide) stereocomplexes: Formation, structure, properties, degradation, and applications. Macromol. Biosci. 2005, 5, 569–597.
2) Pagels R. F., Prud'homme R. K.: Polymeric nanoparticles and microparticles for the delivery of peptides, biologics, and soluble therapeutics. Journal of Controlled Release 2015, 219, 519–535.
3) Biedron T., Brzezinski M., Biela T., et al.: Microspheres from stereocomplexes of polylactides containing ionic liquid end-groups. J. Polym. Sci., Part A: Pol. Chem. 2012, 50, 4538-4547.
4) Bednarek M., Wojtczak E., Pluta M.: Spontaneous formation of polylactide stereocomplex microspheres containing metal ions. Polym. Int. 2017, 66, 108–118.

P029

EFFECT OF THE BULKY CARDO GROUPS ON THE AROMATIC POLYAMIDE MEMBRANE BASED GAS SEPARATION

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Polymer membrane-based gas separation has experienced a substantial growth during past decades as an energy efficient and environmentally friendly separation processes over the conventional industrial methods. However, the trade-off between permeability and selectivity associated with the polymeric membranes has initiated extensive research works to develop new membrane materials. In this present investigation, we try to develop new polyamides (PA s) suitable for gas separation applications.

The gas transport properties of the four series of PAs prepared from four new diamines containing different cardo group and different molecular architecture with five different commercially available aromatic diacids; towards four different gases CH_4, N_2, O_2 and CO_2 at 35 °C and an upstream pressure of 3.5 bar were investigated. The highest permeability ($P_{CO2} = 119.0$ and $P_{O2} = 29.0$ Barrer) was observed for PA XVI, containing tri-*tert*-butylphenol substituted triphenylamine (TPA). The PAs showed excellent gas separation efficiency for O_2/N_2 gas pair and some of them surpassed the 2008 Robeson upper bound. These results signify the PAs containing propeller shaped TPA structure showed interesting gas separation properties.

Keywords: *Polyamides, Bulky pendant groups, Triphenylamine, Gas permeability.*

P030

REVERSIBLE CROSSLINKING OF TELECHELIC POLYDIENES: A NEW APPROACH TOWARD RECYCLABILITY OF ELASTOMERS

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Rubbers can be found into various fields of applications like aerospace, sports equipments or tires. Elasticity, solvent permeability and stress durability are the main characteristics targeted for theses materials. In order to achieve such properties, polymer chains must be crosslinked to form a network. However, irreversibility of the vulcanization which is the main method employed industrially, generates a large amount of waste rubber. Additionally, there is no viable method for recycling these materials. To tackle this issue, various dynamic linkages such as Diels-Alder reaction, metal coordination or hydrogen-bonding have been successfully used on different polymers to create reversible networks.[1,2]

We report here a new method to synthesize polybutadiene and polyisoprene networks based on reversible telechelic covalent or hydrogen bonding. High molar masses polymers were first chemically degraded in order to obtain liquid/viscous polymers.[3] Then, polymers chain ends were modified by furan or ureidopyrimidinone moieties to generate reversible interactions.[4] Thermal stability and elastic properties of the formed reversible networks were analyzed and impact of the chain length, crosslinking density and recyclability of the networks will be particularly discussed.

References

1) A. M. Schenzel, N. Moszner, C. Barner-Kowollik, Polym. Chem. 2017, 8, 414.
2) Z. Tang, J. Huang, B. Guo, L. Zhang, F. Liu, Macromolecules 2016, 49, 1781.
3) F. Sadaka, I. Campistron, A. Laguerre, J.-F. Pilard, Polym. Degrad. Stab. 2012, 97, 816.
4) B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. a. J. van der Rijt, E. W. Meijer, Adv. Mater. 2000, 12, 874

P031

THERMORESPONSIVE HYDROGEL NANOCOMPOSITES WITH TUNEABLE DESWELLING KINETICS

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Hydrogels with environmental sensitivity can provide a way to change some of their properties (i.e. size, optical properties, etc.) in a controlled way making a perfect candidate for actuators, sensors or vehicles for drug delivery systems. Their physical properties often restrict the applicability of pure polymer systems, which can be overcome by nanocomposite hydrogels.

Regardless of the targeted application, the comprehensive understanding and tunability of the nature and kinetics of the response is inevitable. Our aim was to investigate the effect of quality and quantity of carbon nanoparticles with different structure and surface chemistry on the thermal response of nanocomposite system. Carbon nanotubes (CNTs) and graphene oxide (GO), respectively, were incorporated into the poly(N-isopropyl acrylamide) gel matrix. The observed effect of the two nanoparticles is significantly different. The presence of CNT does not alter the character of the response. GO at temperatures significantly higher than the temperature of volume phase transition (VPT) slows down the triggered shrinkage, while at temperatures just above the VPT its hydrophilic character facilitates the expulsion of water and results in a faster deswelling.

P032

SIMULTANEOUS AND SEQUENTIAL SYNTHESIS OF POLYANILINE-G-POLY(ETHYLENE GLYGOL) BY COMBINATION OF OXIDATIVE POLYMERIZATION AND CUAAC CLICK CHEMISTRY: A WATER SOLUBLE INSTANT RESPONSE GLUCOSE BIOSENSOR MATERIAL

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A novel approach for the *in-situ* synthesis of conjugated polyaniline-poly(ethylene glycol) graft copolymer (PA-*g*-PEG) by the combination of oxidative polymerization and copper catalyzed azide–alkyne cycloaddition (CuAAC) click reaction is described. The method pertains to the reduction of the $CuBr_2$ catalyst during the oxidative copolymerization of aniline and aminophenyl propargylether to Cu(I) species, which catalyze the CuAAC reaction between thus formed polyaniline with pendant alkyne groups and independently prepared azide functional PEG in both simultaneous and sequential manner. The obtained water soluble PA-*g*-PEG was used for the construction of glucose biosensor by a simple one-step approach. Combined electrostatic polyanion-polycation and hydrogen bond interactions between PA-*g*-PEG and GOx provided a suitable immobilization matrix for the enzyme resulting in excellent analytical parameters. PA-*g*-PEG based glucose biosensor exhibited a remarkable response time, producing an instant signal upon addition of analyte, making this sensor an attractive alternative for the existing devices.

P033

STATISTICAL COPOLYMERS OF 2-(TRIMETHYLAMMONIUM)ETHYL METHACRYLATE AS NOVEL WATER SOLUBLE DRUG DELIVERY SYSTEMS

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Series of 2-(trimethylammonium)ethyl methacrylate copolymers with methyl methacrylate and methyl acrylate were synthesized via atom transfer radical polymerization (ATRP)[1]. Hydrodynamic diameters determined by dynamic light scattering were smaller for chloride containing copolymer particles (10 nm) than for salicylate ones (150 nm). Release profiles for salicylate ions bonded with copolymer showed 95% efficiency within 180 h. The values of critical micelization concentration below 0,1 mg/ml allowed selection of polymers, which were loaded with non-ionic drugs like erythromycin and quercetin. Resulted in dual drug delivery systems with both ionically and physically interacted bioactive substances were examined for loading and release properties, which were affected by drug structure showing that proposed systems were only appropriate for non-aromatic drugs.

References

1) R. Bielas; A. Mielańczyk; A. Siewniak; D. Neugebauer, ACS Sustain. Chem. Eng. 2016, 4 (8), 4181–4191.

P034

POLYMETHACRYLATE NANOPARTICLES BASED ON FLUORESCENT INITIATORS FOR BIOLOGICAL STUDIES IN PLANTS

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Atom transfer radical polymerization initiator based on pyranine was obtained from bromoesterification with 2-bromoisobutyryl bromide with 90% of yield. Next two series of linear polymers, poly(2-hydroxyethyl methacrylate) and poly(2-trimethylammoniumethyl methacrylate) with polymerization degrees below 100, were obtained by ATRP. Critical micellization concentrations were determined for each polymer resulting values below 0,1 mg/ml. Influence of polymer chain lenght on hydrodynamic diameter was investigated using dynamic light scattering technique. All polymers resulted in particles with sizes below 2 nm, which next were evaluated as a potential tool for cell-to-cell communication studies in plants.

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P035

MECHANOCHEMICALLY ACTIVE NETWORKS FOR THE COPPER(I)-CATALYZED AZIDE/ALKYNE “CLICK” CYCLOADDITION (CuAAC) REACTION

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Polymeric mechanochemistry is of growing interest, as it enables the transformation of destructive effects, like structural damaging or leaking of material properties to constructive applications, usable for example in the field of self-healing and stress-sensing materials[1]. It offers the possibility to activate labile chemical bonds solely by external mechanical force, generating thus an active catalyst for copper(I)-catalyzed-azide/alkyne-“click”-cycloadditions (CuAAC). We designed polymeric and non polymeric Cu(I)-bis(N-heterocyclic-carbene) (NHC) based mechanocatalyst, activable by cleaving one of the shielding NHC-ligand[2,3] by ultrasound in solution or compression in bulk. The thus formed active monocarbene species triggers the fluorogenic-“click”-reaction of non-fluorescent 3-azido-7-hydroxycoumarine and phenylacetylen towards the highly fluorescent 7-hydroxy-3-(4-phenyl-1H-[1,2,3]triazol-1-yl)-coumarine in-situ-probing the stress-sensing properties by the appeared fluorescence.

In order to study substantially the effect of the initial molecular weight onto the mechanophore activation efficiency and to increase the catalytic activity, we designed chain-extended mechanocatalysts, including several Cu(I)-centers within one polymer chain. Additionally, we designed mechanophoric networks, where also the perpendicular to the applied force oriented mechanophores will be activated[4], guaranteeing the force transmission in all directions, enhancing further the cleavage efficiency.

References

1) Li, J.; Nagamani C.; Moore J.S.; Polymer mechanochemistry: from destructive to productive; Chem. Res.; 2015, 48 (8), pp 2181-2190.
2) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P.; Activating catalysts with mechanical force; Nature Chem.; 2009, 1 (2), 133-137.
3) Michael, P.; Binder, W. H., A Mechanochemically Triggered “Click” Catalyst. Angew. Chem. Int. Ed. 2015, 54 (47), 13918-13922.
4) Beiermann, B. A.; Kramer, S. L. B.; Moore, J. S.; White, S. R.; Sottos, N. R., Role of Mechanophore Orientation in Mechanochemical Reactions. ACS Macro Lett. 2012, 1 (1), 163-166.

P036

SMART MICROARRAY PLATFORMS FOR UNDERSTANDING BIOCHEMICAL INTERACTIONS

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There is an urgent need for new technologies to detect and probe bacterial infection and carbohydrate arrays (glycoarrays) have gathered significant interest for this purpose.At the start of the infection process pathogens adhere onto the host cells, commonly through protein-carbohydrate interactions. Probing these interactions can be efficiently achieved by the presentation of carbohydrates in an array format, which can detect bacteria and provide structural information on their adhesion proteins and carbohydrate specificities.

Combining glycoarray technology with polymer surface coatings can provide a route to higher resolution arrays with minimisation of false positive outputs. We have previously described a versatile methodology to functionalise glass and silicon substrates with carbohydrates, producing arrays which are as simple as self-assembling on gold, but with the cost saving of working on glass and silicon.[1] This work now includes the immobilisation of both RAFT-synthesised switchable non-fouling polymers using 'click' type reactions and libraries of glycopolymers,[2] synthesised through tandem post-polymerisation modification methods. The arrays have been extensively characterised [3] and their efficiency for facilitating protein-carbohydrate interactions has been investigated.

References

1) Biggs, C.I. et al., Biomaterials Science, 2015, 3, 175-181
2) Richards, S-J. et al., ACS Macro Letters. 2014, 3, 1004-1008
3) Biggs, C.I. et al., Biomacromolecules, 2016, 17 (8), 2626–2633

P037

ASSEMBLY OF TIO2-B NANOPARTICLES INTO POROUS STRUCTURES USING PDMA-B-PS BLOCK COPPOLYMERS

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Although lithium-ion rechargeable batteries are the heart of portable electronics today, the existing battery systems are far from optimal. An alternative anode material, TiO_2-*Bronze,* is an interesting candidate as the “open” crystal lattice of the TiO_2-*Bronze* phase make that Li-ion diffuse quite easily into the crystal structure. But for excellent performance the final anode material needs 3 characteristics: a high crystallinity of TiO_2-B, a high surface area and a controllable pore size. Our strategy consists of synthesizing TiO_2-B nanocrystals and order them into porous structures using tailor-made block copolymers.

The non-agglomerated TiO_2-B nanocrystals were synthesized using a microwave synthesis method, and could be dispersed in all media, unprecedented for the Bronze phase. The nanocrystal size could be controlled using a design of experiments: Definitive Screening Design. The nanoparticles were assembled into a porous structure using the self-synthesized poly(dimethylacrylamide)-block-polystyrene block copolymer (PDMA-b-PS). This polymer was chosen because of the nanocrystal tethering PDMA segment. In this way the pore size could be controlled and altered if needed. Finally the deposited thin films of nanocrystals were tested for their Li-ion insertion capabilities.

P038

POLYMER-ANALOGUE FUNCTIONALIZATION OF POLY(2-ALKYL-2-OXAZOLINE)S FOR HYDROGEL FORMATION AND CHEMOSELECTIVE COUPLING

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Poly(2-alkyl-2-oxazoline)s (POx) are versatile polymers due to their side chain variability [1]. A variety of monomers have been synthesized to introduce functional groups such as vinyl [2] or thiol functionalities [3]. We are interested in strategies for mild and chemoselective coupling of POx to biological molecules such as peptides or proteins. For this, we described the introduction of cysteines to POx side chains via thiol-ene chemistry using a protected cysteine linker [4].

Here, a similar approach was taken to introduce thiols to POx via post-polymerization functionalization. We quantified the amount of thiols via Raman spectroscopy and Ellman assay and demonstrate hydrogel formation via thiol-ene chemistry. We further use the thiol groups to introduce vinyl dimethylazlactone (VDM). VDM is stable under cell culture conditions and forms stable amide bonds with cysteine containing peptides in a mechanism similar to native chemical ligation [5]. Additionally, it represents an interesting alternative to rather instable thioesters. VDM could be successfully attached to POx and was used to form polymer-peptide conjugates under mild conditions, which could be confirmed via HPLC and NMR.

References

1) Hoogenboom, R. Angew. Chem. Int. Ed. 2009, 48, 7978 – 7994
2) Gress, A.; Völkel, A.; Schlaad, H. Macromolecules 2007, 40, 7928
3) Cesana, S.; Kurek, A.; Baur, M. A.; Auernheimer, J.; Nuyken, O. Macromol. Rapid Commun. 2007, 28, 608–615
4) Schmitz, M.; Kuhlmann, M.; Reimann, O.; Hackenberg, C. P. R.; Groll, J. Biomacromolecules 2015, 16, 1088–1094
5) Schmitt, S. K.; Trebatoski, D. J; Krutty, J. D.; Xie, A. W.; Rollins, B.; Murphy, W. L.; Gopalan, P. Biomacromolecules 2016, 17, 1040–1047

P039

FROM RENEWABLE PHENOLS TO HIGH PERFORMANCE BIOBASED THERMOSET RESINS: THE BENZOXAZINE APPROACH

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The use of epoxy based composites for structural applications is becoming more and more important thanks to their light weight, their strength related to their weight, their corrosion resistance, their design flexibility, etc. Unfortunately, these resins commonly used between the carbon or glass fiber layers exhibit poor thermal and fire resistance and as a consequence the composites retain no mechanical strength after thermal and fire exposure. In this context, benzoxazine resins have recently attracted extensive attention due to their near-zero shrinkage upon curing, high stiffness, excellent thermal properties, lower moisture absorption, better resistance to flammability and to UV radiation than epoxies. Moreover, the development of sustainable polymeric materials from renewable resources has recently become a major challenge in polymer science and is of particular interest for both academics and industrials. In this context and due to the large availability of natural phenolic compounds, benzoxazine resins are emerging as new players in the bio-based polymers thematic. This presentation summarizes our new developments and trends in the field of advanced bio-based polybenzoxazines[1-3].

References

1) L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, "Chavicol benzoxazine: ultrahigh Tg biobased thermoset with tunable extended network", Eur. Pol. J., 81, 337-346 (2016)
2) L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, "High performance bio-based benzoxazine networks from resorcinol and hydroquinone", Eur. Pol. J., 75, 486-494 (2016)
3) L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, "Bio-based high performance thermosets: stabilization and reinforcement of eugenol-based benzoxazine networks with BMI and CNT", Eur. Pol. J., 67, 494-502 (2015)

P040

POLY(GLYCERYL GLYCEROL) - A BUILDING BLOCK FOR MULTI-FUNCTIONAL BIOMATERIALS

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Poly(glyceryl glycerol) (PGG) is a polymer featuring a polyethylene oxide backbone and 1,2-diol groups in every repeating unit. The 1,2-diol side chains can be functionalized in a variety of ways to attach probes, targeting ligands and possibly drugs. In the present work PGG is prepared by monomer-activated ring-opening polymerization of (DL-1,2-isopropylidene glyceryl) glycidyl ether and subsequent acidic deprotection. This allows introduction of a functional head group to each polymer chain that can be utilized for (bio)conjugation.

The usefulness and versatility of PGG for the design of multi-functional biomaterials is illustrated with two examples. First, PGG is conjugated to poly(L-lactide) (PLLA) to obtain amphiphilic block copolymers, which assemble into nanoparticles in aqueous solution.[1] Labeling of the PGG-PLLA particles is achieved by simply mixing with a boronic acid-functional fluorophore due to the strong interaction of PGG with boronic acids. Second, double hydrophilic graft copolymers of PGG and hyaluronic acid are studied as vehicles for sustained intravitreal drug release.

References

1) T. Borke, A. Korpi, F. Pooch, H. Tenhu, S. Hietala, Poly(Glyceryl Glycerol): A Multi-Functional Hydrophilic Polymer For Labeling with Boronic Acids, Journal of Polymer Science Part A: Polymer Chemistry, 2017, DOI: 10.1002/pola.28497.

P041

DESIGN AND CHARACTERISATION OF FUNCTIONAL POLYMERS FOR SOLID DISPERSIONS

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Determining monomer sequence distribution in copolymerisation is important when correlating molecular structure to macroscopic properties. Controlling monomer addition to afford a variety of complex polymeric structures, using either controlled radical or ionic polymerisation, is a topic of interest for many polymer chemists.

The copolymerisation of various methacrylates has been studied to provide sequence distribution data. Free radical copolymerisation reactions were monitored using ^{1}H NMR spectroscopy to estimate reactivity ratios and analyse individual monomer feed depletion as a function of total monomer conversion. Reactivity ratios for the copolymerisation of methyl methacrylate (MMA) and poly(ethylene glycol) methacrylate (PEGMEM) (M_n 500) suggest a near random copolymer structure $r_{MMA} = 1.66$ $r_{PEGMEM} = 0.97$. The monomer reactivity has also been studied qualitatively upon the addition of methacrylic acid. The results also suggest a near random terpolymer structure, despite the evident differences in monomer steric and electronic properties.

Methacrylate reactivity data was used to synthesise more complex polymeric architectures such as block copolymers. The resulting polymers will be subjected to industrial application testing to provide a greater understanding of macroscopic properties as a function of molecular structure.

P042

AN AMPEROMETRIC GLUCOSE BIOSENSOR PLATFORM CONTAINING CARBON NANOTUBES-ZINC PHTHALOCYANINE AND A CONDUCTING POLYMER

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Proper interaction between biomolecules and electrode surface is the fundamental step to construct applicable biosensors. Conducting polymers (CPs) enhance biosensor performance because of their good electrical conductivity and processability. In addition, phthalocyanines are promising electroactive molecules due to their electronic properties and rich redox chemistry. Multi walled carbon nanotubes (MWCNTs) are also well-known matrices since they enhance conductivity and facilitate electron transfer of metallated phthalocyanines. Hence, a new immobilization platform for an amperometric glucose biosensor utilizing a conducting polymer, MWCNTs and a water soluble zinc phthalocyanine (ZnPc) was developed. For biosensor construction, a graphite electrode was firstly modified with poly[9,9-di-(2-ethylhexyl)- fluorenyl-2,7-diyl] end capped with N,N-Bis(4- methylphenyl)-4-aniline (PFLA) and MWCNTs. Then, co-immobilization of GOx with ZnPc onto the surface was performed. The biosensor showed a linear response range between 0.025 - 1.0 mM with a detection limit of 0.018 mM. K_M^{app} and sensitivity values were calculated as 0.53 mM and 82.18 μAmm^{-1}cm^{-2}, respectively. Scanning electron microscopy (SEM) and cyclic voltammetry (CV) techniques were used to investigate the surface modifications. Finally, the constructed biosensor was tested on beverages successfully.

P043

A SUSTAINABLE APPROACH FOR THE PREPARATION OF THERMOPLASTIC POLYURETHANE ELASTOMERS

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The environmental aspect of the plastics industry – in particular relating to the materials and technologies used – has gained importance in recent years. Special emphasis is placed on responsible resource management. We are therefore working to develop thermoplastic polyurethane elastomers (TPUs) containing sustainable alternatives to conventional petroleum-based polyols. An approach aiming to fabricate TPUs with advantageous properties and a high content of eco-friendly building blocks was investigated. A series of TPU formulations with tailored chemical composition was obtained through a solvent-free synthesis procedure and characterized in view of the thermal and mechanical properties. The results indicate that the newly developed TPUs are an attractive option to meet the growing demand for sustainable plastics.

P044

CdS QUANTUM DOTS AS PHOTOINITIATORS IN FREE RADICAL POLYMERIZATIONS

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Quantum dots (QD) generate an electron-hole pair upon photoexcitation, hence have a great potential as photoinitiators (PI) in free radical polymerizations (FRP). Their broad absorption is very advantages compared to most organic photoinitiators (PI), especially for excitation in the visible range. There has been few reports demonstrating the potential of QDs as photo-initiators in aqueous FRP (1-4) where hole scavenging with solvent and/or HO· formation was suggested as a must. Besides, usually bare chalcogenides with unknown luminescence, low quality, and non-colloidal particles have been used and therefore, nanoparticle/polymer mixture (or composites) were not achieved. Here, oleic acid coated colloidal CdS QDs were utilized as PI in FRP of MMA, PEGDA and HDDA in “non-aqueous” medium. Impact of light power, amount of QD on conversion and rate were studied using a Photo-DSC. Different excitation filters (320-390, 320-480, 400-500 nm) were used to investigate the initiation at long wavelengths, as well. CdS/polymer compositions were produced in batch reactions where colloidally stable structures with strong luminescence were achieved. Hydrodynamic size of the QD/polymer, polymer molecular weight and T_g were also studied.

References

1) Hoffman, A. J., et al., The Journal of Physical Chemistry (1992) 96 (13), 5546
2) Strandwitz, N. C., et al., Journal of the American Chemical Society (2008) 130 (26), 8280
3) Zhang, D., et al., Scientific Reports (2013) 3, 1399
4) Dadashi-Silab, S., et al., Polymer Chemistry (2015) 6 (11), 1918

P045

PREPARATION AND CROSS-LINKING OF ALL-ACRYLAMIDE DIBLOCK COPOLYMER NANO-OBJECTS VIA POLYMERIZATION-INDUCED SELF-ASSEMBLY IN AQUEOUS SOLUTION

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Poly(dimethylacrylamide)-poly(diacetone acrylamide) (PDMAC-PDAAM) diblock copolymer nano-objects were prepared by reversible addition-fragmentation chain-transfer aqueous dispersion polymerization, at 70 °C and 20 % w/w solids via polymerization-induced self-assembly. TEM studies indicate that the use of a PDMAC macro-CTA with a mean degree of polymerization (DP) of 68 or higher resulted in the formation of well-defined spherical nanoparticles. In contrast, either highly anisotropic worms or polydisperse vesicles were formed when relatively short macro-CTAs (DP = 40-58) were used. Dynamic light scattering and aqueous electrophoresis studies indicated that, in most cases, these PDMAC-PDAAM nano-objects were surprisingly resistant to changes in either solution pH or temperature. However, $PDMAC_{40}$-$PDAAM_{99}$ worms did undergo partial dissociation on adjusting the solution pH from pH 2-3 to approximately pH 9 at 20 °C, or on heating to 50 °C. Post-polymerization crosslinking of concentrated aqueous dispersions of PDMAC-PDAAM spheres, worms and vesicles was performed at ambient temperature using adipic acid dihydrazide. The formation of hydrazone groups was monitored by FT-IR spectroscopy and afforded covalently-stabilized nano-objects that remained intact on exposure to methanol, a good solvent for both blocks.

P046

BIOARTIFICIAL POLYPEPTIDE CONJUGATES: POST-MODIFICATION OF L-LYSINE PEPTIDE VIA ADMET POLYMERIZATION

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To shed light on the folding and crystallization of proteins, processes involved in the secondary structural transitions and their assembly behaviour have been intensively investigated. [1, 2] Poly-L-lysine (PLK), which exhibits three major secondary structures; namely random-coil, α-helix and beta-sheet, is an ideal *model* for understanding of the « *Protein-Folding*» phenomenon in conjunction with crystallization-phenomena. Therefore it is our aim to modify PLKs with polyethylene *via* ADMET-polymerization to study the structural properties introduced by altered conformational interactions. [3, 4]

PLKs were synthesized by ring opening polymerization (ROP) of *N*-carboxyanhydride (NCA) and the chain end functionalization reactions were performed by amidation of the *N*-terminus. *N*-terminus functionalized PLKs (fPLKs) were fractionated according to their number of repeating units (n) with preparative GPC. Chemical analyses revealed that fPLKs could be separated into fractions (n=5-33) with relatively low PDI values (PDIs=1.02-1.08) serving as central building blocks for ADMET-polymerization. Structural examinations were accomplished by CD-spectroscopy indicating that longer chains (n=33) display α-helicity, while shorter chains (n=5-8) form βII-turns. The fractionated fPLKs together with L-lysine function as building blocks for subsequent ADMET-polymerization to furnish the final biohybrid-polymers.

References

1) Davidson, B. G.; Fasman, D. Biochem. 1967, 6, 6.
2) Dobson, C. M. Nature 2003, 426, 6968.
3) Leonard, J. K.; Hopkins, T. E.; Chaffin, K.; Wagener, K. B. Macromol. Chem. Physic. 2008, 209, 1485.
4) Reimann, S.; Baumeister, U.; Binder, W. H. Macromol. Chem. Physic. 2014, 215, 1963.

P047

MULTIBLOCK COPOLYMER SYNTHESIS WITH GROUP TRANSFER POLYMERISATION

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Recent developments in ‘living’/’controlled’ polymerisation methods have facilitated the synthesis of novel and complex polymeric architectures. Sequential polymerisation has facilitated the synthesis of multiblock copolymers (eg. $(AB)_n$, (ABC…)) with interesting applications that include photonics and lithography. Presently, icosablock[1] and henicosablock[2] (20 and 21 block) copolymers are the most complex structures produced when using a mono-functional initiator. Both polymers were synthesised by RAFT in optimised conditions and the total synthesis exceeded 48 hours. Here, we report the synthesis of well-defined pentadecablock (15 block) copolymers that can be repeatedly synthesised in less than 4 hours. This was a one-pot synthesis using sequential group transfer polymerisation (GTP). A variety of methacrylate monomers were used to produce a bipolymer $(AB)_7$-B and a quintapolymer $(ABCDE)_3$ with low final *Đ* (<1.20) and an M_n of 8-13 kg mol^{-1}.

References

1) Gody, G., Maschmeyer, T., Zetterlund, P. B. & Perrier, S. Rapid and quantitative one-pot synthesis of sequence-controlled polymers by radical polymerization. Nat. Commun. 4, 2505 (2013). doi: 10.1038/ncomms3505.
2) Engelis, N. G. et al. Sequence-controlled methacrylic multiblock copolymers via sulfur-free RAFT emulsion polymerization. Nat. Chem. 1–19 (2016). doi:10.1038/nchem.2634

P048

EXPANDING THE TOOLBOX OF THIOL-X CHEMISTRY: THE THIOL-PARA-FLUORO REACTION AS AN EFFICIENT APPROACH FOR NETWORK FORMATION

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Substantial effort has been made in the last few decades to develop new strategies to build up polymer networks. [i] Among others, thiol based reactions, known for centuries, have just gained consideration and are exploited for functionalization and synthesis of polymeric materials.[ii] Accordingly, the para-fluoro-thiol reaction (PFTR) was employed for surface[iii] or side chain modification of polymers.[iv] In the current work, for the first time PFTR chemistry is applied to network formation. Specifically, a novel three linker containing penta fluoro phenyl moieties was first synthesized in an one-step reaction and subsequently reacted with several multifunctional thiols in an efficient manner. To assist the elucidation of the mechanism of the network formation, a complete analytical characterization of a model reaction with a monothiol is additionally displayed. Moreover, this study addressed the effects of diverse thiol structure on the thermal properties of the respective networks. The versatility of the entire concept is further demonstrated by employing multi armed-thiols. Thus, a novel platform technology for network formation is introduced.

References

i) J. G. Kloosterboer, Advances in Polymer Science, Springer-Verlag: Berlin/Heidelberg, 1988; Vol. 84.
ii) B. D. Fairbanks, T. F. Scott, C. J. Kloxin, K. S. Anseth and C. N. Bowman, Macromolecules, 2009, 42, 211–217.
iii) (a) L. Dumas, E. Fleury and D. Portinha, Polymer, 2014, 55, 2628–2634; (b) K. Babiuch, C. R. Becer, M. Gottschaldt, J. T. Delaney, J. Weisser, B. Beer, R. Wyrwa, M. Schnabelrauch and U. S. Schubert, Macromol. Biosci., 2011, 11, 535–548.
iv) (a) H. Turgut and G. Delaittre, Chem. – Eur. J., 2016, 22, 1511–1521; (b) D. Varadharajan and G. Delaittre, Polym. Chem., 2016, 7, 7488–7499; (c) H. Turgut, A.C. Schmidt, P. Wadhwani, A. Welle, R. Mueller, G. Dellaitre, Polym. Chem., 2017, doi: 10.1039/C6PY02108E.

P049

PRIMARY ALKYL PHOSPHINE-BORANE POLYMERS

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Boron-containing materials show highly interesting physical and chemical properties making them candidates for a range of uses including sensing, electronics, catalysis, biomedical applications, energy storage, and as high energy fuel additives. Phosphine-borane polymers were discovered in the 1950s and comprise an inorganic linear chain of alternating phosphorus and boron atoms [1, 2]. The polymers are formed by dehydrocoupling of phosphine-borane adducts, usually with the aid of a transition metal catalyst and already show potential as solution processable pro-ceramic materials [3].

This work describes the synthesis and characterisation of a new family of phosphine-borane adducts with linear primary alkyl side chains and their polymers. A range of molecular weights from 4.5 kDa to over 30 kDa and narrow polydispersities of 2-3 were observed. The polymers are viscous liquids that are soluble in common organic solvents. They exhibit very low glass transition temperatures down to 204 K (-69°C) and appear to be reasonably stable in the presence of air and water.

This work is funded through the Weapons Science and Technology Centre (WSTC) by the Defence Science and Technology Laboratory (Dstl).

References

1) Burg; Wagner, J. Am. Chem. Soc. 1953, 75, 3872
2) Dorn et al. Angew. Chem. Int. Ed. 1999, 38, 3321
3) Clark et al. Chem. Eur. J. 2005, 11, 4526

P050

TRANSLATING PEPTIDES TO PRECISION POLYMERS: "A GENERAL STRATEGY TOWARDS FUNCTIONAL SYSTEMS"

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Controlling the monomer sequence along polymer chains gives the opportunity to investigate structure-property relationship. In recent years, significant amount of effort has been dedicated to develop strategies for the synthesis of various complex structures with defined sequences.[1-3] As elegant synthesis methodologies have been introduced for the preparation of sequence defined complex architectures, an inevitable need to show the importance of sequential arrangements along the polymer chain in an application arises.

Previously, a peptide sequence was found to be specifically interacting with the water insoluble photodynamic cancer therapy drug tetra(hydroxyphenyl)chlorin (*m*-THPC). To study the structure-property relationship of this peptide sequence, poly(ethylene glycol) (PEG) conjugate of this peptide was synthesized and investigated as a tailor-made solubilizer to overcome the low water solubility of *m*-THPC.[4] Herein, we introduce novel bioconjugates which consist of a PEG chain connected to specifically engineered thiolactone-based precision segment inspired by the peptidic analogue. In this work, we have investigated structure-property relationship of precision segment via novel thiolactone based bioconjugates to improve water solubility of *m* -THPC and adjust release kinetics with comparison to their peptidic analogues.

References

1) 1- Meszynska, A.; Badi, N.; Borner, H. G.; Lutz, J. F. Chem. Commun. 2012, 48, 3887
2) 2- Zuckermann, R. N.; Kerr, J. M.; Kent, S. B. H.; Moos, W. H. J.Am. Chem. Soc. 1992, 114, 10646.
3) 3- Martens, S.; Van den Begin, J.; Madder, A.; Du Prez, F. E.; Espeel, P. J.Am. Chem. Soc. 2016, 138, 14182
4) 4- Wieczorek, S.; Krause, E.; Hackbarth, S.; Roder, B.; Hirsch, A. K.; Borner, H. G. J.Am. Chem. Soc. 2013, 135, 1711

P051

RANDOM CONJUGATED POLYMERS COMPRISING DERIVATIVES OF TRIPHENYLAMINE, BENZODITHIOPHENE AND BENZOTRIAZOLE MOIETIES FOR PHOTOVOLTAIC APPLICATIONS

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In this study, electronic, optical features and photovoltaic applications of two novel organic materials were investigated in order to improve organic photovoltaic properties. With this aim, derivatives of triphenylamine, benzoditophene (as the donor units) and benzotriazole (as the acceptor unit) containing donor/acceptor (D/A) type random conjugated polymers, **P1 & P2**, were synthesized via Stille coupling reaction. Electrochemical characterizations of the polymers were investigated with cyclic voltammetry and UV-Vis-NIR spectrophotometer was used to specify optical features of the polymers. Electronic and optical band gaps of the polymers were recorded as 2.06 eV, 2.16 eV for **P1** and 2.16 eV, 2.11 eV for **P2**, respectively. Device fabrications of these polymers were constructed with ITO coated glass substrate, PEDOT:PSS, (**P1** or **P2**):$PC_{71}BM$, LiF and Al in a given order. Preliminary studies showed that the highest power conversion efficiency (PCE) of these photovoltaic devices were recorded as 2.81 % with V_{oc}; 0.78 V, I_{sc}; 6.80 mA/cm^2 , FF; 0.53 for **P1**:$PC_{71}BM$ (1:2, w/w) in 3% ODCB solution and 3.14 % with V_{oc}; 0.76 V, I_{sc}; 7.96 mA/cm^2,FF; 0.52 for **P2**:$PC_{71}BM$ (1:2, w/w) in 2% chlorobenzene solution.

P052

PS-b-PNIPAM BLOCK COPOLYMERS FOR THERMO-RESPONSIVE MEMBRANE APPLICATIONS

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Stimuli-responsive pores offer anti-fouling and easy-to-clean properties to a membrane[1,2]. Block copolymers are interesting since well-defined nanopores can be obtained[3,4] and stimuli-responsive functions can be incorporated[4,5].

In our study, we synthesized well-defined high molecular weight polystyrene-*b*-poly(*N* -isopropylacrylamide) (PS-*b*-PNIPAM) block copolymers by RAFT polymerization where PNIPAM block acts as the thermo-responsive part due to its lower critical solution temperature (LCST) of 32°C. In principle, the pore sizes of the membrane should increase at temperatures above the LCST of PNIPAM, due to collapsing PNIPAM chains. Membranes were prepared by (a) spin-coating and solvent annealing to a desired morphology or (b) using self-assembly and non-solvent induced phase separation (SNIPS) procedure. Morphological properties of the block copolymer membranes were investigated by a variety of techniques including atomic force microscopy (AFM), grazing incidence small angle X-ray scattering (GISAXS) and scanning electron microscopy (SEM).

Membrane preparation using SNIPS procedure resulted in nanoporous membranes and temperature dependent permeability experiments showed that our membranes exhibit a thermo-responsive character. Reversibility tests proved that the membranes can be used repeatedly at temperatures between 20 and 50°C.

References

1) D. Bhattacharyya, T. Schäfer, S. R. Wickramasinghe, S. Dauner, Responsive Membranes and Materials, 2013, John Wiley & Sons Ltd., UK
2) D. Wandera, S. R. Wickramasinghe, S. M. Hussona, J. Memb. Sci., 2010, 357, 6–35
3) W. A. Phillip, M. A. Hillmyer, E. L. Cussler, Macrom. 2010, 43, 7763–7770
4) S. Rangou, K. Buhr, V. Filiz, J. I. Clodt, B. Lademann, J. Hahn, A. Jung, V. Abetz, J. Memb. Sci., 2014, 451, 266–275
5) S. P. Nunes,A. R. Behzad, B. Hooghan, R. Sougrat, M. Karunakaran, N. Pradeep, U. Vainio, K.-V. Peinemann, ACS Nano, 2011, 5(5), 3516–3522

P053

DYNAMIC ORDERING AND PHASE SEGREGATION IN HYDROGEN-BONDED POLYMERS

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Hydrogen bonds (H-bonds) constitute highly relevant structural units of molecular self-assembly.[1] They bridge biological and synthetic sciences, implementing dynamic properties[2] into materials and molecules, not achieved via purely covalent bonds. Phase segregation[3] on the other hand represents another important assembly-principle, responsible for eg. cell compartimentation, membrane-formation and microphase segregation in polymers.

We here discuss the phase segregation of H-bonding polymers, wherein the molecular recognition elements are based on barbiturate/Hamilton wedge (Ba/HW) element. The specific aggregation of a series of different H-bonding polymers in solution, both linear[4, 5] and dendritic[3, 6] polymers, bearing heterocomplementary H-bonding moieties are described, in particular focusing on the issue of phase segregation. The exploitation of H-bonded supramolecular dendrons with segregating polymer chains leads to the formation of three-phase segregated hierarchical micelles in solution,[3] purely linking the components via H-bonds, displaying a versatile spectrum of different segregated morphologies. We also discuss the discovery of novel functional microphase separated self-healing supramolecular architectures,[2] illustrating dynamic and self-healing properties with an almost complete recovery of the initial mechanical performances within 24 h healing at 30 °C.

References

1) S. Chen; W. H. Binder. Acc. Chem. Res. 2016, 49, 1409-1420.
2) S. Chen; N. Mahmood; M. Beiner; W. H. Binder. Angew. Chem. Int. Ed. 2015, 54, 10188-10192.
3) S. Chen; B.-D. Lechner; A. Meister; W. H. Binder. Nano Lett. 2016, 16, 1491-1496.
4) S. Chen; D. Ströhl; W. H. Binder. ACS Macro Lett. 2015, 4, 48-52.
5) S. Chen; Y. Deng; X. Chang; H. Barqawi; M. Schulz; W. H. Binder. Polym. Chem. 2014, 5, 2891-2900.
6) S. Chen; M. Schulz; B.-D. Lechner; C. Appiah; W. H. Binder. Polym. Chem. 2015, 6, 7988-7994.

P054

CRYSTALLIZATION OF SINGLE CHAINS AND CONCENTRATED SOLUTIONS OF STIFF MACROMOLECULES

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Crystallization of polymers was discovered a long time ago, but still the processes, which play a key role in formation of crystalline structures, are not fully understood. Main aim of our research is an investigation of the mechanisms of formation of crystalline clusters in a solution of semiflexible polymers under various conditions. We perform dissipative particle dynamics (DPD) computer simulations [1] using our own program code, and we consider very long semiflexible chains within tangent spheres model [2]. Different systems have been studied:

- Single chains of 10 000 beads long in poor solvent [3].
- Concentrated solutions of macromolecules of 1000 beads long with different polymer fraction and poor solvent.

We analyze pair density-density correlation function, static structure factor, and perform clustering analysis to characterize the size and the form of obtained crystallites. We have also studied the contact probability between monomer units along the chain.

References

1) R.D. Groot, P.B. Warren, J. Chem. Phys. 107 (11), 1997.
2) C. Vega, C. McBride, and L. G. MacDowell, J. Chem. Phys. 115, 4203, 2001.
3) A. Chertovich and P. Kos, J. Chem. Phys., 141, 134903, 2014.

P055

HETEROGENEOUS COPOLYMERIZATION: INSIGHT FROM COMPUTER SIMULATIONS.

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We introduce a computer simulation methodology to study living radical heterogeneous copolymerization. In our model the spatial segregation of species is accounted for and a microphase separation could occur during the copolymerization process. We performed model verification on the well-studied system of styrene - acrylic acid bulk copolymerization, both for low and high conversion degrees. Our simulations exhibited a perfect agreement with the available literature data and, moreover, allowed us to predict reactive melt 3D structure during the copolymerization process, including long-range ordered states during Polymerization Induced Phase Separation (PIPS).

The natural continuation of this work is an application of this methodology to the various values reaction rates and construction of phase diagram to describe possible regions of microphase separation during the polymerization process. It is intriguing feature if we could be able to predict polymerization parameters which will give long-range ordering in one step process. The other extension of this methodology is the studies of polymerization in initially heterogeneous systems, like emulsion copolymerization, where our method can be directly applied without any modifications.

P056

PUNNELS: SYNTHESIS, CHARACTERISATION AND APPLICATION OF TUNNEL POLYMERS

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The increasing global energy demand and the control of the level of CO_2 emission have been the two main challenges faced by mankind of the 21st century. This has led to the resurgence of interest in the development of renewable alternatives; one of which includes the direct generation of high energy fuels such as molecular hydrogen from water via membrane-based artificial photosynthetic systems. Nafion, a polymer that has been widely used in such systems possesses a number of flaws involving its selectivity, environmental inadaptability[1], moisture dependency for conducting protons and swelling[2]. Among the polymers synthesised as "Nafion alternatives", promising results can be seen in biomimetic membranes made via chemical modification of polyepichlorohydrin (PECH) with liquid crystalline (LC) mesogens[3,4].

In this study, polyethers with novel clickable and clicked pyrene derivatives were prepared. The polymers utilise LC properties contributed by the attached groups to self-assemble into tunnels when baked at a specific temperature; giving it its name Punnels (T**unnel P**olymers). Thus, the synthesis, characterisation and application of Punnels will be discussed.

References

1) B. Tylkowski, N. Castelao, M. Giamberini, R. Garcia-Valls, J. A. Reina and T. Gumí, Mater. Sci. Eng. C, 2012, 32, 105–111.
2) J. M. Spurgeon, M. G. Walter, J. Zhou, P. A. Kohl and N. S. Lewis, Energy Environ. Sci., 2011, 4, 1772.
3) M. G. G. Gilabert Oriol, R. Garcia-Vallas, Segur. y Medio Ambient., 2012, 126.
4) K. A. Bogdanowicz, S. V. Bhosale, Y. Li, I. F. J. Vankelecom, R. Garcia-Valls, J. A. Reina and M. Giamberini, J. Memb. Sci., 2016, 509, 10–18.

P057

A STRAIGHTFORWARD METHOD TO SYNTHESIZE TELECHELIC POLY(DIMETHYLSILOXANE)S

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One of the goals of polymer chemistry is developing new methodologies for the controlled synthesis of polymers with predictable, well-defined structures. Living anionic polymerization provides one of the best methodologies for synthesizing complex macromolecular structures like α, ω-telechelic polymers. These macromolecules are obtained by different synthetic methods, which usually involve the titration of alkyllithiums over double diphenyl ethylene derivatives (DDPE). In this work we report the synthesis of α, ω-telechelic PDMS by employing a novel bifunctional initiator, obtained from a commercial available siloxane precursor, poly(dimethylsiloxane) diglycidylether terminated (PDMS-DGE). The synthetic strategy involves high-vacuum reaction of *sec*-Bu$^-$Li$^+$ with DPE, and subsequently with PDMS-DGE to promote the nuclephilic ring-opening of the epoxide ends. The resulting bifunctional initiator was then employed to polymerize hexamethyl(cyclotrisiloxane) (D_3) by using conventional anionic polymerization methods. Silane (-SiH), vinyl (-CH=CH_2), hydroxyl (-OH), trimethyl and even methacryloyl ended PDMS were obtained. From SEC analysis, narrow molar masses distributions (Mw/Mn < 1.3) and good control over the resulting number-average molar masses were observed. In addition, ^{1}H-NMR and FTIR characterization confirmed the presence of the targeted functional groups in the resulting polymers.

P058

WEAR IS THE ANSWER? ENHANCED PROPERTIES FROM METALLOCENIC ISOTACTIC POLY(PROPYLENE)S WITH SILOXANE-TYPE ADDITIVES

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By using poly(dimethylsiloxane) (PDMS) and PDMS-based copolymers as additives, it is possible to improve and alter the superficial, crystalline, tribological and extrusion properties of commercial polyolefins.[1-6] Moreover, the scratching resistance of polypropylene (PP) can be enhanced with polyester modified siloxane copolymers. This enhancement is becoming increasingly important in several specific applications, such as the automotive industry.[1,2]

Abrasive wear behavior of different metallocenic isotactic propylene (iPP) homo and copolymers was studied along with their mixtures with poly(dimethylsiloxane) (PDMS) homo and copolymers. Mechanical, thermal, microscopic and spectroscopic features were also studied in order to infer the effect of PDMS-based additives in the mixtures. A reduction up to ten times the original wear value of the polyolefins was observed for the samples prepared with PCL-*b*-PDMS copolymers, in which PCL corresponds to poly(caprolactone) block. Blends of iPP with comparable quantities of similar molar masses of PCL or PDMS have a lower decrease in wear or none at all, respectively. However, blends with PDMS of higher molecular weight showed a significant decrease in wear rate.

References

1) I. Alonso, TPE Magazine International. TPE Magazine Int., 2013, 2, 106.
2) J. Markarian, Plastics, Additives and Compounding, 2009, 11, 10.
3) A.J. Satti, E.C. Molinari, A.G.O. de Freitas, W.R. Tuckart, C. Giacomelli, A.E. Ciolino, E.M. Vallés, Mat. Chem. Phys., 2017, 188, 100-108
4) (a) E. Yilgör, T. Sinmazcelik, I. Yilgör, J. Appl. Polym. Sci., 2002, 84, 535, (b) E. Yilgör, I. Yilgör, Prog. Polym. Sci., 2014, 39, 1165.
5) Z. Zhao, W. Yao, R. Du, Q. Zhang, Q. Fu, Z. Qiu, S. Yuan, J. Polym. Sci., 2009, 27, 137-143.
6) S. Zhu, N. T. McManus, C. Tzoganakis, A. Penlidis, Polym. Eng. Sci., 2007, 47, 1309-1316.

P059

COME TOGETHER: ROP + SET-LRP TO SYNTHESIZE BLOCK COPOLYMERS

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A one-pot, two-step method was applied to synthesize 3-arm AB_2-type star block copolymers. First, ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) was carried out in toluene by using either stannous octonoate ($Sn(Oct)_2$) or diphenyl phospate (DPP) as catalyst, and a multifunctional initiator bearing a bromoester moeity and alcohol groups. Then, single electron transfer-living radical polymerizations (SET-LRP) of methylmethacrylate (MA) or isobornylacrylate (IBA) were conducted in the same reaction vessel. Well-defined PMA-*b*-$(PCL)_2$ and PIBA-*b*-$(PCL)_2$ were obtained, with acceptable control of molar mass and polydispersity. The technique developed appears as an easy-to-handle, low-cost and effective experimental procedure, and can be also employed for the synthesis of linear block copolymers.

P060

IN SITU SPECTROSCOPIC STUDIES OF THE SYNTHESIS OF POLY(STEARYL METHACRYLATE)-POLY(2,2,2-TRIFLUORETHYL METHACRYLATE) BLOCK COPOLYMER NANOPARTICLES VIA POLYMERIZATION-INDUCED SELF-ASSEMBLY

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RAFT dispersion polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) was conducted in n-dodecane using a poly(stearyl methacrylate) macro-CTA to produce spherical nanoparticles via polymerization-induced self-assembly (PISA). Under these conditions, the core-forming PTFEMA is contrast-matched with the solvent, which affords highly transparent dispersions even at 30 % solids. This eliminates light scattering problems for visible absorption spectra recorded in situ using a quartz probe. Using a weak 438 nm band assigned to the trithiocarbonate-based RAFT agent, we show that the growing RAFT chain-ends remain stable for at least 6 h at 90 °C during this PISA synthesis. At 97% TFEMA conversion, adding excess initiator removes most of the RAFT end-groups. Moreover, the fluorine atoms in TFEMA enable the polymerisation kinetics to be monitored by ^{19}F NMR spectroscopy. Initially, the growing PTFEMA chains are well-solvated by unreacted monomer, so the polymerising mixture remains homogeneous. After 65 min, nucleation occurs and the ^{19}F polymer signal broadens as the growing chains become less mobile within the monomer-swollen micelles.

P061

UNDERSTANDING THE MECHANISM BEHIND IRON-MEDIATED CONTROLLED RADICAL POLYMERISATION

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Controlled radical polymerisation (CRP) is an important development in polymer chemistry as it offers control over molecular weight and dispersity in reactive radical polymerisations. One strategy to achieve control uses a metal mediator to reversibly cap a growing polymer chain, achieved through either Atom Transfer Radical Polymerisation (ATRP) or Organometallic Mediated Radical Polymerisation (OMRP). Iron presents an exciting opportunity in this field as it is inexpensive, non-toxic and can act through both mechanisms.

Amine–bis(phenolate) (ABP) iron complexes are excellent mediators of styrene and methyl methacrylate polymerisations, achieving dispersities as low as 1.07.[1] Mechanistic investigations suggest both ATRP and OMRP are active.[2,3] However, there has been little work targeting the OMRP-only system. This contribution investigates the mechanism behind the OMRP of vinyl monomers, mediated by the aforementioned iron ABP complexes, with a focus on understanding the balance between propagation and termination reactions. Surprisingly, the OMRP of both methyl methacrylate and styrene show living behaviour under specific conditions. The potential for multi-mechanism copolymerisations is also considered.

References

1) L. E. N. Allan et al., Macromol. Rapid Commun., 2012, 33, 414–418.
2) L. E. N. Allan, et al., Macromolecules, 2014, 47, 1249–1257.
3) H. Schroeder, et al., Macromolecules, 2015, 48, 4329–4338.

P062

AMPHIPHILIC POLYETHER-BASED ARCHITECTURES AS VERSATILE STRUCTURES FOR BIOMEDICAL APPLICATIONS

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Long-circulating liposomes, usually designated stealth liposomes, are polymer-coated vesicles with a poly(ethylene glycol) corona and are applied as drug carriers to minimize serious side effects of toxic drugs.[1] Due to the lack of multiple functional groups in the PEG backbone, the development of multifunctional polyether-based lipids is of high interest, as these structures permit further functionalization that enables, e.g. active targeting.[2]

We developed different cholesterol- and dialkyl-based amphiphilic structures of polyethers with various architectures (linear and hyperbranched polyglycerol as well as copolymers with PEG). The polymers employed were characterized via NMR and SEC measurements and had defined architectures with molecular weights in a range of 2500 to 8000 g/mol and narrow size distributions. These hetero-functional lipids were incorporated into liposomal nanocarriers which were investigated via electron microscopy analysis and light scattering. In the course of our studies the behavior of the carriers in human blood serum as well as the circulation time *in vivo* was examined.[3] In addition, the attachment of target functions was analyzed and the polymers were modified with acid-labile linkages which is promising to improve the drug delivery systems.

References

1) Sharma, A. International Journal of Pharmaceutics. 1997, 154 (2), 123–140.
2) a) Hofmann, A. M.; Wurm, F.; Hühn, E.; Nawroth, T.; Langguth, P.; Frey, H. Biomacromolecules. 2010, 11 (3), 568–574; b) Thomas, A.; Müller, S. S.; Frey, H. Biomacromolecules. 2014, 15 (6), 1935–1954.
3) a) Mohr, K.; Müller, S. S.;Müller, L. K.; Rusitzka, K.; Gietzen, S.; Frey, J.; Schmidt, M. Langmuir 2014, 30, 14954–14962. b) Reibel, A. T.; Müller, S. S.; Pektor, S.; Bausbacher, N.; Miederer, M.; Frey, H.; Rösch, F. Biomacromolecules 2015, 16, 842–851.

P063

THERMO-RESPONSIVE COPOLYMERS OF VINYL METHYL ETHER AND VINYL ACETATE: SYNTHESIS, CHARACTERIZATION AND LCST DEMIXING BEHAVIOUR IN WATER

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A range of thermo-responsive copolymers of vinyl methyl ether[1] and vinyl acetate, having different chemical composition, was synthesized by side chain modification of well-defined poly(vinyl acetate) (PVAc) for the first time. Thanks to the side chain modification strategy, all the copolymers have the same chain length and chain ends, and only differ in chemical composition. The PVAc was synthesized using cobalt mediated radical polymerization (CMRP) which has been proven recently to be one of the best ways to make PVAc polymers with predetermined molar masses and narrow distributions.[2-4] The synthesized PVAc was characterized by ^{1}H NMR and size exclusion chromatography. Differential scanning calorimetry (DSC) and optical microscopy were used to study the influence of copolymer chemical composition on the solubility behaviour of the copolymers in water. The obtained results indicate that the ether function improves the solubility thanks to its ability to form hydrogen bonds with water molecules, whereas the acetate function decreases the solubility of the copolymer in water.

References

1) D. Markova, D. Christova and R. Velichkova, Polym Int, 2003, 52, 1600-1604.
2) A. Debuigne, J.-R. Caille and R. Jérôme, Angewandte Chemie, 2005, 117, 1125-1128.
3) A. Debuigne, Y. Champouret, R. Jérôme, R. Poli and C. Detrembleur, Chemistry – A European Journal, 2008, 14, 4046-4059.
4) A. N. Morin, C. Detrembleur, C. Jérôme, P. De Tullio, R. Poli and A. Debuigne, Macromolecules, 2013, 46, 4303-4312.

P064

EFFECT OF SIDE CHAIN LENGTH ON STRUCTURE AND MECHANICAL PROPERTIES OF STARCH TRIESTERS

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Starch is an abundant and cheap raw material usually considered as a promising candidate for the substitution of petroleum-based polymers. However, starch presents some drawbacks such as a high hydrophilicity, a limited processability and poor mechanical properties as compared to synthetic polymers. Plasticization is commonly used to overcome these limitations. A lot of studies is focused on chemical modifications of starch such as esterification. Although the synthesis and thermal properties of starch triesters have been already described in literature. The relation between the alkyl chain length and the structural organization remains still unclear and there are scarce data regarding their mechanical behavior.

This study shows the self-organization of macromolecules into a layered structure constituted of the starch backbones separated by the alkyl chains oriented perpendicular to those planes. Moreover, this work reveals that the mechanical behavior of starch triesters depends on both the alkyl chain length and the botanical origin of starch, suggests the possibility of tunable mechanical properties.

With this respect, a modulation of the properties will be attempted by blending various starch triesters with different alkyls chain length.

P065

TO MODIFY A POLYMER'S SURFACE, OR TO MODIFY A SURFACE WITH POLYMERS: TAD'S THE WAY

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Triazolinediones (TADs) are known to be one of the strongest ene- and diene-ophiles in organic chemistry, allowing for a wide range of additive-free and atom efficient reactions at ambient conditions.[1] Because of a reaction time from seconds to minutes, they were already found to be an excellent tool for the modification of unsaturated polymers. Moreover, when an indole is used as a reaction partner, an adduct is formed that is stable at room temperature yet becomes dynamic at elevated temperatures.

Here, we introduce the use of tailor-made triazolinediones to alter the surface of different – organic and inorganic – materials via two distinct strategies. On the one hand, fluorinated TADs were applied as reactive additives for polydienes. Depending on the exact TAD compound and the modification procedure, the fluorinated groups were found to have a varying effect on the wetting properties of the final material.[2] On the other hand, silicon and glass substrates were functionalised with a TAD-tagged ATRP initiator via microcontact chemistry. By subsequent surface initiated ATRP, it was possible to graft micropatterned polymer brushes from the surface.[3]

References

1) K. De Bruycker, S. Billiet, H. A. Houck, S. Chattopadhyay, J. M. Winne, F. E. Du Prez, Chem. Rev. 2016, 116, 3919-3974.
2) K. De Bruycker, M. Delahaye, P. Cools, J. Winne, F. E. Du Prez, submitted 2017.
3) O. Roling, K. De Bruycker, B. Vonhören, L. Stricker, M. Körsgen, H. F. Arlinghaus, B. J. Ravoo, F. E. Du Prez, Angew. Chem. Int. Ed. 2015, 54, 13126-13129.

P066

ATTACHMENT OF NANOPARTICLE DRUG-RELEASE SYSTEMS ON "SHISH-KEBAB"-FUNCTIONALIZED POLY(ε-CAPROLACTONE) NANOFIBERS

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The use of biocompatible and biodegradable materials as implants is a promising approach to temporarily replace endogenous functions and replace tissue during a healing process. Electrospun fiber mats can be used in the field of tissue engineering and to engineer tendon/ligament-to-bone interfaces, [1] showing high surface to volume ratio and a good roughness, which is promising for initial cell attachment and growth. [2] Using Polycaprolactone (PCL) as a basic material for implants is favorable because of its good mechanical properties and its slow degradation. However, due to its hydrophobic characteristics PCL is an unfavorable material for cell attachment. Multiple approaches have been made to improve the cellular behavior such as plasma treatment or chemical modification. Another approach uses a “shish-kebab” coating of the electrospun fibers. Chitosan (CS)-PCL graft copolymers (CS-g-PCL) can spontaneously crystallize as kebabs on PCL nanofibers which act as shishes. [3] The “shish-kebab” coating of CS-g-PCL onto electrospun PCL fibers is a fast and scalable approach to create fibermats which are more attractive for human cells and allow further modification with nanoparticular drug-release systems by electrostatic adsorption.

References

1) Font Tellado et al., Advanced drug delivery reviews 2015, 94, 126–140.
2) Mirjalili, M.; Zohoori, S., J Nanostruct Chem 2016, 6 (3), 207–213.
3) Jing et al., ACS Appl. Mater. Interfaces, 2015, 7 (12), pp 6955–6965

P067

DESIGN OF REPROCESSABLE PCL-BASED SHAPE-MEMORY MATERIALS BY REVERSIBLE TAD CHEMISTRY

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A chemically cross-linked but remarkably (re)processable shape-memory polymer (SMP) was designed by crosslinking poly(ε-caprolactone) (PCL) stars via the efficient triazolinedione click chemistry, based on the very fast and reversible Alder-ene reaction of 1,2,4-triazoline-3,5-dione (TAD) with indole compounds.[1]

Shape-memory polymers (SMPs) are remarkable materials able to switch from a temporary shape to their initial permanent shape by the application of a stimulus, such as heat or light. Typically, the shape-memory effect is generally observed for chemically or physically cross-linked polymers that exhibit an elastomeric behavior above a phase transition, e.g. glass or melting transition. cross-linked semi-crystalline PCL is widely studied for the development of SMPs. As most of SMPs are irreversibly cross-linked material, their reprocessing is impossible preventing any recycling. Thereby, reversible reactions, allowing the formation/cleavage of the network, raise tremendous interest for the development of new SMPs.[2-4]

As demonstrated by the stress relaxation measurement, the labile character of the TAD-indole adducts under stress allowed for the remolding at will of the raw cross-linked material by compression molding, while keeping excellent shape-memory properties.[5]

References

1) S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne, F. E. Du Prez, Nat Chem 2014, 6, 815.
2) T. Defize, R. Riva, J.-M. Raquez, P. Dubois, C. Jérôme, M. Alexandre, Macromolecular Rapid Communications 2011, 32, 1264.
3) T. Defize, R. Riva, C. Jérôme, M. Alexandre, Macromolecular Chemistry and Physics 2012, 213, 187.
4) T. Defize, J.-M. Thomassin, M. Alexandre, B. Gilbert, R. Riva, C. Jérôme, Polymer 2016, 84, 234.
5) T. Defize, R. Riva, J. M. Thomassin, M. Alexandre, N. Van Herck, F. Du Prez, C. Jérôme, Macromolecular Rapid Communications 2017, 38.

P068

INDUCTION OF CHIRALITY IN β-TURN MIMETIC POLYMER CONJUGATES VIA POSTPOLYMERIZATION „CLICK“ COUPLING

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Inspired by helical biopolymers such as proteins or DNA, various synthetic helices have been constructed; among them a variety of dynamic helical polymers, giving the opportunity to induce chirality by a small chiral bias.[1-2]We were interested in studying the interplay of induced chirality during the polymerization in competition to a chiral center attached by postpolymerization chemistry. We therefore synthesized helical poly(*n*-hexyl isocyanate)s (PHICs) using chiral or achiral alkyne-functional organotitanium catalysts. The obtained helical polymers were coupled with chiral β-turn mimetic structures using the copper-catalyzed azide/alkyne cycloaddition (CuAAC) reaction,[3] in turn allowing to tune the distance between the PHIC-helix and the chiral center from 7 to 14 Å. The successful linkage of the PHIC-helix to the β-turn mimetic was confirmed by SEC, HPLC and MALDI-ToF MS. Circular dichroism spectra confirmed chirality induction from the chiral β-turn mimetic structure to the polymer backbone of the achiral PHIC over five chemical bonds *via* postpolymerization modification. In contrast, a linkage effect leading to reduced chirality was observed when an additional linker unit was incorporated in-between the β-turn mimetic structure and the polymer backbone.[4]

References

1) Green, M. M.; Peterson, N.C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. Science 1995, 268 (5219), 1860-1866.
2) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. Chem. Rev. 2009, 109 (11), 6102-6211.
3) Malke, M.; Barqawi, H.; Binder, W. H. ACS Macro Lett. 2014, 3 (4), 393-397.
4) Deike, S.; Binder, W. H. Induction of Chirality in β-Turn Mimetic Polymer Conjugates via Postpolymerization “Click” Coupling, Macromolecules 2017, accepted.

P069

INTERNALLY CATALYSED COVALENT EXCHANGE REACTIONS FOR (RE-)PROCESSABLE POLYMER NETWORKS

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Because of its dimensional stability, creep resistance and mechanical properties, thermosets are often the materials of choice in modern society. However, due to their fixed crosslinked nature, thermosets have to be made in their desired shape and in contrast with thermoplasts, they cannot be reprocessed or recycled. An attractive chemical strategy to achieve the combination of plastic and thermosetting properties in a synthetic material is offered by the introduction of reversible bonds into a polymer network, which are also known as covalent adaptable networks or CANs.[1,2] To achieve a swift exchange reaction, usually a catalyst needs to be included as a material additive,[3] resulting in problems with catalyst ageing or leaching. A possible solution to this problem is the use of internal catalysis or neighbouring group participation (NGP). In this work, the effect of neighbouring carboxylic acids in the transesterification reaction is investigated. The results of a preliminary model study are transferred on a material level to obtain CAN's without the use of an external catalyst.

References

1) C. J. Kloxin, T. F. Scott, B. J. Adzima & C. N. Bowman, Macromolecules, 2010, 43, 2643-2653.
2) W. Denissen, J. M. Winne & F. E. Du Prez, Chemical Science, 2016, 7, 30-38.
3) M. Capelot, M. M. Unterlass, F. Tournilhac & L. Leibler, ACS Macro Lett., 2012, 1, 789-792.

P070

DYNAMIC IMINOBORONATE-BASED BOROXINE CHEMISTRY FOR THE DESIGN OF AMBIENT HUMIDITY-SENSITIVE SELF-HEALING POLYMERS

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Developing intrinsic self-healing polymeric materials is of great interest nowadays to extend material lifetime and/or to prevent the replacement of damaged pieces [1]. Spontaneously humidity-sensitive healable polymer network built around the dynamic covalent B-O bonds [2] was templated through iminoboronate-based boroxine derivatives.

Combining the dynamic boroxine/boronic acid equilibrium [3] and the iminoboronate chemistry [4], it could be first possible to synthetize and characterize molecular models of low molecular weight to demonstrate our approach. We secondly inserted these modules within a polymer matrix to design polymeric materials able to self-heal without requiring any energy demanding external activation. Interestingly, this novel family of iminoboronate adduct-based materials can be readily produced upon a relatively simple and straightforward synthesis between boronic acid and diamine-based compounds. When using diamino-polypropylene glycol and 2-formylbenzeneboronic acid, we obtained a stretchy rubber polymer capable to self-heal when exposed at ambient humidity and allowing us to regenerate cut into species with a recovery of up to 90% its mechanical properties.

This work paves undoubtedly the way towards spontaneous healing applications for, e.g., coatings.

References

1) S. R. White et al., Nature, 409, 794–797 (2001)
2) S. J. Rowan et al., Angew. Chemie Int. Ed., 41, 898–952 (2002)
3) A. L. Korich, P. M. Iovine, Dalton Trans., 39, 1423–1431 (2010)
4) A. Bandyopadhyay, J. Gao, Chem. – A Eur. J., 21, 14748–14752 (2015)

P071

UNPRECEDENTED FLUOROALKENE-BASED COPOLYMERS THROUGH COBALT-MEDIATED RADICAL POLYMERIZATION

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The precision design of fluorinated copolymers is challenging but also attractive for future developments in a wide range of applications involving fluoropolymers, such as advanced coatings or purification membranes.[1–3] In particular, controlling the radical polymerization of fluoroalkenes remains extremely difficult because of the high reactivity of these monomers due to the lack of resonance stabilizing group on their double bond. Herein, Cobalt-Mediated Radical Polymerization (CMRP) was used to efficiently control the bulk copolymerization of perfluorohexylethylene (PFHE) and vinyl acetate (VAc). Well-defined statistical poly(PFHE-*stat*-VAc) copolymers with different compositions ($0 < F_{\mathrm{PFHE}} < 0.5$) were obtained accordingly. In some cases, fluorinated monomer content as high as ~80 % by weight were achieved. Reactivity ratios were determined ($r_{VAc} = 0.18$ and $r_{PFHE} = 0$) and emphasized a clear tendency for alternation. Single step approach and sequential polymerization were assessed for the synthesis of novel PFHE/VAc block copolymers. Finally, the acidic hydrolysis of the pendant ester groups of these block copolymers led to the formation of novel highly amphiphilic macromolecules bearing a PVOH hydrophilic segment and a hydrophobic PFHE-based block.

References

1) Moore, A. L. Fluoroelastomers Handbook: The Definitive User's Guide and Databook.; Plastic Design Library, William Andrew Publishing: Norwich, New York, 2005.
2) Cui, Z.; Drioli, E.; Lee, Y. M. Recent Progress in Fluoropolymers for Membranes. Prog. Polym. Sci. 2014, 39 (1), 164–198.
3) Ameduri, B.; Sawada, H. Fluorinated Polymers; Polymer Chemistry Series; The Royal Society of Chemistry, 2017.

P072

A VESICLE-TO-WORM TRANSITION PROVIDES A NEW HIGH-TEMPERATURE OIL THICKENING MECHANISM

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Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization is utilized to prepare diblock copolymer vesicles via polymerization-induced self-assembly (PISA)[1-3] directly in mineral oil. Poly(stearyl methacrylate)$_{13}$ -poly(benzyl methacrylate)$_{96}$ (PSMA$_{13}$-PBzMA$_{96}$) vesicles undergo a vesicle-to-worm transition on heating to 150 °C, as judged by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).[4] Variable temperature ^{1}H NMR spectroscopy indicates that this transition is the result of surface plasticization of the membrane-forming block by hot solvent, effectively increasing the volume fraction of the stabilizer block and so reducing the packing parameter for the copolymer chains. The rheological behavior of a 10% w/w copolymer dispersion in mineral oil is strongly temperature-dependent: the storage modulus increases by five orders of magnitude on heating above the critical gelation temperature of 135 °C, because the non-interacting vesicles are converted into weakly interacting worms. Detailed analysis of the SAXS data indicate that each vesicle produces on average three worms. Such vesicle-to-worm transitions offer an interesting new mechanism for the high-temperature thickening of oils.

References

1) N. J. Warren and S. P. Armes, J. Am. Chem. Soc., 2014, 136, 10174-10185.
2) M. J. Derry et al., Prog. Polym. Sci., 2016, 52, 1-18.
3) S. L. Canning et al., Macromolecules, 2016, 49, 1985-2001.
4) M. J. Derry et al., Angew. Chem. Int. Ed., 2017, DOI: 10.1002/anie.201609365

P073

PREPARATION OF CONCANAVALIN A DECORATED P(PEGMA-co-NMAS) POLYMERIC SURFACES AND UTILIZATION IN BACTERIAL CELL DETECTION

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Functional surfaces have a keen interest in biomedical applications like immunoassays, bio-sensing and cell adhesion because of easy modification with small molecules or polymers and controllable surface properties. In this study, Concanavalin A decorated P(PEGMA-*co*-NMAS) polymeric chains were synthesized on glass surfaces and used for detection of *E.coli* expressing green fluorescence gene. Briefly, glass surface has been treated with Piranha solution, (3-aminopropyl)triethoxysilane, and 2-bromo-butyrylbromide-triethylamine solution to obtain bromide functionalized surface initiator. Successively, polymeric hairy glass surfaces prepared by copolymerization of poly(ethylene glycol)methacrylate (PEGMA) and *N*-methacrylamido succinimide (NMAS) monomers on glass surfaces via surfaced induced atom transfer radical polymerization yielding an amine reactive polymeric surface. A lectin protein, Concanavalin A (Con A), was conjugated to the polymer surface via succinimidyl esters. Con A interacts with glycoprotein receptors containing mannose and glucose as *E.coli* expresses on the cell surface. This study has a great potential for development of a new diagnostic tool with high sensitivity and easy modification. Experimental steps were characterized by FT-IR, contact angle measurement and fluorescence microscopy. This work was financially supported by the TUBITAK (Project#: 2150139).

P074

SYNTHESIS OF PH SENSITIVE HYPERBRANCHED P(PLA-b-(PEGMA-co-NMAS)) POLYMERS VIA RING OPENING POLYMERIZATION AND ATOM TRANSFER RADICAL POLYMERIZATION

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Stimuli-responsive polymers have been employed in various biomedical applications due to their superior properties. Among such polymers, pH sensitive polymers allow controllable response in different pH level. Briefly, we attempt to synthesize pH sensitive hyperbranched P(PLA-*b*-(PEGMA-*co*-NMAS)) polymers which have a hydrophobic core and hydrophilic shell. Firstly, an acrylate based macromonomer of PLA (MPLA) was synthesized via ROP of the lactide monomer. An inimer, 2-(vinyloxy)ethyl 2-bromobutanoate, containing hemiacetal bond between acrylate and bromo functionality as the acid cleavable linkage was synthesized and utilized in ATRP of M-PLA yielding a bromo end-functional hyperbranched polymer [P(M-PLA)]. Subsequently, PEG methacrylate (PEGMA) and *N*-methacrylamido succinimide (NMAS) were copolymerized via ATRP with P(MPLA). PLA-based polymers have been studied extensively in delivery of hydrophobic drugs. Incorporation of P(PEGMA) provide solubility and biocompatibility, and succinimidyl moieties offer handle for conjugation of amine groups. Therefore, water soluble hyperbranched P(PLA-*b*-(PEGMA-*co*-NMAS)) polymers may take attention from the view point of solubility. All polymers were successfully characterized by GPC and NMR. This work was financially supported by Yildiz Technical University (Project # 2013-07-04-GEP01).

P075

FROM CARBON-SUPPORTED COPPER NANOMATERIALS TO SELF-HEALING NANOCOMPOSITES

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The exploitation of carbon-supported polymer nanocomposites has created an ambitious vision in material science, researching on self-healing materials repairing themselves autonomously after (mechanical) impact.[1-2]

We here describe the preparation of highly dispersed copper(I) nanoparticles immobilized onto graphene-oxide therefore obtaining a highly active, heterogeneous catalyst for the copper(I)-catalyzed azide-alkyne "click" (CuAAC) reaction.[3-4] Consequently, the reaction kinetics of crosslinking liquid and multivalent azides and alkynes was studied in solution *via* NMR spectroscopy as well as in bulk *via* DSC and rheology proving an excellent catalytic activity as well as a good recyclability.[3-4] In the next step, we have used this catalyst for the preparation of carbon-supported "click"-triggered self-healing epoxy nanocomposites enabling self-healing *via* fast and efficient "click" crosslinking while additionally showing good mechanical and conductive properties.[5] Therefore, the multivalent crosslinking agents have been either encapsulated or directly embedded into the epoxy matrix and the self-healing performance of the so obtained carbon-supported nanocomposites was investigated by DMA demonstrating an efficient crack healing at room temperature related to the high catalytic activity of the immobilized copper(I) nanoparticles as well as an enhanced tensile performance.[5]

References

1) L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, A. Mariconda, W. H. Binder, Smart Mater. Struct. 2014, 23, 045001.
2) W. H. Binder, Wiley-VCH, Weinheim, 2013, 440.
3) A. Shaygan Nia, S. Rana, D. Döhler, W. Osim, W. H. Binder, Polymer 2015, 79, 21-28.
4) A. Shaygan Nia, S. Rana, D. Döhler, X. Noirfalise, A. Belfiore, W. H. Binder, Chem. Commun. 2014, 50, 15374-15377.
5) S. Rana, D. Döhler, A. S. Nia, M. Nasir, M. Beiner, W. H. Binder, Macromol. Rapid Commun. 2016, 37, 1715-1722

P076

VINYLOGOUS URETHANE VITRIMERS: CONTROLLING THE VISCOELASTIC PROPERTIES VIA CATALYSIS

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Vinylogous urethane vitrimers are polymer networks that can undergo rapid network rearrangements, stress relaxation and viscoelastic flow through swift addition/elimination reactions of free amines. In this work, simple additives like acids and bases have been incorporated, which were found to significantly influence the covalent exchange kinetics on a molecular level and gave a wide range of viscoelastic properties on a material level. This strategy thus offers exquisite control of the viscoelastic properties of the vinylogous urethane materials, useful in the rational design of vitrimer elastomers with short relaxation times at elevated temperatures, but negligible exchange at service temperature, thus avoiding undesired elastomer creep.

References

1) Denissen, W., Rivero, G., Nicolaÿ, R., Leibler, L., Winne, J. M. and Du Prez, F. E. (2015), Vinylogous Urethane Vitrimers. Adv. Funct. Mater., 25: 2451–2457.
2) Denissen, W., Droesbeke, M., Winne, J. M. and Du Prez, F. E., Nature Communications, Accepted article

P077

ABSTRACT CANCELLED

P078

NOVEL PHOSPHONATE- AND BISPHOSPHONATE-FUNCTIONALIZED POLY(BETA-AMINO ESTER) NETWORK POLYMERS

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Poly(β-amino ester)s [PBAEs] are important as biomaterials due to their pH sensitivity, biodegradability and high biocompatibilities. In this work, we report on new biomaterials produced by incorporating phosphorus-containing building blocks into PBAEs, to combine the biodegradable, hemocompatible, protein adsorption resistant nature and strong affinity for hydroxyapatite-based tissues (such as dentin, enamel, and bone) of phosphonates and bisphosphonates with those of PBAEs.

Novel phosphonate and bisphosphonate-functionalized secondary diamines were prepared from the reactions of 1,4-butanediamine, 1,6-hexanediamine or 4,9-dioxa-1,12-dodecanediamine with diethyl vinyl phosphonate or tetraethyl vinylidene bisphosphonate, respectively. The PBAE macromers were prepared from Michael addition reaction of these amines to 1,6-hexane diol diacrylate (HDDA) and poly(ethylene glycol) diacrylate (PEGDA) efficiently without any catalyst and photopolymerized to give gels. The mass loss of the gels was found to be affected by the chemical structure of the network polymers. Also PBAE macromers were copolymerized with HEMA to produce hydrogels with customizable degradation rate. The degradation products are biocompatible with NIH 3T3 mouse embryonic fibroblast cells. The results support the use of the PBAEs produced as candidates for nontoxic degradable biomaterials.

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P079

SYNTHESIS AND EVALUATION OF BOTH PHOSPHONIC- AND BISPHOSPHONIC ACID FUNCTIONALIZED MONOMERS FOR LONGER-LASTING DENTAL FILLINGS

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It is possible to increase the lifetime of dental restorations by increasing the performances of 'self-etching' dental adhesives. In this work, the first monomers containing both phosphonic and bisphosphonic acid functionalities are synthesized since it was conjectured that they will have an interaction with tooth structure; and their properties are analyzed. For their synthesis, two amines having both phosphonate and bisphosphonate functionalities were synthesized via Michael addition reaction between diethyl 2-aminoethylphosphonate or diethyl 6-aminohexylphosphonate and tetraethyl ethylidenebisphosphonate. Reaction of these amines with acryloyl chloride or 2-isocyanatoethyl methacrylate gave new monomers with both phosphonate and bisphosphonate functionalities. Some of these monomers were converted to acid monomers by selective cleavage of these functionalities. Copolymerization reactivity of monomers with commercial monomers used in dental adhesives was studied using photo differential scanning calorimeter. The interaction of the acid monomers with HAP was investigated using Raman, XPS and XRD techniques.

This work was supported by a grant from the Scientific and Technological Research Council of Turkey (TÜBİTAK) (215Z060).

P080

SYNTHESIS AND CHARACTERIZATION OF POLYMER LINKER SYSTEMS FOR T-CELL ACTIVATION

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In the field of biomedicine specifically designed polymer brush systems gained much interest due to their ability to control a number of important architectural features[1] for the creation of particular biointerfaces[2] and applications in nanotechnologies on different substrates[3].

In this study it was of special interest to prepare a polymer linker system to glass substrates for monitoring of specific cell interactions via total internal reflection microscopy. Thus, uniform polymer brushes were prepared using reversible addition fragmentation chain transfer polymerization (RAFT), which facilitates a polymerization under gentle temperatures, without toxic catalysts, providing low dispersity and defined molecular weights. Poly-(N-acryloylmorpholine) and poly-(N-(3-methoxypropyl)acrylamide) polymers generated by RAFT with a MW of approximately 20 kDa were investigated via SLS, DLS and SAXS to determine their size, shape and structural stability in aqueous environments. The results of these measurements showed, that strong aggregation occurred in aqueous solution, and that the formed aggregates exhibited a Kholodenko-worm-like shape in water and PBS, indicating potential suitability for the targeted polymer brush system. Further approaches for grafting of polymers from glass substrates were analyzed via contact angle and ellipsometry.

References

1) Krishnamoorthy, M.; Hakobyan, S.; Ramstedt, M.; Gautrot, J. E. "Surface-Initiated Polymer Brushes in the Biomedical Field: Applications in Membrane Science, Biosensing, Cell Culture, Regenerative Medicine and Antibacterial Coatings"; Chemical Reviews 2014, 114 (21), 10976-11026
2) Xu, F. J.; Neoh, K. G.; Kang, E. T. "Bioactive surfaces and biomaterials via atom transfer radical polymerization"; Progress in Polymer Science 2009, 34 (8), 719-761
3) Ayres, N. "Polymer brushes: Applications in biomaterials and nanotechnology"; Polymer Chemistry 2010, 1 (6), 769-777.

P081

PROTONATION AND COMPLEXATION INDUCED SWITCHING OF INITIATORS FOR NITROXIDE MEDIATED POLYMERIZATION

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Recently, a new concept of pH-switchable agents for reversible addition–fragmentation chain transfer (RAFT) polymerization has been introduced by Benaglia et al.[1] Hereafter we extended the concept of pH-switchable mediators to nitroxide mediated polymerization (NMP) by employing nitroxides and alkoxyamines with basic or acidic groups as controlling agents. The alkoxyamines under investigation possess protonable groups in alkyl and nitroxyl parts. Consequently, we observed that protonation of alkyl part of alkoxyamine leads to the increase of homolysis rate constant k_d,[2] whereas protonation of nitroxide fragment decreases k_d.[3] The difference in k_d can be up 10 20 times. Hereinafter, we explored the influence of complexation on homolysis of alkoxyamine. For that we prepared complexes of $Zn(hfac)_2$ and $Cu(hfac)_2$ with alkoxyamines based on SG1-nitroxide.[4] Up to 20-fold-increase in k_d has been observed for complexes, thus becoming to be efficient way to activate homolysis. The influence of protonation and complexation of mediators on NMP was also investigated.

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References

1) Benaglia et al., J. Am. Chem. Soc.2009, 131, 6914–6915
2) Bagryanskaya et al., Macromolecular rapid communications 2012, 33, 152-157.
3) Edeleva et al. The Journal of organic chemistry 2011, 76, 5558-5573.
4) Audran et al. Inorganic Chemistry Frontiers 2016, 3, 1464-1472.

P082

DUAL INITIATOR ALKOXYAMINES WITH SG1 NITROXIDE MOIETY FOR PREPARATION OF BLOCK-COPOLYMERS

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Dual initiators for controlled radical/ionic polymerization reactions attract much attention in terms of preparation of new materials. We studied the potential of dual-initiator alkoxyamines based on both on para-substituted aromatic ring for external triggering or initiation of orthogonal polymerization and on N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) for nitroxide-mediated polymerization (NMP) with various monomers such as styrene, styrene sulphonate, 2-vinyl pyridine or methylmethacrylate. Alkoxyamines under investigation were found to be as efficient in the NMP process as N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl)hydroxylamine (so called SG1-MAMA, 1).

Moreover, in contrast to TEMPO-based alkoxyamines, our alkoxyamines are suitable for the co-polymerisation of MMA by NMP with different co-monomers such as styrene and 2-vinylpyridine and thus could be used for preparation of metal-crosslinked polymers. In general, SG1-based alkoxyamines are more efficient in NMP than those based on TEMPO. The carboxylic function in our alkoxyamines is reactive enough for both pre- and post-functionalisation as demonstrated by the preparation of PS-b-PEG via both approaches, with preservation of the main features of 1 in NMP.

P083

SYNTHESIS AND CHARACTERIZATION OF DIELS-ALDER MEDIATED POLY (ETHYLENE GLYCOL) BASED HYDROGELS

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Diels–Alder (DA) reactions are important organic reactions between conjugated dienes and substituted alkenes. For the past few decades, the interest in the application of such reaction mechanisms in polymer chemistry synthesis pathways have gradually improved due to ease in moiety formation and thermally reversible properties of end products.

In the present study, furan containing poly(ethylene glycol) (PEG) based polymeric intermediates were synthesized via ring opening reactions of PEG diglycidylether (Mn:500 g/mol) with furfurylamine. The obtained materials were characterized using ^{1}H-NMR, FT-IR and GPC. A subsequent crosslinking reaction of the pre-synthesized polymeric intermediate materials with different ratios of dimaleimide containing molecules were performed to obtain a stable hydrogel network. The hydrogels were then characterized using DSC, TGA and FTIR. In addition, the swelling properties, degradation properties and rheological properties of the hydrogels were evaluated to demonstrate suitable performance and applicability in drug delivery applications.

P084

PROTEIN ENCAPSULATION INTO NANOSTRUCTURED CACO3 MICROPARTICLES TEMPLATED BY PEO-b-POLYPHOSPHOESTER USING A SUPERCRITICAL CO2 PROCESS

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The use of calcium carbonate microparticles is becoming more and more attractive in biomedical applications as proteins carriers for their controlled delivery in the body. We investigate the protein encapsulation by *in situ* precipitation of calcium carbonate particles prepared by a process based on supercritical CO_2 and using a new type of degradable well-defined double hydrophilic block copolymer composed of poly(ethylene oxide) and polyphosphoester block with an affinity for calcium like poly(phosphotriester)s bearing pendent carboxylic acids on each repeating monomer unit[1] which evidenced an efficient structure for templating the formation of $CaCO_3$ leading to unprecedented small-sized particles[2]. Lysozyme was chosen as a model for therapeutic protein for its availability and ease of detection. It was found that by this green process, loading into the $CaCO_3$ microparticles with a diameter about 2 μm can be obtained as determined by scanning electron microscopy. A protein loading up to 6.5% active lysozyme was measured by a specific bioassay (*Micrococcus lysodeikticus*). By encapsulating fluorescent-labelled lysozyme (lysozyme-FITC), the confocal microscopy images confirmed its encapsulation and suggested a core–shell distribution of lysozyme into $CaCO_3$.

References

1) Z. Ergul Yilmaz, T. Cordonnier, A. Debuigne, B. Calvignac, C. Jérôme and F. Boury. Int. J. Pharm., 2016, 513, 130
2) Z. Ergul Yilmaz, A. Debuigne, B. Calvignac, F. Boury and C. Jérôme. J. Mater. Chem. B, 2015, 3, 7227

P085

PROTEIN ENCAPSULATION INTO NANOSTRUCTURED CaCO3 MICROPARTICLES TEMPLATED BY PEO-b-POLYPHOSPHOESTER USING A SUPERCRITICAL CO2 PROCESS

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The use of calcium carbonate ($CaCO_3$) microparticles is becoming more and more attractive in biomedical applications as proteins carriers for their controlled delivery in the body. We investigate the protein encapsulation by in situ precipitation of calcium carbonate particles prepared by a process based on supercritical CO_2 and using a new type of degradable well-defined double hydrophilic block copolymer composed of poly(ethylene oxide) and polyphosphoester block with an affinity for calcium like poly(phosphotriester)s bearing pendent carboxylic acids on each repeating monomer unit[1] which evidenced an efficient structure for templating the formation of $CaCO_3$ leading to unprecedented small-sized particles[2]. Lysozyme was chosen as a model for therapeutic protein for its availability and ease of detection. It was found that by this green process, loading into the $CaCO_3$ microparticles with a diameter about 2 μm can be obtained as determined by scanning electron microscopy. A protein loading up to 6.5% active lysozyme was measured by a specific bioassay (Micrococcus lysodeikticus). By encapsulating fluorescent-labelled lysozyme (lysozyme-FITC), the confocal microscopy images confirmed its encapsulation and suggested a core–shell distribution of lysozyme into $CaCO_3$.

References

1) Z. Ergul Yilmaz, T. Cordonnier, A. Debuigne, B. Calvignac, C. Jérôme and F. Boury. Int. J. Pharm., 2016, 513, 130
2) Z. Ergul Yilmaz, A. Debuigne, B. Calvignac, F. Boury and C. Jérôme.. J. Mater. Chem. B, 2015, 3, 7227

P086

WETTING PROPERTIES AND APPLICATIONS OF FLUORINATED POLYMER BLEND FILMS

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The control of surface wetting properties is very useful for many practical applications. Therefore, many methods have been developed to prepare polymer surfaces with desired wetting properties. Among these methods, blending is one of the most effective and can easily combine the beneficial properties of each component into one blended material. Fluorinated polymers have recently attracted much attention in both science and industry because of their ultralow surface energy, unique water and oil repellency, self-cleaning property, and excellent thermal and chemical stability. In order to control the wetting properties of commercially available polymers, in this study, fluorinated polymers with short fluorinated side chains were used as the blend components and their electrical and biological applications were suggested.

P087

AMYLOID BETA AGGREGATION IN THE PRESENCE OF TEMPERATURE-SENSETIVE POLYMERS

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The formation of amyloid fibrils is considered to be one of the main causes for many neurodegenerative diseases, such as Alzheimer's, Parkinson's or Huntington's disease [1]. Current knowledge suggests that amyloid-aggregation represents a nucleation-dependent aggregation process in vitro, where a sigmoidal growth phase follows an induction period. Here, we studied the fibrillation of amyloid β 1-40 (Aβ40) in the presence of thermoresponsive polymers, expected to alter the Aβ40 fibrillation kinetics due to their lower critical solution behavior [2-6]. To probe the influence of the molecular weight and the end groups of the polymer on its lower critical solution temperature (LCST) poly(methoxy di(ethylene glycol)acrylate)s with different LCSTs were synthesized. Also considering its concentration dependence in the presence of buffer-salts needed for the aggregation studies of Aβ40 mixtures in varying concentrations and a conjugate of Aβ40 with poly(methoxydi(ethylene glycol)acrylate)s were investigated via time-dependent measurements of the thioflavin T (ThT) fluorescence. The studies revealed that amyloid fibrillation was accelerated, accompanied by a reduction of the lag phase of Aβ40 fibrillation in the presence of poly(methoxy di(ethylene glycol)acrylate)s [6].

References

1) Chiti, F.; Dobson, C.M., Annu. Rev. Biochem. 2006, 75, 333
2) Hamley, I.W., Angew. Chem. Int. Ed. 2007, 46, 8128
3) Hamley, I.W., Chem. Rev.2012, 112, 5147
4) Sgarbossa, A., Int. J. Mol. Sci. 2012. 13(12): 17121
5) Arosio, P.; Cukalevski, R.; Frohm, B.; Knowles, T.P.J.; Linse, S., J. Am. Chem. Soc. 2014, 136, 219
6) Funtan, S.; Evgrafova, Z.; Adler, J.; Huster, D.; Binder, W.H., Polymers 2016, 8, 178

P088

STARCH BASED BRANCHED POLYACRYLAMIDE SYNTHESIZED BY Cu0-MEDIATED LIVING RADICAL POLYMERIZATION

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Starch based functional materials can in principle be prepared by a "grafting from" approach. In particular the homogeneous grafting of acrylamide from starch may allow the preparation of a water-soluble material that can profit from the branched structure of starch for a peculiar rheological behaviour. In this work waxy potato starch was dissolved in dimethylacetamide with the assistance of lithium chloride[1] and a water soluble macroinitiator (StBr) was then synthesized homogeneously by esterification of starch with 2-bromopropionyl bromide. After that the homogeneous grafting of polyacrylamide from StBr was carried out by aqueous Cu^0-mediated living radical polymerization with CuBr/Me_6Tren as catalyst[2]. ^{1}H-NMR, ^{13}C-NMR, gHSQC and FTIR were employed for the characterization of the starch-based macroinitiator while the starch-g-polyacrylamide (St-g-PAM) was characterized by ^{1}H-NMR and FTIR[3]. The molecular weight and polydispersity of PAM side chains were analysed by gel permeation chromatography (GPC) after hydrolysing the starch backbone. The kinetics of polymerization was determined according to the conversion rate of acrylamide monitored by gas chromatography (GC). A preliminarily rheological study was also performed on aqueous solutions of the prepared materials in this research.

References

1) Zhang, C., et al., Dissolution mechanism of cellulose in N,N-dimethylacetamide/lithium chloride: revisiting through molecular interactions. J Phys Chem B, 2014. 118(31): p. 9507-9514.
2) Jones, G.R., et al., Rapid Synthesis of Well-Defined Polyacrylamide by Aqueous Cu(0)-Mediated Reversible-Deactivation Radical Polymerization. Macromolecules, 2016. 49(2): p. 483-489.
3) Jane, J.-l., Starch: Structure and Properties, in Chemical and functional properties of food saccharides, P. Tomasik, Editor. 2004, CRC Press.

P089

IN SITU SCREENING OF POLYMERIC AMPHIPHILES FOR NUCLEIC ACID DELIVERY

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Here we describe a new method to synthesise and in situ screen polymeric amphiphiles and evaluate them in the delivery of small interfering RNA (siRNA). A poly(acryloyl hydrazide) scaffold is modified using readily available aldehydes to explore of a broad range of functionalities suitable for membrane permeability. The activity of the formed "modulated" polymeric amphiphiles (MAPs) can be in situ evaluated using both model membranes and model cell lines, without MAPs isolation and purification. This method constitutes an improved alternative to current screening methods and can underpin the discovery of new functional polymers with complex chemical functionality.

References

1) Priegue, J. M., Crisan, D. N., Martinez-Costas, J., Granja, J. R., Fernandez-Trillo, F., and Montenegro, J. (2016) In Situ Functionalized Polymers for siRNA Delivery. Angew. Chem., Int. Ed. 55, 7492–7495.

P090

PEPTIDE CHEMISTRY AND NANOTECHNOLOGY FOR THE TARGETED AND RESPONSIVE DELIVERY OF ANTIMICROBIALS

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Here we present the synthesis of new enzyme-responsive polyion complex (PIC) nanoparticles for the delivery of antimicrobials. Our efforts to optimise degradation kinetics, multivalency and charge density in our enzyme-responsive peptides will be described. Similarly, we will show how these enzyme responsive PIC nanoparticles are selectively degraded in the presence of *P. aeruginosa* elastase without being affected by other endogenous elastases. Moreover, these enzyme-responsive particles can exert an specific antimicrobial effect against *P. aeruginosa* without affecting non-pathogenic strains of these bacteria.

References

1) Insua, I., Wilkinson, A., and Fernandez-Trillo, F. (2016) Polyion complex (PIC) particles: Preparation and biomedical applications. Eur. Polym. J. 81, 198–215.
2) Insua, I., Liamas, E., Zhang, Z., Peacock, A. F. A., Krachler, A. M., and Fernandez-Trillo, F. (2016) Enzyme-responsive polyion complex (PIC) nanoparticles for the targeted delivery of antimicrobial polymers. Polym. Chem. 7, 2684–2690.
3) Insua, I., Majok, S., Peacock, A. F. A., Krachler, A. M., and Fernandez-Trillo, F. (2016) Preparation and antimicrobial evaluation of polyion complex (PIC) nanoparticles loaded with polymyxin B. Eur. Polym. J. doi: 10.1016–j.eurpolymj.2016.08.023.

P091

AMPHIPHILIC POLYMERIC ANTIOXIDANTS. A NEW PARADIGM FOR FAST DEGRADATION OF PLASTIC POLLUTION IN WATER

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In our research we have studied in aqueous environment the effect of ageing and degradation of styrene–butadiene rubber (SBR) and polyethylene (PE) modified with polymeric antioxidants. The molecular structure of the polymeric antioxidants represents a hydrophilic PEG polymer containing hydrophobic antioxidants moieties, namely 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate or 2-benzamido-3-(3,5-di-tert-butyl-4-hydroxyphenyl) acrylate, as end-groups that differ in activity and hydrophobicity. By simple variation of PEG molecular weight, the hydrophobic-hydrophilic balance could be easily tuned providing an ideal tool for creation of amphiphilic polymers.

P092

STRUCTURALLY DIVERSE, MULTIFUNCTIONAL NORBORNENE POLYMERS BASED ON THIOLACTONE CHEMISTRY

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Norbornene is mostly used in ring-opening metathesis polymerization (ROMP), resulting in high T_G, high transparency polymers with good electric properties, but only lately, involvement in the formation of more complex, functionalized polymer structures, has started.

Thiolactone chemistry has become more and more important in contemporary polymer research, combining the convenience and safety of protected thiols with the advantages and multiplicity of ‘thiol-X’ chemistries as well as easy-to-do one-pot double polymerization and modification reactions.

This poster describes the successful combination of appreciated properties of norbornene polymers, e.g. increased T_G, resilience etc., and the versatility of thiolactone chemistry using three different approaches: two thiolactone monomers with differently substituted norbornene moieties were synthesized and their potential for conjugated amine-thiol-ene polymerization, free radical (*co-*) polymerization (FRP) and ring-opening metathesis polymerization (ROMP) was evaluated, whereas only 5-norbornenemethyl (2-oxotetrahydrothiophen-3-yl) carbamate resulted in polymers in all three cases. For amine-thiol-ene polymerization, different amines, solvents and initiator concentrations were screened for their influence on molecular weight and T_G. The ROMP and FRP derived polymers were submitted to post-polymerization modification (PPM).

P093

CRYSTALLIZATION AND AGGREGATION BEHAVIOR OF POLYMER PEPTIDE CONJUGATES

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Proteins are among the most abundant macromolecules in nature, composed of amino acids (AA) and able to form usually complex architectures. Thus, well defined folding is a basic requirement for their unique properties and specific biological functions.[1] Especially the understanding of the secondary structure formation from polypeptides is essential as it depends strongly on their (bio)chemical environment.

We investigate the aggregation and crystallization behavior of various poly(AA)/poly(ethylene) (PE) hybrid-polymers. For that purpose, we synthesized several alkene-functionalized oligo-AA, able to induce secondary structures, which were subsequently converted by acyclic-diene-metathesis (ADMET) polymerization to higher molecular weight poly(AA)-PE-copolymers. Poly-L-glutamic acid, poly-L-aspartic acid and poly-L-leucine were selected as AA as they are known displaying a large conformational variability and dynamic α-helical-to-coil-transition.[2,3] Furthermore, single AA were polymerized *via* ADMET to achieve a periodic distribution of functional AA units along the PE-backbone.[4,5] In both cases the influence of the AA-defects onto the crystallization behavior of the PE chain was investigated *via* DSC- and WAXS-measurement revealing fully amorphous polymers for unpolar AA (L-leucine) and partially crystalline polymers the for polar AA (L-glutamic acid and L-aspartic acid).

References

1) Lee, D.; Redfern, O.; Orengo, C.,Nat. Rev. Mol. Cell. Biol., 2007, 8, 995-1005.
2) Novotná, P.; Urbanová, M., Vib. Spectrosc. 2013, 66, 1-7.
3) Miranda, R. A.; Finocchio, E.; Llorca, J.; Medina, F.; Ramis, G.; Sueiras, J. E.; Segarra, A. M., Phys. Chem. Chem. Phys. 2013, 15, 15645-59.
4) Reimann, S.; Baumeister, U.; Binder, W. H., Macromolecular Chemistry and Physics 2014, 215, 1963-1972.
5) Hopkins, T. E.; Wagener, K. B., Macromolecules 2003, 36, 2206-2214.

P094

MECHANOCATALYTICALLY ACTIVE POLYMER NETWORKS FOR FORCE-INDUCED COPPER(I)-CATALYZED AZIDE/ALKYNE “CLICK” REACTIONS

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Mechanochemistry allows to redirect destructive processes, triggered by the impact of mechanical energy, to defined chemical processes.[1] Polymeric bis(*N*-heterocyclic carbene) (NHC) copper(I)-complexes show mechanoresponsive behavior since they can be switched from their latent state to their active state by cleaving-off one of the shielding carbene ligands after applying mechanical stress by ultrasound in solution or compression in bulk. Thus, a catalytic active monocarbene Cu(I)-complex is formed, displaying catalytic activity for the copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC) for self-healing and damage-sensing applications.[2-4]

To increase the mechanochemical cleavage-efficiency, we incorporate the latent NHC copper(I)-complexes into the repetitive unit of elastin-like polypeptide (ELP) chains to obtain polymer networks where the latent Cu(I)-centers act as crosslinking points. It is assumed that the crosslinked polymer network acts as a handle improving the force-transmission to the labile copper-NHC bond, facilitating the bond-cleavage and subsequently the activation of the incorporated latent catalytic Cu(I)-centers. Consequently the efficiency of the CuAAC increased significantly compared to linear, non-crosslinked polymeric mechanocatalysts. ELPs were chosen as force-transmitting polymers because of their helical structure, implementing a high chain flexibility and a lever-effect.[5-6]

References

1) Li, J.; Nagamani, C.; Moore, J. S. Acc. Chem. Res. 2015, 48, 2181.
2) Michael, P.; Binder, W. H. Angew. Chem. Int. Ed. 2015, 54, 13918.
3) Gragert, M.; Schunack, M.; Binder, W. H. Macromol. Rapid Commun. 2011, 32, 419.
4) Rana, S.; Döhler, D.; Shaygan Nia, A.; Nasir, M.; Beiner, M.; Binder, W. H. Macromol. Rapid Commun. 2016, 37, 1715-1722.
5) Smits, F. C. M.; Buddingh, B. C.; van Eldjik, M. B.; van Hest, J. C. M. Macromol. Biosci. 2015, 15, 36.
6) Klukovich, H. M.; Kouznetovsa, T. B.; Kean, Z. S.; Lenhardt, J. M.; Craig, S. L. Nat. Chem. 2013, 5, 110-114

P095

MALEIMIDE- AND THIOL-FUNCTIONALIZED POLYOXAZOLINES FOR BIOCONJUGATION AND SURFACE FUNCTIONALIZATION

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Preventing surface biofouling is a key factor for the development of biosensors, medical implants, and microarray applications.[1] For many years, poly(ethylene glycol) (PEG) has been considered the main choice for these purposes. However, drawbacks such as immunogenicity, have sparkled a renewed interest for substitute materials.[2]

Poly(2-alkyl-2-oxazoline)s (PAOxs) appear as a promising alternative because variants with methyl and ethyl side chains share the physical characteristics of PEG,[3] with the advantage of an easier synthetic setup and the possibility to adjust their properties.[4]

For most of the aforementioned applications end-reactive PEG surrogates are required. In this line, we designed novel functional initiators for the ring-opening polymerization of 2-oxazolines, which allow the quantitative incorporation of a functional group at the α-chain end. [5] This leaves the more commonly employed ω-chain end available for further modification. The controlled polymerization of 2-ethyl-2-oxazoline using the new nosylate-based initiators was successfully shown via kinetics experiments monitored by GC and SEC. Structural details were obtained using NMR spectroscopy and ESI-MS. The functional PAOxs were used to graft onto proteins and surfaces, to study the resulting properties.

<u>References</u>

1) R. Konradi, C. Acikgoz, M. Textor. Macromol. Rapid Commun. 2012, 33, 1663–1676.
2) K. Knop, R. Hoogenboom, D. Fischer, U. S. Schubert. Angew. Chem. Int. Ed. 2010, 49, 6288–6308.
3) R. Hoogenboom. Angew. Chem. Int. Ed. 2009, 48, 7978–7994.
4) R. Hoogenboom, H. Schlaad. Polymers. 2011, 3, 467–488.
5) G. Gil Alvaradejo, M. Glassner, R. Hoogenboom, G. Delaittre. Submitted.

P096

µPET IMAGING OF THE BIODISTRIBUTION OF POLY(2-ETHYL-2OXAZOLINE) IN COMPARISON TO POLY(ETHYLENE GLYCOL)

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Poly(2-oxazoline)s (PAOx) are a promising class of polymers for biomedical applications and a versatile alternative to poly(ethylene glycol)s (PEG).[1-3] Therefore, it is of fundamental importance to gain an in-depth understanding of the biodistribution profile of PAOx. In the present contribution we investigate the biodistribution of well defined ^{89}Zr-labeled poly(2-ethyl-2-oxazoline)s (PEtOx) in a molar mass range of 5 to 110 kDa and a ^{18}F labeled 5 kDa PEtOx compared to ^{89}Zr-labeled PEG of 20 and 40 kDa by micro Positron Emission Tomography (µPET) molecular imaging in mice.[4, 5] As previously described for other classes of non-ionic polymers, the blood clearance of PEtOx decreased with molar mass. The cut off for glomerular filtration of PEtOx is likely to be around 40 kDa. While [^{18}F]-PEtOx displays a rapid and efficient clearance from the kidneys, 5 kDa [^{89}Zr]-Df-PEtOx is not efficiently cleared over the time course of the study, which is most likely caused by trapping of ^{89}Zr-labeled metabolites in the renal tubules and not the polymer itself, demonstrating the importance of selecting the appropriate label for biodistribution studies.

<u>References</u>

1) Luxenhofer, R.; Han, Y.; Schulz, A.; Tong, J.; He, Z.; Kabanov, A. V.; Jordan, R.; Macromol. Rapid Commun. 2012, 33, 1613-1631.
2) Sedlacek, O.; Monnery, B. D.; Filippov, S. K.; Hoogenboom, R.; Hruby, M.; Macromol. Rapid Commun. 2012, 33, 1648-1662.
3) de la Rosa, V. R.; J. Mater. Sci. - Mater. Med. 2014, 25, 1211-1225.
4) wyffels, L.; Verbrugghen, T.; Monnery, B. D.; Glassner, M.; Stroobants, S.; Hoogenboom, R.; Staelens, S.; J. Controlled Release 2016, 235, 63-71.
5) Glassner, M.; Palmieri, L.; Monnery, B. D.; Verbrugghen, T.; Deleye, S.; Stroobants, S.; Staelens, S.; wyffels, L.; Hoogenboom, R.; Biomacromolecules 2017, 18, 96-102.

P097

POLYMER FUNCTIONAL NANODIAMONDS BY LIGHT-INDUCED REACTIONS

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Nanodiamonds (NDs) are accessible in large quantities and with low cost from the detonation of carbon containing explosives. To introduce targeting functions and enhance the colloidal stability, their light-triggered modification in the absence of any catalyst and at ambient temperature is reported. For instance, *o*-methyl benzaldehyde groups – forming *o* -quinodimethanes (photoenols) upon UV irradiation – were attached to the surface of the NDs. The photoenol groups undergo Diels-Alder reactions with electron deficient double bonds, such as maleimides. For this purpose, various maleimide end group functional polymers were linked covalently to the NDs showing the modularity of the approach.[1] In addition to the direct light-driven homo-grafting, a strategy for the co-grafting of various functional polymers to graphitic nanodiamonds generated by thermal annealing of detonation nanodiamonds *via* the light-induced photo-enol reaction in only two subsequent reaction steps is reported.[2] The in-depth characterization of the NDs is supported by the investigation of the effect of the polymer chain length on the grafting efficiency of the glycopolymer functional NDs.

References

1) Wuest, K. N. R.; Trouillet, V.; Goldmann, A. S.; Stenzel, M. H.; Barner-Kowollik, C. Macromolecules 2016, 49, 1712-1721.
2) Wuest, K. N. R.; Trouillet, V.; Köppe, R.; Roesky, P. W.; Goldmann, A. S.; Stenzel, M. H.; Barner-Kowollik, C. Polym. Chem. 2017, in press.

P098

LIGHT-INDUCED CHEMISTRIES FOR MACROMOLECULAR PRECISION DESIGN

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The contribution highlights light-triggered chemistries employed in our team for macromolecular materials design. It will be demonstrated how such light-triggered conjugation chemistries can be employed in macromolecular synthesis as well as to alter the chemical and physical properties of various substrates. The specific protocols to be addressed include photo-induced cycloaddition reactions such as nitrile-imine tetrazole-ene cycloaddition (NITEC), phenacylsulfide chemistry, azirine chemistry as well as photoenol chemistry, some offering the possibility to be activated with visible light.The selected concepts offer vast possibilities for macromolecular precision design as well as for the modification of surface properties of various substrates on demand by spatially directed photonic fields.e.g. [1]-[5]

References

1) Hiltebrandt, K.; Elies, K.; D´hooge, D. R.; Blinco, J. P.; Barner-Kowollik, C. J. Am. Chem. Soc. 2016, 138, 7048–7054.
2) Delaittre, G.; Goldmann, A. S.; Mueller, J. O.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 11388–11403.
3) Claus, T. K.; Richter, B.; Hahn, V.; Welle, A.; Kayser, S.; Wegener, M.; Bastmeyer, M.; Delaittre, G.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2016, 55, 3817-3822.
4) Zydziak, N.; Konrad, W.; Feist, F.; Afonin, S.; Weidner, S.; Barner-Kowollik, C. Nat. Commun. 2016, 7, 13672.
5) Lederhose, P.; Chen, Z.; Müller, R.; Blinco, J.P.; Wu, S.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2016, 55, 12195-12199.

P099

SILOXANE FEATURES AND THEIR EFFECT ON THE OPTICAL PROPERTIES OF SILOXANE POLYCARBONATE COPOLYMERS.

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Polycarbonate-siloxane copolymers have improved lower temperature impact and release properties over BPA based polycarbonate and find wide application in many markets. Through the siloxane chain length and content the siloxane microphase segregation can be controlled and transparent PC-siloxane can be produced. Many factors that determine the transparency of PC-siloxanes are known and involve: polydimethylsiloxane content, polydimethylsiloxane chain length, the distribution over the copolymer chain, and are controlled through the reaction process conditions. Despite this knowledge often variation in transparency and haze is observed when using a given siloxane chain length and content.

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THE POWER OF CHAIN TRANSFER IN THE FIELD OF PHOTOPOLYMER APPLICATIONS

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Multifunctional (meth)acrylate-based thermosetting resins are state-of-the-art materials for modern photopolymer applications such as 3D structuring, dental medicine, tissue engineering, or microelectronics. However, highly-crosslinked, irregular photopolymer networks are created due to an unregulated, radical chain-growth curing mechanism. Resulting materials often suffer from low toughness and high polymerization-induced shrinkage stress.[1] Chain transfer strategies have been developed in order to regulate the radical curing process (e.g. thiol-ene chemistry[2]) and create tunable photopolymers with improved mechanical performance. We have adapted different chain transfer strategies (i.e. addition fragmentation chain transfer reagents,[3,4] silane-ene chemistry[5]) for the advancement of this strategy. With the presented tools we were able to create photopolymer networks with reduced shrinkage stress, high final conversion, tunable thermomechanical properties and improved toughness. First application oriented tests outline the potential of such photopolymers for lithography-based 3D structuring.[6]

References

1) S. C. Ligon-Auer, M. Schwentenwein, C. Gorsche, J. Stampfl and R. Liska, Polym. Chem., 7, 257-286 (2016)
2) C. E. Hoyle and C. N. Bowman, Angew. Chem., Int. Ed., 49, 1540-1573 (2010).
3) G. Moad, E. Rizzardo and S. H. Thang, Polymer, 49, 1079-1131 (2008).
4) C. Gorsche, T. Koch, N. Moszner and R. Liska, Polym. Chem., 6, 2038-2047 (2015).
5) J. Steindl, A. Svirkova, M. Marchetti-Deschmann, N. Moszner, C. Gorsche, Macromol. Chem. Phys., submitted.
6) C. Gorsche, K. Seidler, P. Knaack, P. Dorfinger, T. Koch, J. Stampfl, N. Moszner and R. Liska, Polym. Chem., 7, 2009-2014 (2016).

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SYNTHETIC MIMICS OF AFGPs, NOVEL ICE RECRYSTALISATION INHIBITORS

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Antifreeze glycoproteins (AFGPs) are found in many Arctic fish species, and enable them to survive at sub-zero temperatures. One of their key properties is to inhibit intracellular ice crystal growth which is often associated with cell death during cryopreservation. Therefore, AFGPs could have many applications in cell and tissue storage, enabling future regenerative medicine treatments. However, AFGPs are difficult to synthesise or extract from natural sources.

We are developing new mimics of AFGPs based on simple synthetic polymer scaffolds to both understand how they function and to translate to cell storage, reducing the need for toxic solvent-based cryoprotectants such as glycerol and DMSO. Here we will show our 2nd generation polymers which have been designed to mimic AFGPs and their application in cryopreservation.

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UNDERSTANDING PC-SILOXANE COPOLYMER BLENDS AND IMPACT ON SURFACE AESTHETICS

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Current trends for the use of plastics in consumer electronics applications show the need for improved thin-wall molding capabilities along with excellent molded part aesthetics. Polycarbonate-siloxane (PC-siloxane) copolymers and blends have been used frequently in these applications because of their good impact resistance. In this paper, we will present the results of atomic force microscopy (AFM) and color measurements on a range of PC-siloxane copolymer blends. This study has helped us to gain a better understanding of the relation between copolymer blend morphology and aesthetics.

P103

UNDERSTANDING THE EFFECT OF NANOPARTICLE RIGIDITY ON CELLULAR UPTAKE

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Polymeric nanoparticles have become increasingly relevant in biomedicine, with applications such as drug delivery and diagnostics. Our understanding of the mechanism by which these interact with biological systems has become less clear as nanoparticle design has become more complex. Herein we show a systematic study of the effect of nanoparticle rigidity on the degree of cellular uptake. We synthesised a library of PEGylated core-shell nanoparticles of 50 and 100 nm diameters, *via* RAFT emulsion polymerisation, with three different core polymer compositions of various T_g to modify nanoparticle rigidity. Nanoparticle uptake was monitored by flow cytometry and confocal microscopy. Our findings may aid future nanoparticle design.

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INKJET PRINTABLE SUPRAMOLECULAR POLYMERS: FROM 2D INTO 3D

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Inkjet printing is an attractive patterning technology[1] which has become increasingly accepted in industrial and scientific applications. The ability to deposit small volumes of liquid (pL) at precise locations in well-defined arrays makes it ideal for high-throughput coding, prototyping and materials fabrication[2] in such fields as graphics, textiles, electronics, nanotechnology, additive manufacturing and tissue engineering.[3]

In order to realise advanced applications from printable polymers, key parameters such as molecular weight, mechanical properties and formulation require consideration when designing materials. Whilst high molecular weight polymers are desirable in many applications, these can be challenging to print as a result of high solution viscosity. To address this, low viscosity formulations based on supramolecular polymers ($M_w < 3000$ Da) which are able to self-assemble on the substrate surface to form *pseudo* -high molecular weight polymer networks with attractive physical characteristics have been investigated.

Initial studies[4] focused on forming 2D images for high-throughput industrial coding from electronically complementary π-π stacking polymers using two different printing techniques (Drop-On-Demand and Continuous Inkjet). Complex 3D printed biocompatible structures[5] were then explored for regenerative medicine using hydrogen bonding polymer networks.

References

1) P. Calvert, Chem. Mater., 2001, 13, 3299–3305.
2) I. M. Hutchings and G. D. Martin, Inkjet Technology for Digital Fabrication, John Wiley & Sons Ltd., 2012.
3) M. Singh, H. M. Haverinen, P. Dhagat and G. E. Jabbour, Adv. Mater., 2010, 22, 673–685.
4) L. R. Hart, J. L. Harries, B. W. Greenland, H. M. Colquhoun and W. Hayes, ACS Appl. Mater. Interfaces, 2015, 7, 8906–8914.
5) L. R. Hart, S. Li, C. Sturgess, R. Wildman, J. R. Jones and W. Hayes, ACS Appl. Mater. Interfaces, 2016, 8, 3115–3122.

P105

RESPONSIVE POLYMER CONJUGATES OF CYCLIC PEPTIDE NANOTUBES AS NEXT GENERATION ANTIBIOTICS

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The formation of nanotubes from cyclic peptides was pioneered 1993 by Ghadiri.[1] One outstanding property is their anti-microbial activity based on the interaction with bacterial membranes.[2] As this mechanism is less susceptible to the development of resistances, such systems are ideal candidates to prevent a “post-antibiotic era” as predicted by the WHO.[3]

However, the aggregation of the cyclic peptide nanotubes (CPNT) into large assemblies, as well as their toxicity against mammalian cells display major drawbacks. By conjugation of polymers to CPNT, aggregation as well as tubular length can be restricted.[4] We herein present CPNT that are reversibly connected to a polymeric shell in order to achieve a stimuli responsive antimicrobial activity. Stealth polymers as poly(2-ethyl-2-oxazoline) or poly(ethylene glycol) containing brush polymers were used as a shell forming polymer to restrict unspecific toxicity.[5]

The connection between CPNT and polymer was designed to cleave upon reduction or the presence of virulence factors as proteases. Stimuli responsive membrane disruption was investigated via light scattering, dye leakage studies on artificial membrane models as well as using bacterial growth inhibition experiments.

References

1) Fernandez-Lopez, S.; Kim, H.-S.; Choi, E. C.; Delgado, M.; Granja, J. R.; Khasanov, A.; Kraehenbuehl, K.; Long, G.; Weinberger, D. A.; Wilcoxen, K. M.; Ghadiri, M. R., Nature 2001, 412, 452-455.
2) Fletcher, J. T.; Finlay, J. A.; Callow, M. E.; Callow, J. A.; Ghadiri, M. R., Chem. Eur. J. 2007, 13, 4008-4013.
3) WHO Antimicrobial resistance: Global report on surveillance; 2014; http://www.who.int/drugresistance/documents/surveillancereport/en/
4) Chapman, R.; Danial, M.; Koh, M. L.; Jolliffe, K. A.; Perrier, S., Chem. Soc. Rev. 2012, 41, 6023-6041.
5) Knop, K.; Hoogenboom, R.; Fischer, D.; Schubert, U. S., Angew. Chem. Int. Ed. 2010, 49, 6288-6308.

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SEQUENCE-DEFINED PEPTIDE-PEPTOID HYBRIDS

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Synthetic peptide and peptoid macromolecules are well-known for their secondary and tertiary structures as well as aqueous self-assembly.[1-3] However, only little is known about peptide-peptoid hybrids. Herein, we introduce a synthesis strategy for the modification of peptides, the synthesis of sequentially functionalised peptide-peptoid hybrids and oligopeptoids. Using solid-phase chemistry,[4] peptoid sequences can be synthesised from amino acids via Ugi-4-component reaction. Each peptoid sequence synthesised, which is generally sterically demanding and conformationally constrained, contains two independent R-groups, selected from hydrocarbons, sugars, or polymers, which provides a high chemical diversity for the synthesised macromolecules. Amongst, amphiphilic hybrids were manufactured and analysed for their self-assembly properties. Depending on the architecture, they displayed different self-assembly behavior.

This method may open avenues for the facile synthesis of precisely modified peptides or peptide-peptoid hybrids, and perhaps even artificial proteins that contain sequence-specifically inserted peptoid sequences. Finally, we have investigated the self-assembly behavior of relatively short peptide-peptoid hybrids synthesised using this process.

References

1) A. S. Knight, E. Y. Zhou, M. B. Francis, R. N. Zuckermann, Adv. Mater. 2015, 27, 5665.
2) J.-F. Lutz, J.-M. Lehn, E. W. Meijer, K. Matyjaszewski, Nat. Rev. Mater. 2016, 1, 16024.
3) J.-F. Lutz, M. Ouchi, D. R. Liu, M. Sawamoto, Science 2013, 341, 1238149.
4) R. J. Simon, R. S. Kania, R. N. Zuckermann, V. D. Huebner, D. A. Jewell, S. Banville, S. Ng, L. Wang, S. Rosenberg, C. K. Marlowe, Proc. Natl. Acad. Sci. 1992, 89, 9367.

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ZOOMING IN ON POLYMER FLOW REACTIONS VIA ON-LINE MASS SPECTROMETRY: A FACILE TOOL FOR EFFICIENT REACTION OPTIMIZATION

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On-line mass spectrometry analysis of continuous flow processes provides real time data and thus allows for rapid kinetic screening and in consequence efficient optimization of chemical reactions. A combination of both – continuous flow processing and on-line monitoring – constitutes an ideal tool in any chemical synthesis optimization. Especially for polymers, the classical spectroscopic on-line analysis tools (UV-Vis, infrared and NMR)[1] are not sufficient for a complete understanding of the reactions. Techniques such as ESI-MS to determine specific product patterns are much more valuable for modern precision polymer design.

The Passerini three-component reaction (Passerini–3CR)[2] is studied via on-line microreactor/ESI-MS reaction monitoring. Nowadays the isocyanide based multicomponent reaction suffers from high reagent excesses and long reaction times to obtain high yields. In here, a reaction protocol is proposed for excellent Passerini product yields (> 95%) within minutes reaction time and led to the development of block copolymer conjugation with variable block length, a synthesis target that was before not identified for Passerini reactions.

References

1) Haven J. J., Vandenbergh, J. and Junkers T., Chem. Commun., 2015, 51, 4611–4614.
2) Passerini M. and Simone L., Gazz. Chim. Ital., 1921, 51, 126.

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CAPILLARY BREAKUP EXTENSIONAL RHEOMETRY OF SUPRAMOLECULAR WATER SOLUBLE BUILDING BLOCKS

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Supramolecular polymeric assemblies provide a framework with a huge versatility compared to covalent polymeric systems. Metal-ligand bonded systems are in particular interesting because their bond characteristics can be easily tuned [1]. To understand how such systems behave under flow, the extensional rheological behavior of supramolecular solutions was investigated with Capillary Breakup Extensional Rheometry (CaBER) [2]. Linear and star-like poly(ethylene oxide) was functionalized with terpyridine [3]. The obtained telechelic polymers were dissolved in water and mixed with transition-metal salts. The formed bond between terpyridine moieties and metal ions led to supramolecular associations resulting in chain extension or, respectively, network formation [4]. Tuning the system by altering the ratio of metal ions to ligands, the polymer concentration or the metal ion nature, influences the extensional relaxation time which can be extracted from an elasto-capillary balance. This is expected to be related to a varying amount of formed assemblies.

References

1) Holyer, R. H., Hubbard, C. D., Kettle, S. F. A., and Wilkins, R. G. The kinetics of replacement reactions of complexes of the transition metals with 2, 2’, 2”-terpyridine. Inorg. Chem. 5, 4 (1966), 622–625.
2) Clasen, C., Plog, J. P., Kulicke, W. M., Owens, M., Macosko, C., Scriven, L. E., Verani, M., and McKinley, G. H. (2006). How dilute are dilute solutions in extensional flows? J. Rheol., 50(6):849–881.
3) Lohmeijer, B. G. G., and Schubert, U. S. Water-soluble building blocks for terpyridine-containing supramolecular polymers: Synthesis, complexation, and ph stability studies of poly(ethylene oxide) moieties. Macromol. Chem. Phys. 204, 8 (May 2003), 1072–1078.
4) Seiffert, S., and Sprakel, J. Physical chemistry of supramolecular polymer networks. Chem. Soc. Rev. 41, 2 (2012), 909–930.

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PHOTOACTIVE CELLULOSE NANOFIBRILS: A PLATFORM FOR FUNCTIONAL MATERIALS

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Due to their superior mechanical properties and biocompatible nature, cellulose nanofibrils (CNFs) attract significantly interests as functional and bioactive building blocks.[1, 2] Beside the outstanding mechanical properties, CNFs offer a high specific surface area providing a high density of functional groups available for subsequent modification. Recent studies demonstrated photo-induced nitrile imine mediated tetrazole-ene cycloaddition (NITEC) as a versatile route towards light-reactive molecularly dissolved cellulose or classical filter paper.[3]

Herein, we focus on colloidal CNFs equipped with tetrazole, and describe their synthesis in water, as well as their functionalization through photochemically complementary maleimide-carrying building blocks using NITEC. We will discuss that by the choice of maleimide compound, the properties of the hybrid materials can be modified on demand. In addition, we demonstrate the ability of a spatially resolved fluorescent self-reporting conjugation system on otherwise optically transparent hybrid CNF nanopapers. The approach serves as an instructive platform for a new field of applications based on materials from CNFs.

References

1) J. G. Torres-Rendon, T. Femmer, L. De Laporte, T. Tigges, K. Rahimi, F. Gremse, S. Zafarnia, W. Lederle, S. Ifuku, M. Wessling, J. G. Hardy, A. Walther, Adv. Mater. 2015, 27, 2989.
2) A. J. Benítez, F. Lossada, B. Zhu, T. Rudolph, A. Walther, Biomacromolecules 2016, 17, 2417.
3) A. Hufendiek, A. Carlmark, M. A. R. Meier, C. Barner-Kowollik, ACS Macro Lett. 2016, 5, 139.

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A MULTIFUNCTIONAL SYNTHETIC PROTOCOL FOR NOVEL, SEQUENCE-DEFINED MACROMOLECULES USING THIOACRYLATE CHEMISTRY

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Man-made polymers are unable to match the absolute control, i.e. precision in monomeric sequence order and conformational complexity that is found within bio-polymers such as DNA. Sequence-defined chemistry hopes to address this key challenge of synthetically copying Nature.

We have collaborated to further progress our work in sequence-defined chemistry. At UGhent, our expertise in thiolactone chemistry have enabled the development of new protocols that push the boundaries of precision synthesis and control over macromolecular architectures. [1–3] Whilst at QMUL, extensive work into the synthesis of thioacrylates resulted in a new class of functional monomers which were successfully polymerised by RAFT polymerisation. [4]

At UGhent we have developed a new, thiolactone-based, protecting group free, iterative protocol. [1] Automated equipment has demonstrated the versatility and huge potential of this thiolactone-based strategy. We hereby present the combination of a novel protocol to synthesise precise, sequence-defined structures using the aforementioned thioacrylates, yielding sequence-defined architectures which not only gave an extension to the monomeric alphabet but offer new potential properties and applications by using thioacrylates as functional pendant groups.

References

1) S. Martens, J. Van Den Begin, A. Madder, F. E. Du Prez and P. Espeel, J. Am. Chem. Soc., 2016, 138, 14182–14185.
2) P. Espeel, L. L. G. Carrette, K. Bury, S. Capenberghs, J. C. Martins, F. E. Du Prez and A. Madder, Angew. Chemie - Int. Ed., 2013, 52, 13261–13264.
3) P. Espeel and F. E. Du Prez, Eur. Polym. J., 2015, 62, 247–272.
4) S. Aksakal and C. R. Becer, Polym. Chem., 2016, 7, 7011–7018.

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MICROPARTICLES BASED ON POLYLACTIDE AND POLY(METHYL METHACRYLATE) BLENDS FOR CONTROLLED RELEASE OF HYDROPHOBIC BIOACTIVE AGENTS

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Partially biodegradable porous materials with incorporated bioactive agents prepared by simple techniques possess an enormous interest in tissue engineering applications. Polylactide-poly(methyl methacrylate) blends and methyl chavicol (hydrophobic bioactive agent) were utilized for microparticle preparation by oil-in-water solvent evaporation technique. The microparticles were characterized by scanning electron microscopy, particle size analysis and differential scanning calorimetry. Connected with methyl chavicol incorporation to the formulations the release was studied to determine the microparticles suitability for controlled drug delivery applications. The efficiency of encapsulation and release kinetics of methyl chavicol were evaluated by SPME-HS gas chromatography method.

Results showed the spherical shape, index polydispersity less than 2.0 and the microparticles with different glass-transition temperature. The porous structure obtained in the case of microparticles with incorporating methyl chavicol after hydrolytic degradation indicates the promising polymer blend compositions for long-lasting release applications.

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ANIONIC RING-OPENING ALTERNATING COPOLYMERIZATION PROMOTED BY A PHOSPHAZENE BASE

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During the recent development of organocatalytic polymerization, particular attention has been paid to the phosphazene superbase, *t*-BuP$_4$, because of its capability of activating various acidic groups without attacking the monomers, which has allowed for in situ (co)polymerization of epoxides from substrates carrying such initiating sites. So far, various polyether-based macromolecular architectures have been achieved in this manner including random, gradient, block, star, graft, and end-functionalized (co)polymers.1 Recently, a new member has been added in the club, the alternating copolymers. We have proven the feasibility to copolymerize several commonly used epoxides with a phenolic lactone, 3,4-dihydrocourmain, in an alternating manner from alcoholic initiators by the aid of *t*-BuP$_4$. The products are shown to have precisely alternating sequence distribution, and are composed of both linear and cyclic structures ascribed to the occurrence of intramolecular transesterification reaction. The major benefit of this system is the viability of using mono-, di-, tri-, or multi-hydroxy initiators to facilely achieve ω-hydroxy, α,ω-dihydroxy, three-arm star or brush-like alternating copolymers, which have exhibited good thermal stability and higher glass transition temperatures compared with the corresponding polyethers.2

References

1) Zhao, J.; Hadjichristidis, N.; Gnanou, Y. Polimery 2014, 59, 49.
2) Hu, S.; Dai, G.; Zhao, J.; Zhang, G. Macromolecules 2016, 49, 4462.

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AMINOLYSIS OF ACTIVATED CYCLIC MONOMERS—A POWERFUL SYNTHETIC TOOL FOR FUNCTIONALIZED BUILDING BLOCKS

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Aminolysis is typically a reaction where labile carboxylic acid derivatives react with amines resulting in the corresponding amide-containing product. Aliphatic polyesters and polycarbonates are susceptible to free amine-containing chemicals and chain scissions often occur. While it might detrimentally impact the chemical and physical properties of the products, the aminolysis chemistry by itself casts light on a synthetic pathway towards functional monomeric building blocks. Recent studies have shown efficient aminolysis chemistry for the ring-opening of thiol-lactones where the formed amide-thiols are readily available for "thiol-ene" chemistry.[1] Telechelic cyclic carbonates functionalized oligomers have also been studied extensively in the synthesis of isocyanate-free polyurethanes.[2]

We have designed an array of functional monomers using the aforementioned aminolysis chemistry. A more conventional sugar-derived lactone was used as the starting material and the resulting multifunctional amide monomers were applied as the building block for hydrogels, that proved to be highly efficient heavy-metal ion adsorbents.[3] Multifunctional hydroxyl-urethanes monomers were also constructed through aminolysis of cyclic carbonates and the urethane monomers were, again, crosslinked to a hydrophilic gel that after modification had high antibacterial qualities.

References

1) F. Goethals, S. Martens, P. Espeel, O. van den Berg and F. E. Du Prez, Macromolecules, 2014, 47, 61–69.
2) J. L. J. van Velthoven, L. Gootjes, D. S. van Es, B. A. J. Noordover and J. Meuldijk, Eur. Polym. J., 2015, 70, 125–135.
3) G. Hua and K. Odelius, ACS Sustain. Chem. Eng., 2016, 4, 4831–4841.

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ORGANOCATALYTIC COPOLYMERIZATION OF CO2 AND OXETANE: STEP FORWARDS IN GREEN CHEMISTRY FROM C1 SYNTHON TO POLYMER

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Carbon dioxide (CO_2), a renewable C1 feedstock, has been researched in producing valuable chemicals [1] for years. The success of synthesizing useful compounds derived from CO_2 not only affords alternative route to mitigate the emission of green gas but also allows the utilization of fossil fuel in decreasing. Therefore, developing efficient catalytic system to transform CO_2 into chemicals is still a great challenge in research field. Based on our previous research on the cycloaddition of CO_2 and epoxide under very mild conditions [2], herein we report a novel synthetic approach to copolymer by coupling CO_2 and oxetane using iodine and co-catalysts under low pressure. CO_2-based copolymer was obtained (M_n = 5.9kDa, $Đ_M$ = 1.43) from the characterization of ^{1}H-NMR and size exclusion chromatography (SEC).

References

1) Q. Liu, L. Wu, R. Jackstell, M. Beller, Nature Communications 2015, 6, 5933.
2) O. Coulembier, S. Moins, V. Lemaur, R. Lazzaroni, P. Dubois, Journal of CO2 Utilization 2015, 10, 7-11.

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THIOL-MALEIMIDE MICHAEL ADDITION AS A POWERFUL PLATFORM FOR BUILDING UNIMOLECULAR MACROMOLECULES

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Unimolecular macromolecules with uniform molecular weight, precise microstructures and well-defined topology, are challenging to synthesize, but they are crucial for an accurate and reliable investigation on structure-property relationships. In this article, metal-free, mild and “click” thiol-maleimide Michael addition was firstly used to synthesize unimolecular macromolecules on a gram scale *via* Iterative Exponential Growth strategy. A monomer with a furan-protected maleimide and a thioacetate group was designed and prepared, in which the maleimide and thiol group could be orthogonally deprotected in convenient ways. Unimolecular macromolecules with MW up to 27.4 kDa (128mer, 7.9 g) were prepared *via* this approach. Furthermore, unimolecular macromolecules with dendritic topology were formed by a second round thiol-maleimide Michael addition reaction. Upon simultaneous de-protections of maleimide and thiol groups, cyclic topology was also fabricated in high dilution. Moreover, using pre-designed cross thiol-maleimide Michael additions, a defined unit sequence was created, which was “easy to read” by MALDI-TOF-TOF owing to the breakable succinimide thioether bonds. This work thiol-maleimide Michael addition as a powerful platform for fabricating unimolecular macromolecules, which would facilitate the sophisticated structure-property research and applications of polymer-based materials.

References

1) Lutz, J.-F., Lehn, J.-M., Meijer, E. & Matyjaszewski, K. From precision polymers to complex materials and systems. Nature Reviews Materials 1, 16024 (2016).
2) Binauld, S., Damiron, D., Connal, L. A., Hawker, C. J. & Drockenmuller, E. Precise synthesis of molecularly defined oligomers and polymers by orthogonal iterative divergent/convergent approaches. Macromol. Rapid Commun. 32, 147-168 (2011).
3) Barnes, J. C. et al. Iterative exponential growth of stereo- and sequence-controlled polymers. Nature Chem. 7, 810-815 (2015).
4) Jiang, Y. et al. Iterative Exponential Growth Synthesis and Assembly of Uniform Diblock Copolymers. J. Am. Chem. Soc. 138, 9369-9372 (2016).
5) Lutz, J. F., Ouchi, M., Liu, D. R. & Sawamoto, M. Sequence-controlled polymers. Science 341, 1238149 (2013).

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STRUCTURE PROPERTY RELATIONSHIP OF LIGNIN INSPIRED PHENOLIC POLYETHERS SYNTHESIZED VIA ADMET

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In the past years, there has been a strong development in the field of polymer synthesis from renewable monomers, to provide alternatives to or replacements for crude oil based monomers. A significant share of industrially relevant polymers contains aromatic entities to ensure certain thermal and mechanical properties. Lignocellulosic biomass is an especially promising resource since it is abundant and does not compete with food or feed.

Key intermediates in the synthesis of renewable aromatic building blocks from lignin are vanillin, 4-hydroxybenzaldehyde, and syringaldehyde, which can be converted into diols.[1] A platform, consisting of dienes, was synthesized from potentially renewable lignin derived diols containing an aromatic moiety and other renewable diols with a related structure (14 diols in total). Subsequently, ADMET polymerization was performed on these dienes to investigate the influence of the monomer structure on the resulting thermal properties of the polymers. The remaining double bonds of the polymers, synthesized by ADMET polymerization, allow for further fine-tuning of the material properties by post-polymerization functionalization or crosslinking via triazolinedione chemistry.[2]

References

1) Caillol, S., et al. Green Chemistry. 2014;16(4):1987-1998.
2) Vlaminck, L., et al. Polymer Chemistry 2016, 7, 5655-5663.

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COMBINATION OF PHOSPHAZENE BASE AND LEWIS ACID : A TOOL FOR CHALLENGING ANIONIC POLYMERIZATION

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Phosphazene bases, which are characterized by an exceptional basicity, have been used in the domain of anionic polymerization.[1] They are very efficient to deprotonate very low acidic molecules, generating highly reactive species associated with bulky phosphazenium cations.[2] However phosphazene base catalyzed anionic polymerizations have demonstrated some drawbacks and limitations. Despite the high reactivity of the "propagating center / phosphazenium cation" system, attempts to polymerize low reactivity monomers, such as *N* -glycidylphthalamide, have failed.[3] Quite the opposite, this high reactivity has led during oxirane polymerizations to transfer reactions by the occurrence of nucleophilic attacks when carbonyl moieties are present on the initiator.[2, 4]

In this presentation, we will show that the addition of Lewis acid in the polymerization mixtures provides a solution to these seemingly contradictory problems. In a first example, the first anionic polymerization of *N* -glycidylphthalamide was performed using a phosphazene base and triisobutylaluminum system according to an activated monomer mechanism. In a second example, urethane initiators were stabilized by triisobutylaluminum and used in combination with *t* $\mathrm{BuP_4}$ to initiate the living ring-opening polymerization of butylene oxide.

References

1) Boileau, S., N. Illy: Prog. Polym. Sci., 2011, 36, 1132-1151.
2) Dentzer, L., Bray, C., Noinville, S., Illy, N., Guégan, P.: Macromolecules, 2015, 48, 7755-7764.
3) T. Isono, S. Asai, Y. Satoh, T. Takaoka, K. Tajima, T. Kakuchi and T. Satoh, Macromolecules, 2015, 3217-3229
4) J. Zhao, D. Pahovnik, Y. Gnanou, N. Hadjichristidis, Macromolecules, 2014, 47, 1693.

P118

2D NANOSTRUCTURES VIA CRYSTALLISATION-DRIVEN SELF-ASSEMBLY; SHAPE EFFECTS ON NANOCOMPOSITE HYDROGELS

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The widespread use of nanoparticles in medicine has been severely disadvantaged by low delivery efficiencies to targeted areas, where most particles are subject to the mononuclear phagocytic system and renal clearance pathways.[1] Major improvements in nanoparticle delivery and their interaction with cells are clearly needed, both in terms of administration of particles *in vivo* and in tuning of particle chemistry and morphology.

An emerging approach is the use of hydrogel delivery systems, though non-covalently cross-linked hydrogels often exhibit low mechanical strength, which limits their use in *in vivo* applications. The incorporation of polymeric particles can offer advantages in not only improved mechanical properties, but also in ease of tuning functionality for purpose.[2] Beyond spherical constructs, we have explored the use of crystallisation-driven self-assembly approaches to prepare 1D cylindrical and 2D platelet morphologies, which have been shown to display longer *in vivo* circulation times and improved cellular uptake.[3] Our results indicate that the morphology of our nanoscale additives plays a key role in determining the strength of alginate hydrogels.

References

1) S. Wilhelm, A. J. Tavares, Q. Dai, S. Ohta, J. Audet, H. F. Dvorak and W. C. Chan, Nat. Rev. Mater., 2016, 1, 16014.
2) L. Xiao, C. Liu, J. Zhu, D. J. Pochan and X. Jia, Soft Matter, 2010, 6, 5293-5297.
3) Y. Geng, P. Dalhaimer, S. Cai, R. Tsai, M. Tewari, T. Minko and D. E. Discher, Nat. Nanotechnol., 2007, 2, 249-255.

P119

NEW BN-EPOXY COMPOSITES OBTAINED BY THERMAL LATENT CATIONIC CURING WITH ENHANCED THERMAL CONDUCTIVITY

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Novel thermosetting epoxy materials were prepared by homopolymerization of DGEBA with a latent thermal cationic initiator, N-(p-methoxybenzyl)-N,N-dimethylanilinium hexafluoroantimonate[1] and glycerol.

The thermal conductivity was enhanced up to 300% by adding 5 to 20 wt. % of BN particles to the formulation. The addition of BN decelerated the curing but did not affect the latency of the curing agent, being the formulation stable for at least 3 months kept at room temperature. T_gs measured were around 130 ºC.

Rheological measurements allowed to determine viscoelastic properties and the percolation threshold, calculated to be 6.9 wt. % of BN. The Newtonian range decreased by the addition of filler. Both the conversion and time to reach the gelation decreased on increasing the proportion of BN.

Mechanical and dielectrical performance improved with the proportion of filler. Young modulus increased more than 50% and impact strength in 75%. Knoop microindentation hardness reached a maximum increase of 25% in the material with 10% of BN and shear strength was maintained up to 15 % of BN. Thermal expansion coefficient in the glassy state was reduced from 75 to 58 ppm/ºC.

References

1) S. Nakano, T. Endo. Cationic polymerization of glycidyl phenyl ether by benzylammonium salts. J. Polym. Sci.: Part A: Polymer Chemistry 33 (1995) 505-512.

P120

SYNTHESIS AND SELF-AGGREGATION OF POLY(2-OXAZOLINE)-BASED PHOTO-AND THERMO-RESPONSIVE BLOCK AND RANDOM COPOLYMERS

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Poly(2-alkyl-2-oxazoline)s (POxs) are bio-inspired polymers and termed as pseudopeptides due to structural similarity with polypeptides. POxs possesses all characteristics features required for different potential applications. Designing of poly(2-oxazoline)-based various multi-stimuli-responsive amphiphilic copolymers, their self-assembly behavior into micellar nanostructures and their applications in dye encapsulation/release is demonstrated. For example, poly(2-oxazoline)-based photo-responsive block copolymer (BCP), poly(2-ethyl-2-oxazoline)-*block* -poly(2-nitrobenzyl acrylate) (PEtOx-*b*-PNBA) is synthesized by CROP and ATRP.[1] The BCP self-assembles into primary micelles in THF/H_2O, which undergo secondary aggregation into compound micelles. Upon UV irradiation, photocleavage of PNBA block leads to disruption of micelles. Encapsulation of a guest molecule, nile red (NR), into BCP micellar core in H_2O and its UV-triggered release is investigated. A random copolymer poly(oligo(2-ethyl-2-oxazoline)acrylate)-*ran*-PNBA (P(OEtOxA)-*ran*-PNBA) with dual thermo- and photo-responsiveness is also achieved with via CROP and RAFT techniques. The P(OEtOxA)-*ran*-PNBA exhibits LCST-type phase behavior and effect of UV-irradiation on T_{cp} of P(OEtOxA)-*ran*-PNBA is investigated. Amphiphilic nature of copolymer causes them to self-assemble into spherical micelles in H_2O and effect of UV light/temperature on copolymer assemblies is also explored. Finally, thermo- and photo-triggered release of NR from copolymer micelles is demonstrated.

References

1) J. Phys. Chem. B, 2016, 120 (4), pp 813–824

P121

MOLECULAR LOGIC GATES BASED ON MULTI-STIMULI RESPONSIVE PHOTOCHROMIC POLY(2-ETHYL-2-OXAZOLINE) S

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Due to the increasing demands of information technology for miniaturization, the design and construction of molecular systems capable of information processing has attracted considerable attention in recent years[1,2]. Molecular logic describes a concept of computation using chemical structures and has recently gained certain attention[3]. Logic gates are switches whose output state (0 or 1) depends on the input conditions (0 or 1). Molecular logic gates which can simultaneously treat multiple inputs are interesting as intelligent "bottom-up" materials. Polymer based logic gates have the advantage of being much more processable and more versatile in the type of output and input signals than logic gates based on small molecules[4]. Poly(2-ethyl-2-oxazoline) is a typical polymer with sharp phase transition behavior in water in response to changes in temperature. Also, narrow distributions can be obtained by living cationic polymerization and various functional groups can be easily introduced to both initiation and termination ends[5].

In this communication, we report colorimetric logic gates or smart sensors with a sharp response based on the most important input parameters temperature, light and pH.

References

1) J. Ling, B. Daly, V.A.D. Silverson, A.P. de Silva, Taking baby steps in molecular logic-based computation, Chemical Communications 51(40) (2015) 8403-8409.
2) J.R. Nilsson, M.C. O'Sullivan, S. Li, H.L. Anderson, J. Andreasson, A photoswitchable supramolecular complex with release-and-report capabilities, Chemical Communications 51(5) (2015) 847-850.
3) A.P. de Silva, S. Uchiyama, Molecular logic and computing, Nat Nano 2(7) (2007) 399-410.
4) P. Schattling, F.D. Jochum, P. Theato, Multi-stimuli responsive polymers - the all-in-one talents, Polymer Chemistry 5(1) (2014) 25-36.
5) K. Lava, B. Verbraeken, R. Hoogenboom, Poly(2-oxazoline)s and click chemistry: A versatile toolbox toward multi-functional polymers, European Polymer Journal 65 (2015) 98-111.

P122

H2O2 ENABLES CONVENIENT REMOVAL OF RAFT END-GROUPS FROM BLOCK COPOLYMER NANO-OBJECTS PREPARED VIA POLYMERIZATION-INDUCED SELF-ASSEMBLY IN WATER

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RAFT synthesised polymers are often coloured and malodorous due to the presence of the sulfur-based RAFT end-group(s). In principle, such RAFT end-groups can be removed by treating molecularly-dissolved copolymer chains with excess free radical initiators or amines or oxidants.[1,2] Herein we report a convenient method for the removal of RAFT end-groups from aqueous dispersions of diblock copolymer nano-objects using hydrogen peroxide. This oxidant is relatively cheap, has minimal impact on the copolymer morphology and produces benign side-products that can be readily removed via dialysis. We investigate the efficiency of end-group removal for various nano-objects prepared using either dithiobenzoate or trithiocarbonate CTAs using UV GPC.[3]

References

1) Harvison, M. A.; Roth, P. J.; Davis, T. P.; Lowe, A. B. Aust. J. Chem. 2011, 64, 992.
2) Willcock, H.; O'Reilly, R. K. Polym. Chem. 2010, 1, 149.
3) Jesson, C. P.; Pearce, C. M.; Simon, H.; Werner, A.; Cunningham, V. J.; Lovett, J. R.; Smallridge, M. J.; Warren, N. J.; Armes, S. P. Macromolecules 2017, 50, 182.

P123

MESOPOROUS POLYSTYRENE FUNCTIONALIZED WITH BENZYL-PHENYLTRIAZOLES USING CLICK CHEMISTRY.

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The synthesis of a triazole end functionalized styrene mesoporous polymer with capability to complex metal cations is reported. Segregation and selective degradation of the block copolymer (PS-b-PLA) strategy was selected to prepare this material. The poly(styrene) block was chain-end functionalized with a triazole group and a poly(lactic acid) which was chosen as the sacrificial block. The copolymer was prepared with a sequential ATRP-ROP polymerization, started with the preparation of PS macroinitiator with a trifunctional initiator, 2-hydroxyethyl-2-bromo-2-(4-(mercaptomethyl) phenyl)propanoate, this compound bears α-halo carbonyl, hydroxyl and thiol moieties. The synthesis starts with the carboxy-alkylation of 4-chloro styrene with CO, methanol and palladium triphenylphospine as catalyst.

The methyl-2-(4-(chloromethyl)phenyl)propanoate was further modified through ultrasonic reaction with NaHS, hydrolyzed with NaOH and esterified with ethyleneglycol, finally bromated with NBS. The initiator was polymerizated with styrene to produce a macroinitiator which was co-polymerized with d,l-lactide using microwave energy. The azide group was introduced through thiol-ene reactions. The mesoporous polymer was obtained after the phase segregation with a thermal sheer stress process and alkaline hydrolysis to remove the PLA block, the resulting material show cylindrical cavities.

P124

HEXADIENE GLYCIDYL ETHER: A VERSATILE PLATFORM FOR ULTRA-FAST CROSSLINKING AND FUNCTIONALIZATION OF POLYETHERS BY TRIAZOLINEDIONE CLICK

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Poly(ethylene glycol) (PEG) is known as the “gold standard” biocompatible water-soluble polymer. Multi-functional polyethers can be synthesized by ring opening polymerization of epoxide derivatives.[1] Especially functional moieties which can be addressed via “click” reactions like Diels-Alder reactions are favorable due to their mild reaction conditions. Furan moieties have been proven to be a suitable group for [4+2] cycloaddition with maleimides. A major drawback is the usually occurring retro Diels-Alder reaction at elevated temperatures and in some cases low conversion. To overcome this issue, 4-substituted 1,2,4-triazoline-3,5-diones (TADs) can be used instead of maleimides. TADs are known to be highly reactive dienophiles.[2] We report the synthesis of hexa-2,4-diene glycidyl ether (HDEGE), a novel diene functional epoxide monomer which is suitable as a diene compound for DA “click” reactions. Polyethers based on HDEGE, ethoxyethyl glycidyl ether, propylene oxide and ethylene oxide were prepared via monomer activated technique[3] to obtain copolymers with varying HDEGE content. The HDEGE moieties were further reacted with 4-phenyl-1,2,4-triazole-3,5-dione and 4,4’-(4,4’-diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione) (BisTAD) as dienophile leading to quantitative, irreversible functionalization within seconds. In case of BisTAD highly crosslinked networks are obtained.

References

1) Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F. R.; Frey, H. Chem. Rev. 2016, 116 (4), 2170-2243
2) Billiet, S.; de Bruycker, K.; Driessen, F.; Goossens, H.; van Speybroeck, V.; Winne, J. M.; Du Prez, F. E. Nature chemistry 2014, 6 (9), 815–821.
3) Deffieux, A.; Carlotti, S.; Desbois, P. Macromol. Symp. 2005, 229 (1), 24–31.

P125

IN SITU SMALL-ANGLE X-RAY SCATTERING STUDIES OF THE FORMATION AND GROWTH OF DIBLOCK COPOLYMER NANOPARTICLES DURING POLYMERISATION-INDUCED SELF-ASSEMBLY IN ALCOHOLIC MEDIA

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In principle, *in situ* small-angle X-ray-scattering (SAXS) enables monitoring of the formation and growth of diblock copolymer nanoparticles via polymerisation-induced self-assembly (PISA). The specific PISA formulation examined in this work is the reversible addition−fragmentation chain transfer (RAFT) alcoholic dispersion polymerisation of benzyl methacrylate (BzMA) using poly(2-(dimethylamino)ethyl methacrylate) (PDMA) as the RAFT macro-CTA. Varying the mean degree of polymerisation (DP) of each block enables access to three different copolymer morphologies: spherical micelles, worm-like micelles or vesicles. SAXS enables the evolution in particle size to be studied as a function of monomer conversion for kinetically-trapped $PDMA_x$-$PBzMA_y$ spheres. When targeting $PDMA_x$-$PBzMA_y$ vesicles, the gradual evolution of copolymer morphology during PISA from spheres to worms to vesicles is confirmed. Within vesicle phase space, the membrane thickness (T_m) increases monotonically with PBzMA DP while the overall vesicle diameter remains constant. Thus, the constrained vesicles grow inwards, as recently reported for both aqueous and non-polar PISA formulations. This ultimately leads to vesicle instability (or vesicle ‘death’) and suggests a universal vesicle growth mechanism for all PISA formulations.

P126

ADSORPTION OF SMALL CATIONIC NANOPARTICLES ONTO LARGE ANIONIC PARTICLES FROM AQEUOUS SOLUTION: A MODEL SYSTEM FOR UNDERSTANDING PIGMENT DISPERSION AND THE PROBLEM OF EFFECTIVE PARTICLE DENSITY

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Reversible addition−fragmentation chain transfer (RAFT) alcoholic dispersion polymerisation was used to synthesise diblock copolymer nanoparticles. The steric stabiliser block was poly(2-(dimethylamino)ethyl methacrylate) (PDMA) and the core-forming block was poly(benzyl methacrylate) (PBzMA). Aqueous electrophoresis measurements confirmed that these $PDMA_{71}$−$PBzMA_{100}$ nanoparticles acquired cationic character when transferred from ethanol to water. Electrostatic adsorption of these nanoparticles from aqueous solution onto 470 nm silica particles led to either flocculation at submonolayer coverage or steric stabilisation at or above monolayer coverage. DLS indicated that saturation coverage was achieved on addition of approximately 465 copolymer nanoparticles per silica particle. TEM studies indicated that the cationic nanoparticles remained intact on the silica surface after electrostatic adsorption, while aqueous electrophoresis confirmed that surface charge reversal occurred below pH 7. The relatively thick layer of adsorbed nanoparticles leads to a significantly reduced effective particle density; from 1.99 g cm^{-3} for the silica particles to approximately 1.74 g cm^{-3}, as judged by disk centrifuge photosedimentometry (DCP). Combining the DCP and SAXS data suggests that essentially no deformation of the PBzMA cores occurs during nanoparticle adsorption onto the silica particles.

P127

ENHANCED IONIC CONDUCTIVITY OF A 1,2,3-TRIAZOLIUM-BASED POLY(SILOXANE IONIC LIQUID) HOMOPOLYMER

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A 1,2,3-triazolium-based poly(siloxane ionic liquid) (PSIL) is synthesized by UV-triggered thiol-ene ligation between poly[(mercaptopropyl)methylsiloxane] and a tailor-made vinyl-functionalized triethylene glycol-based 1,2,3-triazolium ionic liquid. The quantitative nature of the thiol-ene coupling is demonstrated by ^{1}H and ^{13}C NMR whereas properties of this new PSIL are discussed based on solubility, size exclusion chromatography, differential scanning calorimetry, thermogravimetric analysis and broadband dielectric spectroscopy measurements. Besides exhibiting low glass transition temperature (T_g = –62 °C) and high thermal stability (T_{d10} = 284 °C) this new class of poly(1,2,3-triazolium) demonstrates the highest value of bulk anhydrous ionic conductivity reported to date for PILs ($\sigma_{DC} = 7 \times 10^{-5}$ S.cm^{-1} at 30 °C).

References

1) M. M. Obadia and E. Drockenmuller, Chem. Commun., 2016, 52, 2433–2450.
2) A. Jourdain, A. Serghei and E. Drockenmuller, ACS Macro Lett., 2016, 5, 1283–1286.

P128

SEQUENCE-CODED POLYURETHANE BARCODES FOR PLASTIC MATERIALS LABELLING

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Anti-counterfeit technologies have become very important during the last decades, for example in the domains of food and pharmaceutical packaging, paper currency, luxury products and high-value artworks. These technologies require novel techniques for tracing commercial products that are extremely difficult to be copied but very efficient for discriminating original products from fraud ones. In this context, sequence-coded polymer barcodes have recently been proposed as an interesting new option. In the present work, digitally-encoded polyurethanes, synthesized by orthogonal solid-phase synthesis, were tested as molecular barcodes. The inclusion of these sequence-coded labels into commodity plastics, such as polystyrene films, photopolymerized 3D methacrylate prints and intraocular implants, was studied and their extraction was investigated by mass spectrometry and NMR. In all cases, the labels were efficiently extracted from the plastic materials and their coded sequences were easily deciphered by tandem mass spectrometry. These results indicate that sequence-coded polyurethane tags represent a promising class of polymers for product labeling and traceability.

References

1) J.-F. Lutz, M. Ouchi, D. R. Liu, M. Sawamoto, Science 2013, 341, 1238149.
2) H. Colquhoun, J.-F. Lutz, Nat. Chem. 2014, 6, 455.
3) H. Mutlu, J.-F. Lutz, Angew. Chem., Int. Ed. 2014, 53, 13010.
4) U. S. Gunay, B. E. Petit, D. Karamessini, A. Al Ouahabi, J.-A. Amalian, C. Chendo, M. Bouquey, D. Gigmes, L. Charles, J.-F. Lutz, Chem 2016, 1, 114-126.
5) D. Karamessini, B. E. Petit, Michel Bouquey, L. Charles, J.-F. Lutz, Adv. Funct. Mater 2017, 27, 1604595

P129

NEW QUINOXALINE CONTAINING DONOR-ACCEPTOR TYPE CONJUGATED POLYMERS FOR ORGANIC SOLAR CELLS

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Quinoxaline demonstrates electron accepting properties due to imine nitrogens. Benzotriazole derivatives with their electron withdrawing imine groups in their structures also lead to exhibit high electron transporting ability. Benzodithiophene moieties demonstrate electron donor property due to the structure of benzene with coherent thiophene units. Bringing together these groups yields a conjugated copolymer with broad absorption band in the visible region. In this study, random copolymers including quinoxaline derivatives; 5,8-dibromo-2,3-di(thiophen-2-yl) quinoxaline,5,8-dibromo-2,3-diphenylquinoxaline, 10,13-dibromo-8b,14a-dihydrodibenzo(a,c)phenazine)), and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy) benzo[1,2-b:4,5-b′]dithiophene and 4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole were synthesized.1H and 13C-NMR spectroscopy were used to investigate the structure of monomers and polymers. Optical studies were performed in order to investigate absorption behaviour of polymers. P1, P2 and P3 demonstrate maximum absorption peaks around 374/539, 493/535 and 488/532 nm and their band gap values were calculated as 1.74, 1.87 and 1.70 eV respectively. Bulk heterojunction photovoltaic devices were fabricated using the synthesized polymers as electron donors with fullerene derivatives where power conversion efficiencies were found as 0.97 and 0.95% for P1 and P2. Device fabrication of P3 and enhancement studies for P1 and P2 are underway.

P130

EPOXY BASED HYBRID ELECTROLYTE FOR STRUCTURAL ENERGY STORAGE DEVICE

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We prepare epoxy-based networked polymer electrolytes including Li salts with either ionic liquids or plastic crystals. The epoxy resins are particularly attractive as polymer matrices for solid polymer electrolytes due to their high mechanical performance combined with good adhesive properties. The selected electrolyte components are allowed to boost ionic conductivity owing to solvating the lithium cation and plasticizing the epoxy matrix. As a result, the curing of a homogeneous mixture of epoxy and electrolyte can generate a two-phase system in which the epoxy phase is selected to provide mechanical strength and the electrolyte phase is selected to maximize ionic conductivity. This can be the strategy to achieve the simultaneous improvement in both mechanical and ion conduction properties of polymer electrolytes. Here, we conduct an investigation of the effect of electrolyte types and their concentration on the conductometric/dielectric/rheological properties of epoxy-based networked polymer electrolytes. We measure ionic conductivity, dielectric constant and viscosity of a series of epoxy-based polymer electrolytes, where the concentration of epoxy resin and electrolyte is varied, using dielectric relaxation spectroscopy and oscillatory shear.

P131

SYNTHESIS OF DABCO BASED CATIONIC POLYMERS WITH ROMP TECHNIQUE AND EXAMINATION OF THEIR ANTIBACTERIAL ACTIVITY

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Bacterial infection, as a global problem, become more important especially in the last decades due to rising death rates. The new generation antibiotics are quite important for fighting against the bacteria. Basically, there are two main categories of new generation antibiotics: the host defense peptides and their synthetic analogues of host defense peptides. Antimicrobial synthetic polymers are one of the most important mimics for host defense peptides. It is also well known that amphiphilic polymers disrupt the cell membranes of the bacteria and can realize the cell death.

This paper focuses on the synthesis of polymers with well defined architecture derived by Ring Opening Metathesis Polymerization technique.In the scope of this work, the monomers containing DABCO and pyridine have been used to synthesize polymers with molecular weights of 3000 g/mole and 10000 g/mole.The synthesized polymers have a cationic structure with the advantage of having high interaction with the anionic surfaces of the bacteria. The hemolytic concentration and Minimum inhibitory concentration values of DABCO based polymers have been measured as 400 µg/mL and 4 µg/mL respectively.

P132

INVESTIGATION OF FIBRINOGEN ADSORPTION ON POLYURETHANE FILMS USING BROWNIAN DYNAMICS SIMULATIONS

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Controlling protein adsorption is very important for the implementation of materials in different biomedical applications, however it is a very challenging task due to numerous properties of proteins, solutions and surfaces. Various studies try to bring different perspectives to enlighten the effect of individual properties in this complex phenomena, but their synergetic effects make this task difficult. In this study, fibrinogen adsorption on polyurethane (PU) surfaces is investigated using Brownian dynamics simulations, where the effect of properties of PUs and proteins could be studied individually. PU films are modeled as grid surfaces with different degrees of roughness, crystallinity and hard/soft domains patterns, being important surface properties of PUs in protein adsorption [1]. The highly flexible fibrinogen molecule is described as three spherical nodes connected by springs. Simulations with simplified bonded and non-bonded interactions give testable results on which PU property is the most effective on fibrinogen adsorption. The effect of shape and flexibility of proteins on adsorption is also investigated by comparing results from previous simulations with one spherical node model of albumin on same PU film models.

References

1) Kurkcuoglu, O. and Guner, F. S., 2015. Polyurethane Surfaces: Protein Adsorption, Encyclopedia of Biomedical Polymers and Polymeric Biomaterials, 9, 6724-6742.

P133

EXPLORING MOLECULAR INTERACTIONS IN DRUG LOADED PECTIN-ZEOLITE BASED HYDROGELS FOR CONTROLLED DRUG DELIVERY

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Pectin imparts many advantages for wound dressing such as ability for binding bioactive molecules, having antimicrobial, anti-inflammatory and antibacterial properties. This study aims to develop pectin-zeolite based drug delivery systems with two different synthesis methods leading to two different diffusion mechanisms: diffusion into membrane and into matrix. Different concentrations of cross-linker $CaCl_2$, Zn^{2+}- or Na^+-zeolite and drug theophylline were studied. To explain the drug release mechanism, water vapor and oxygen permeabilities, FTIR, ICP, XRD, SEM-EDS analyses and molecular dynamics simulations of pectin-metal-drug systems were conducted. Our synthesis method leading to diffusion into matrix mechanism resulted into composites with more controlled-drug delivery. Na^+-zeolite composites had much higher swelling ratios and drug releases as compared to Zn^{2+}-zeolite films, except one critical formulation leading to a more controlled drug-delivery. We visited thermodynamic theories Gibbs-Donnan equilibrium, Flory-Rehner and Debye-Hückel theory to shed light on the drug release mechanism, which is clearly affected by intermolecular interactions before cross-linking and ion-exchange in the system that together control the swelling in pectin-zeolite hydrogels. Cyctotoxicity analysis indicated that pectin hydrogels promoted cell proliferation.

P134

GLYCO-FUNCTIONALIZED POLYMERSb WITH THIOL FUNCTIONALITY

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Naturally occurring glycoconjugates possess carbohydrate moieties that fulfill essential roles in many biological functions.[1] Along with serving as recognition sites, carbohydrates are a major source of energy. Carbohydrate transport through the cell membrane is facilitated by special membrane bound carbohydrate transporters, i.e. GLUT 1-14.[2] Hence, targeting organs via specific GLUT transporters is an appealing approach in drug delivery. For example, transporters GLUT 1 and GLUT 3 are mostly expressed by brain cells, while GLUT 2 and GLUT 9 by the liver and kidney cells. Furthermore, an overexpression of GLUT 1 by cancer cells has been observed, as they have a high energy demand for growth and multiplication.[3]

By mimicking naturally occurring glycoconjugates, efficient targeting and increased uptake of glyco-functionalized macromolecules is anticipated. In this work, glucose was functionalized with vinyl acrylate and methacrylate via transesterification. Through combination of glucose and xanthate monomers via RAFT polymerization, glyco-thiol copolymers were obtained. We are currently working on modification of the glyco-thiol copolymers via thiol-chemistry, which will make them a versatile biomaterial for building bio-mimicking macromolecular structures, such as nanoparticles or hydrogels.

References

1) V. Ladmiral; E. Melia; Haddleton, D. M., Synthetic glycopolymers: an overview. European Polymer Journal 2004, 40 (3), 431-439.
2) Zhao, F. Q.; Keating, A. F., Functional Properties and Genomics of Glucose Transporters. Current Genomics 2007, 8 (2), 113-128.
3) Patra, M.; Awuah, S. G.; Lippard, S. J., Chemical Approach to Positional Isomers of Glucose–Platinum Conjugates Reveals Specific Cancer Targeting through Glucose-Transporter-Mediated Uptake in Vitro and in Vivo. Journal of the American Chemical Society 2016, 138 (38), 12541-12551.

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PHOTOBASE GENERATORS AS LATENT CATALYSTS FOR DUAL-CURABLE THERMOSET SYSTEMS: A KINETIC AND THERMAL STUDY

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Photobase generators (PBGs) are invaluable in formulating dual-curable thermoset systems with latent reactivity. In this work, we synthesized PBGs based on tetraphenyl borate salts of 1,3,5-Triazabicyclo[4.4.0]dec-5-ene (TBD), 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), 4-(N,N-dimethylamino)pyridine (DMAP), and 1-methylimidazole (MI) [1–3]. We showed that for thiol-epoxy click reactions, reaction onset temperature varies between 60 and 150ºC depending on PBG type and method of activation (by heat or UV light). We then focused on the PBG based on TBD and studied thiol-acrylate-epoxy systems whose dual-curing process consists of UV-initiated thiol-acrylate click Michael addition carried out at room temperature (Stage 1) followed by thiol-epoxy click reaction at moderately elevated temperatures (Stage 2). We studied viscoelastic properties of formulations with different acrylate/epoxide proportions and acrylate structures. Although not as influential as the epoxy content, higher functional and more rigid acrylates resulted in higher glass transition temperatures at both stages. Final glass transition temperatures ranged from -13 to 32ºC, depending on monomer structure. Finally, we demonstrated the ability of the same PBG to catalyze sequential thiol-acrylate and acetoacetate-acrylate Michael additions for the preparation of thiol-acetoacetate-acrylate thermosets.

References

1) X. Sun, J.P. Gao, Z.Y. Wang, Bicyclic guanidinium tetraphenylborate: A photobase generator and a photocatalyst for living anionic ring-opening polymerization and cross-linking of polymeric materials containing ester and hydroxy groups, J. Am. Chem. Soc. 130 (2008) 8130–8131. doi:10.1021/ja802816g.
2) S. Chatani, T. Gong, B.A. Earle, M. Podgorski, C.N. Bowman, Visible-light initiated thiol-Michael addition photopolymerization reactions, ACS Macro Lett. 3 (2014) 315–318. doi:10.1021/mz500132j.
3) Y. Jian, Y. He, Y. Sun, H. Yang, W. Yang, J. Nie, Thiol-epoxy/thiol-acrylate hybrid materials synthesized by photopolymerization, J. Mater. Chem. C. 1 (2013) 4481–4489. doi:10.1039/c3tc30360h

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CHITOSAN HYDROGEL BASED NANO-COMPOSITE SYSTEM WITH SELF-HEALING ABILITY: FILMS AND PATCHES

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Bio-polymeric hydrogel system prepared from chitosan cross-linked with glycerol possesses the self-healing ability, which enables this fantastic hydrogel material to form smooth films or coating. By successful utilization of this self-healing ability possessed by this hydrogel material we have fabricated different types of nano-composite hybrid biomaterials. In the first approach chitosan nano-composite hydrogel was fabricated by using carbon dots (CDs) synthesized from commercially available Assam CTC tea. The films obtained from this chitosan-CDs nano-composite hydrogel system showed UV-blocking ability along with the improved mechanical and thermal property. A composite nanomaterial was also synthesized by coating the surface of graphene oxide by the iron oxide nanoparticle and this composite nanomaterial was used to fabricate chitosan-iron oxide coated graphene oxide nanocomposite hydrogel films. The films formed from this nanocomposite hydrogel system was robust with superior mechanical and thermal property along with another interesting property; the antimicrobial activity. This chitosan based hydrogel system was also used to fabricate a kind of super absorbent patch using cotton wool and made it antimicrobial by incorporating graphene oxide (GO) into this hydrogel system.

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DEGRAFTING OF PNIPAM BRUSHES FROM TiO2 SURFACES WITH UV LIGHT

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Surface-grafted poly(N-isopropylacrylamide) (PNIPAM) is one of the most widely investigated examples of polymer brushes due to its thermoresponsive properties originating from lower critical solution temperature (LCST). PNIPAM brushes are typically synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP). However, in aqueous media ATRP of NIPAM can be challenging due to high K_{ATRP} and k_p values, and often results in uncontrolled polymerization. Furthermore, precise determination of molecular weight and dispersity of polymer brushes is difficult as they need to be cleaved from the surface before the measurement. Here, a straightforward approach to de-graft PNIPAM brushes from TiO_2 under UV irradiation is proposed. Well-defined PNIPAM was grafted from TiO_2 wafers and nanoparticles modified with bromoisobutyrate-functionalized nitrodopamine by ATRP in water at 0 °C. PNIPAM was then detached by exposing the substrates to UV light for 200 min, and analyzed by gel permeation chromatography (GPC) and ^{1}H NMR. Additionally, by using shorter irradiation times the grafting density of the brushes could be tuned.

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VERSATILE SINGLE CHAIN POLYMERIC NANOPARTICLES VIA THIOL-MICHAEL ADDITION

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Single chain polymer nanoparticles (SCNPs) are individual polymer chains that are intramolecularly cross-linked into individual nanoparticles. Through exclusively intramolecular cross-links, SCNPs can be prepared an order of magnitude smaller in size than conventional polymer nanoparticles, without the requirement of complex synthetic strategies.[1,2]

In this work, SCNPs were prepared via intramolecular thiol-Michael addition of thiol-functional vinyl polymers with bifunctional acrylates. The polymers are prepared via RAFT polymerization and careful choice of the monomers enables controlling the general physicochemical properties of the resulting nanoparticles, such as solubility and hydrophobicity/hydrophilicity. Furthermore, a clear dependence of the particle sizes on the precursor chain length is demonstrated.

Through employing solketal methacrylate, polymers were achieved that can be rendered water-soluble by hydrolysis at low pH. The resulting diglycol copolymer was successfully crosslinked with a PEG-based cross-linker, both in water as well as in DMSO. The resulting nanoparticles were imaged via AFM and a diameter of 12 nm was confirmed by DLS and STEM. These particles are currently under investigation in cell studies and are tested on barrier models.

References

1) Mavila, S., Eivgi, O., Berkovich, I., Lemcoff, N. G. Chem. Rev., 2016, 116, 878–961
2) Altintas, O., Barner-Kowollik, C. Macromol. Rapid Commun., 2016, 37, 29–46.

P139

NOVEL CROSS-LINKED ALIPHATIC POLYCARBONATE ELASTOMERS BASED ON CO2 AND EPOXIDES

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Carbon dioxide (CO_2) is a renewable carbon source which is easily available in high purity and is utilised as a comonomer in the direct ring-opening-polymerisation (ROP) of epoxides to obtain aliphatic polycarbonates (APCs).[1] Novel degradable aliphatic polycarbonate terpolymers were synthesised via catalytic polymerisation of CO_2 and functional epoxide monomers. In addition, the novel polymers were cross-linked via Diels-Alder reaction.[2] Catalytic polymerisation of CO_2 with 1,2-propylene oxide (PO), 1,2-butylene oxide (BO) and furfuryl glycidyl ether (FGE) afforded the corresponding co- and terpolymers poly(1,2–propylene carbonate) (PPC), poly(1,2–butylene carbonate) (PBC) and poly(1,2-butylene carbonate-*co*-furfuryl glycidyl ether carbonate) (P(BC-*co*-FGEC)). Terpolymers with low FGE-contents could be achieved without polyether defects. The polymerisation proceeded at low temperatures and high CO_2 pressure utilizing the binary catalytic system of (*R, R*)-(salen)-CoCl/[PPN]Cl. Furthermore thermal and elastic properties of the obtained polycarbonates were compared. The linear polymers were characterised by NMR and FT-IR spectroscopy as well as DSC, SEC and TGA and rheologic measurements. The cross-linked polymers were characterised by DSC, TGA and rheologic measurements as well.

References

1) a) Y.-F. Liu, K. L. Huang, D. M. Peng, S. Q. Liu, H. Wu, Chin. Chem. Lett. 2007, 18, 209–212; b) Y. Hu, L. Qiao, Y. Qin, X. Zhao, X. Chen, X. Wang, F. Wang, Macromolecules 2009, 42, 9251–9254.
2) J. Hilf, M. Scharfenberg, J. Poon, C. Moers, H. Frey, Macromol. Rapid Comm. 2015, 36, 174–179.

P140

IMPROVING CONTROL IN PHOTO-RAFT PROCESS OF NON-CONJUGATED MONOMERS BY PREVENTING DECOMPOSITION OF THIOESTER MOIETIES

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In this work, we report photochemical initiation system in RAFT processes of non-conjugated vinyl monomers, such as vinyl acetate, vinyl pyrrolidone, and vinyl amides. UV irradiation along with thioester chain transfer agents has been widely used in radical polymerization process. However, the mechanism is different from the RAFT process in terms of the instability of the growing polymer chain ends under UV irradiation, and is known as 'photoiniferter' process that is generally less controlled over the polymerization at higher conversion. The control in the polymerization could be improved by preventing the photochemical stability of the thioester moieties, in chain transfer agent and growing polymer chain ends, by right selection of chain transfer agent and wavelength of the applying light source. The polymerization showed living characteristics of controlled molecular weight and its distribution. Also we could lower the polymerization temperature to prepare polymers with higher stereoregularity. Detailed discussion about the system will be made.

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EFFECTS OF PROCESSING PARAMETERS ON THE ABSORBENCY OF CROSS-LINKED POLY(ITACONIC ACID) PREPARED BY INVERSE SUSPENSION POLYMERIZATION

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This paper is devoted to the synthesis and characterization of superabsorbent polymers (SAPs) based on poly(itaconic acid) using potassium persulfate as a free radical initiator in the presence of tetra ethylene glycol diacrylate as a cross-linker. These SAP materials were prepared by performing inverse suspension polymerization of an aqueous solution of monomers dispersed in a continuous organic phase. The dispersion was stabilized by the introduction of a surfactant like SPAN 80. Further influence of cross-linking ratio, initial monomer concentration, and process conditions were studied on the base of a model recipe. These results led to optimization of swelling and absorption behaviors.

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METAL-FREE ATRP WITH LIGHT AS THE SMALLEST ACTIVATOR: VISIBLE AND NIR LIGHT FOR SYNTHESIS OF TAILOR-MADE POLYMERS

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Metal-free ATRP has received increased importance for tailor-made synthesis of different polymers[1]. Recently, photo-ATRP was reported as an alternative to synthesize polymers according to controlled reaction mechanism[2,3]. From this point of view, photo-redox systems with reversible equilibria form a prerequisite for controlled polymer synthesis[2,3]. Particular synthesizers with absorption in the visible range (Eosin Y, Erythrosin B) work well in conjunction with amines and halide sources resulting in a polydispersity <1.5 showing that controlled deactivation occurs while a small fraction of uncontrolled radical polymerization still takes place in the reaction system[4].

Furthermore, we used NIR-LEDs emitting at around 800nm to initiate photo-ATRP by using NIR sensitizers derived from heptamethine derivatives. This can be seen as a new approach to initiate radical photopolymerization. Modification of those polymethine sensitizers tunes depending on the molecular pattern its absorption either hypsochromic or bathochromic and facilitates an optimal overlap with emission of available NIR-LEDs[5]. Only those sensitizers exhibiting no netto charge resulted in formation of polymer; that is a barbiturate in the mess-position. On the other hand, cationic sensitizers are inefficient in combination with typical activators/initiators.

References

1) K. Matyjaszewski, T. P. Davis, Handbook of Radical Polymerization, 2002, John Wiley & Sons, Hoboken.
2) S. Dadashi-Silab, S. Doran, Y. Yagci, Chem. Rev. 2016, 116, 10212-10275.
3) X. Pan, M. A. Tasdelen, J. Laun, T. Junkers, Y. Yagci, K. Matyjaszewski, Prog. Polym. Sci. 2016, 62, 73-125.
4) C. Kutahya, F. S. Aykac, G. Yilmaz, Y. Yagci, Polymer Chemistry 2016, 7, 6094-6098.
5) B. Strehmel, C. Schmitz, T. Bromme, A. Halbhuber, D. Oprych, J. S. Gutmann, Journal of Photopolymer Science and Technology 2016, 29, 111-121.

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CONTROLLED/LIVING RING-OPENING POLYMERIZATION OF E-CAPROLACTONE WITH IONIC LIQUID AS CATALYST

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ABSTRACT

Aliphatic polyesters such as as poly(lactide), poly(ε-caprolactone) and their copolymers have attracted considerable attention due to their biodegradability and biocompatibility and have applications in biomedicine and pharmaceutics. [1] They are conveniently synthesized by metal-catalysed ring-opening polymerization (ROP) of cyclic esters (Lactide, ε-caprolactone...). The drawback of these homogeneous systems is the contamination of the resulting polyesters by residual metal that should be avoided for medical use. Therefore, organocatalyzed ROP has emerged as a promising alternative to its metal-catalyzed counterpart.[2] Recently, the ROP of lactones and lactides was described in imidazolium based ionic liquids in the presence of a nucleophilic catalyst such as *in-situ* generated carbene[3]. Herein, we describe, the first controlled ROP of ε-CL in bulk catalyzed by ionic liquids, thus avoiding the use of metal catalyst, solvent and base. These mild conditions led to living polymerization with good conversions and molecular weight distributions of poly(ε-caprolactone). Finally, an activation mechanism is suggested based on the results of an *in-situ* FTIR polymerization analysis using various ionic liquid catalysts.

References

1) Jérôme and P. Lecomte, Adv. Drug Deliv. Rev., 2008, 60, 1056.
2) L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick and C. G. Wade, Macromolecules, 2007, 40, 4154.
3) A. P. Dove, R. C. Pratt, B. G. G. Lohmeijer, R. M. Waymouth and J. L. Hedrick, J. Am. Chem. Soc., 2005, 127, 13798; R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth and J. L. Hedrick, Macromolecules, 2006, 39, 7863.

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EMULSION TEMPLATED POROUS POLYMERS AS SCAFFOLDS FOR ANTERIOR CRUCIATE LIGAMENT TISSUE ENGINEERING

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The emulsion templating process offers a route to highly porous polymers with well-defined morphologies. The process, whereby the continuous phase of a high internal phase emulsion (HIPE) is polymerized, results in materials referred to as polyHIPEs. These porous materials have found application in a wide range of areas including catalysis, organic synthesis, and in biotechnology.

This presentation will describe the preparation of such materials from monomers including multifunctional thiols and acrylates, and styrenic monomers, and their efficacy as scaffolds for anterior cruciate ligament (ACL) tissue engineering discussed. Fibroblast cell lines have been cultured on polyHIPE scaffolds for up to 14 days, indicating the polyHIPEs are biocompatible. The deposition of ligament extracellular matrix proteins, including collagen I, collagen III, and tenascin C, has been assessed by immunohistochemistry, fluorescence staining, and Western blotting. The results obtained suggest that polyHIPE scaffolds may be suitable for use in ACL tissue engineering.

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SYNTHESIS OF FUNCTIONAL γ-THIOLACTONES AND APPLICATIONS TO POLYMER SYNTHESIS AND MODIFICATION

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Du Prez et *al.* have recently found new applications for thiolactones in polymer chemistry, with a particular focus on the 5-membered γ-thiolactones.[1,2] This simple, catalyst-free synthetic procedure allows polymer synthesis under stoichiometric conditions at mild temperature without the need for tedious and costly purification. Despite the increasing development of thiolactone-based polymer synthesis and modifications, simple general methods for the preparation of functional thiolactones are still lacking.

We here report a modular strategy for the synthesis of functional γ-thiolactones with various substituents such as alkyl, perfluoroalkyl or phosphonate bonded to the ring using a single set of elementary reactions. A library of mono- and disubstituted thiolactones is described. These new thiolactone building blocks for polymer chemistry using amine-thiol-ene conjugation is presented with successful end-functionalization of amino-terminated polymers and step-growth polymerizations. The many possibilities of functionalization and this versatile method for making functional thiolactones should find broad applications to prepare new materials with original properties.

References

1) Espeel, P.; Goethals, F.; Du Prez, F. E. J. Am. Chem. Soc. 2011, 133 (6), 1678-1681.
2) Espeel, P.; Du Prez, F. E. Eur. Polym. J. 2015, 62, 247-272.

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BIOMIMETIC MATERIALS - CONTROLLING THE CELLULAR FATE

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Multiple biopolymers with different structural and mechanical properties, which physically interact with each other, make the mechanical environment of a cell *in vivo* much more complicated than the environment of a cell in a single-component artificial matrix.[1]

The mechanics of natural biopolymer gels, however, are very different from most synthetic hydrogels because they show strain-stiffening behaviour.[2,3] Reconstituted networks of natural extracellular matrices (ECMs), such as collagen or fibrin show a large increase in stiffness upon an applied stress or deformation.[2,3] Recently a new biomimetic hydrogel was developed, based upon oligo(ethylene glycol) grafted polyisocyanopeptides.[4] These extremely stiff helical polymers form gels upon warming at concentrations as low as 0.005 %-wt polymer, with materials properties almost identical to those of intermediate filaments and ECMs.[3,4] The unique ability of these materials and their application in cell growth and drug therapeutics revealed the importance of polymer stiffness and material non-linear mechanics.[5,6]

Approaches of how to control the hydrogel properties, how to study them in detail and the influence of strain-stiffening on cellular fate will be presented.

References

1) Janmey, P. A.; et al. PLoS ONE, 2009, 4, e6382; Place, E. S.; et al. Nat. Mater. 2009, 8, 457; Thiele, J.; et al. Adv. Mater. 2014, 26, 125; Huber, F.; et. al. Curr. Opin. Cell Biol. 2015, 32, 39; Nagelkerke, A.; et al. Semin. Cancer Biol. 2015, 35, 62.
2) Storm, C.; et al. Nature, 2005, 435, 191.
3) Jaspers, M.; et al. Nature Comm. 2014, 5, 5808; Jaspers, M.; et al. Adv. Funct. Mater. 2015, 25, 6503.
4) Kouwer, P. H. J.; et al. Nature, 2013, 493, 651.
5) Mandal, S.; et al. Chem. Sci., 2013, 4, 4168; Mandal, S.; et al. ACS Bio 2015, 10, 485.
6) Das, R. K.; et al. Nat. Mater. 2016, 15, 318.

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SYNTHESIS AND SEQUENCING OF DIGITALLY-ENCODED POLY(ALKOXYAMINE-AMIDE)S

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It was recently evidenced that information can be stored in synthetic polymers using a controlled sequence of monomers[1]. For instance digital information can be written in a polymer using two monomers that are arbitrarily defined as 0 and 1 bits. In this presentation, the synthesis and properties of digitally-encoded poly(alkoxyamine-amide)s will be described. These polymers are synthesized via a protecting-group-free solid-phase iterative process involving three sub-monomers[2]: a nitroxide spacer and two coding anhydrides. This facile procedure allows synthesis of monodisperse sequence-defined macromolecules[3]. Furthermore, the digital messages stored in the chains can be read by tandem mass spectrometry. In particular, it was found that the fragile alkoxyamine C-ON bonds in the polymers facilitate fragmentation and sequencing[4]. Among potential applications, digitally-encoded poly(alkoxyamine-amide)s could be used as molecular barcodes in anti-counterfeiting technologies. Such barcodes can be long linear coded chains but also intentionally-polydisperse oligomer mixtures that are even easier to synthesize[5]. These potential new applications of sequence-controlled polymers will be described in details in this presentation.

References

1) H. Colquhoun, J.-F. Lutz, Nat Chem, 6, 455-456 (2014)
2) T.T. Trinh, C. Laure, J.-F. Lutz, Macromol. Chem. Phys., 216, 1498-1506 (2015)
3) R.K. Roy, A. Meszynska, C. Laure, L. Charles, C. Verchin, J.-F. Lutz, Nat. Commun., 6,7237 (2015)
4) L.Charles, C.Laure, J.-F. Lutz, R.K. Roy, Macromolecules, 48, 4319–4328 (2015)
5) C. Laure, D. Saranti-Karamesini, L. Charles, J.-F.Lutz, Angew. Chem., Int. Ed, 55, 36, 10722-10725 (2016)

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Cu(II) METAL-ORGANIC FRAMEWORKS AS EFFICIENT AND RECYCLABLE CATALYSTS FOR ARGET ATRP

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Owing to the comprised metallic element and the physical skeleton resulting from ionic bonding, Cu(II) MOF, can serve as an efficient ligand/ catalyst complex for activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) for comprehensive polymer synthesis, from typical poly(benzyl methacrylate) (PBzMA), poly(styrene) (PS) to poly(isoprene) (PI) and poly(4-vinylpyridine) (P4VP) in a controlled fashion.

Moreover, the Cu(II) MOF, which is composed of photo-addressable metal sites and potential reducing agent is utilized as an efficient catalyst for controlled photopolymerization under visible light, even without the utilization of specialized photoinitiators or dye sensitizers. Simply triggering by light, photoinduced reduction converts the intrinsic Cu(II) to active Cu(I), facilitating controlled polymerization. Surpassing the conventional homogenous ionic catalysts, the ionic-bonding framework imparts to the Cu(II) MOF with higher stability and robustness, enabling the comprised metallic element to attract and activate monomers with high nucleophilicity, such as 4VP, 2-vinylpyridine (2VP), and 2-(dimethylamino)ethyl methacrylate (DMAEMA). As a heterogeneous catalyst, the catalytic complex can be separated, recovered and repeatedly catalyzed for alternative ARGET ATRP or photopolymerization at least six times.

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SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT CONJUGATED POLYMER DOTS HYBRIDIZED WITH INORGANIC MATERIALS FOR RESPONSIVE PROPERTIES

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Conjugated polymers gain a great deal of attention in various applications such as light-emitting diodes, transistors, photovoltaic cells and solar cell, because of their excellent electrically conducting and optical properties. Among various applications, nanoparticles fabricated from such conjugated polymers have advantages, including strong fluorescence, good dispersion in water and easy functionalization on surface. Using such properties of the nanoparticles, many investigations on the conjugated polymer nanodots have been carried out for bio-imaging, bio-sensing, and chemical detection.The surface modification of conjugated polymer dots is found to be intriguing in biology-related fields because of the colloidal stability of the conjugated polymer nanodots in aqueous solution. We are demonstrating new, versatile conjugated polymer-based nanodots that hybridized with inorganic materials for varying optical properties as well as a specific detection of target analytes.

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CORE-CROSSLINKED POLY(2-OXAZOLINE) NANOGELS AS DOXORUBICIN CARRIERS FOR CANCER THERAPY

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The severe side-effects of cytostatic drugs reflect the main issue regarding cancer therapy success. Enhancing the specific cellular uptake using polymer-based nanocarriers is one possibility to reduce side-effects while maintaining the cytostatic characteristics of the drugs.

Recently, poly(2-oxazoline)s became interesting candidates in biomedical applications.[1,] Their synthesis *via* the living cationic ring-opening polymerization using the microwave technique leads to defined macromolecules[2] with a versatile functionalization chemistry, *e.g. via* introduction of primary amino groups.[3]

We present the synthesis of doubly hydrophilic block copolymers, consisting of an amino-functionalized block suitable for core cross-linking and covalent binding of doxorubicin. The second block, constituting the shell of the nanocarrier, was composed of 2-ethyl-2-oxazoline to facilitate biocompatibility and stealth behavior. The nanogels were characterized *via* dynamic light scattering and transmission electron microscopy[4] and investigated regarding their cytotoxicity and cellular uptake *in vitro*.[5] Finally, an *in vivo* cancer therapy study in nude was performed, showing that the doxorubicin loaded nanogels inhibit the tumor growth even at drug concentrations

References

1) R. Luxenhofer, Y. Han, A. Schulz, J. Tong, Z. He, A. V. Kabanov, R. Jordan, Macromol. Rapid. Commun. 2012, 33, 1613-1631.
2) F. Wiesbrock, R. Hoogenboom, C. H. Abeln, U. S. Schubert, Macromol. Rapid. Commun. 2004, 25, 1895-1899.
3) M. Hartlieb, D. Pretzel, K. Kempe, C. Fritzsche, R. M. Paulus, M. Gottschaldt, U. S. Schubert, Soft Matter 2013, 9, 4693-4704.
4) M. Hartlieb, D. Pretzel, M. Wagner, S. Hoeppener, P. Bellstedt, M. Gorlach, C. Englert, K. Kempe, U. S. Schubert, J. Mater. Chem. B 2015, 3, 1748-1759.
5) M. Hartlieb, T. Buś, J. Kübel, D. Pretzel, S. Hoeppener, M. N. Leiske, K. Kempe, B. Dietzek, U. S. Schubert, submitted.

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FULLERENE-FREE SOLUTION-PROCESSED BULK HETEROJUNCTION ORGANIC PHOTOVOLTAICS

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Our present society has come to the understanding that the development of a complementary set of **sustainable energy resources** is of utmost urge and importance, both from an economic and ecological point of view.[1] Solar energy stands out because of its abundance and global character, and various photovoltaic (PV) technologies have been developed to harness this energy.[2] Because of the high absorptivity of organic semiconductors and the use of non-toxic and cheap carbon-based active materials, **organic photovoltaics** (OPV) have grown into an attractive complementary PV type, offering particular advantages in terms of aesthetics and design freedom (e.g. color and uniformity), low-light performance and narrow spectral width. **Bulk heterojunction** organic photovoltaics are based on a solution-processed active layer blend comprising of an organic electron donating and an electron accepting material. Until very recently, fullerenes turned out to be the superior electron acceptors, but in the last year, the promises of more generic and versatile low-cost **non-fullerene acceptors** has been fulfilled and have the same efficiencies [3] (above 10%) as fullerene OPV's.[4] A poster will show our latest work in this field.

References

1) R. E. Smalley, MRS Bull. 30, 412 (2005)
2) K. A Mazzio, Chem. Soc. Rev. 44, 78 (2015)
3) J. Hou; H. Ade, Adv. Mater., 28, 9423 (2016)
4) H. Yan, Nat Energy, 1, 15027 (2016)

P152

Cu(0)-RDRP: AN INVESTIGATION INTO OXYGEN TOLERANCE

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Copper(0)-mediated reversible-deactivation living radical polymerization (RDRP) is a well-established robust technique for the synthesis of well-defined functional polymers. In a typical polymerization, thorough removal of the oxygen is required, either via repetitive freeze-pump-thaw cycles or by degassing the reaction mixture with nitrogen. This can be time-consuming and overall an arduous and expensive task. Herein, we show that under well optimized conditions Cu(0)-wire polymerizations can proceed effectively in the presence of air while exhibiting low dispersity values, high end group fidelity and narrow molecular weight distributions. The versatility of this technique is further demonstrated by the polymerization of both acrylates and methacrylates in a range of solvents, initiators and ligands.

References

1) Anastasaki, A.; Nikolaou, V.; Haddleton, D. M. Polym. Chem. 2016, 7, 1002.
2) B. M. Rosen and V. Percec, Chem. Rev., 2009, 109, 5069– 5119.

P153

PREPARATION OF CYCLO-BASED POLYMERIC STRUCTURES BY TRIAZOLE (MULTI)FUNCTIONALIZATION

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The preparation of cyclic macromolecules has always represented a challenging task in polymer science mainly due to difficulties in connecting chain extremities together. Initiated by the pioneering works of Jacobson and Stockmayer, preparative pathways to cyclic polymers have been considerably improved within the last two decades thanks to the advent of both controlled polymerization mechanisms and efficient coupling reactions in organic chemistry.

Using some high-efficient coupling reactions, several pioneer works have opened the doors to *cyclo*-based polymers and these research have been comprehensively reviewed in the very recent years.[1,2]

In this work, both preparation and characterization by modern mass spectrometry techniques of *cyclo* -polylactide (*c*PLA) based structures is presented. To that end, pristine *c*PLA obtained by the Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) ring-closure technique are quaternized and functionalized on their triazole node by *Menshutkin* reaction.[3]

The functionalization of cycles including one triazole allows the preparation of structures such as tadpoles or dumbbells. *Cyclo*-polylactide including multiple triazole nodes can also possibly be prepared through an iterative divergent-convergent process, the quaternization of such macrocycles giving access to jellyfish structures.

References

1) Laurent, B. A. et al., Chem. Soc. Rev. 2009, 38, 2202–2213
2) Josse, T. et al., Angew. Chem. Int. Ed. 2016, 55, 13944-13958
3) Mudraboyina, B. P. et al., Eur. Polym. J. 2015, 62, 331-337

P154

DESIGNER POLYMER COMPOSITE TAPES FOR SURGICAL TENDON REPAIR

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Electrospun biodegradable films have been popular for a range of tissue engineering applications for some time. Among them, poly(ε-caprolactone) (PCL) is one of the most widely used materials, due to its well-controlled biocompatibility and biodegradability[1] . However, with a major limitation of PCL is its hydrophobic nature, whilst it also lacks functional groups on its backbone, limiting its ability to interact with cells[2]. In order to address this issue, in the current study PCL-*block*-glycopolymers were synthesized via a combination of ring opening polymerization and atom transfer radical polymerization. Polymers were electrospun to make films, which were studied *in vitro* to investigate cell affinity, toxicity, activity and adhesion with these materials. The results indicated that incorporating sugar moieties into the membranes significantly reduced the toxicity of the membrane and increased cellular interaction with the material.

References

1) Lam, C. X.; Hutmacher, D. W.; Schantz, J. T.; Woodruff, M. A.; Teoh, S. H., Evaluation of polycaprolactone scaffold degradation for 6 months in vitro and in vivo. J. Biomed. Mater. Res. A 2009, 90 (3), 906-919.
2) Zhang, H.; Lin, C.-Y.; Hollister, S. J., The interaction between bone marrow stromal cells and RGD-modified three-dimensional porous polycaprolactone scaffolds. Biomaterials 2009, 30 (25), 4063-4069.

P155

SUSTAINABLE SYNTHESIS OF BIOBASED DEGRADABLE THERMOSETS

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Nowadays, the awareness about environmental deterioration and about our dependency on depleting fossil feedstocks forces research to find solutions in order to design a more sustainable future. To reach this goal, in addition to the use of renewable resources, it is crucial to implement as many *green chemistry principles* as possible for the production of polymers, including the use of safer synthetic procedures and catalytic reagents, as well as the consideration of factors such as waste prevention.

In this context, the design of biobased thermosets with a cleavable linkage, thus enabling the network degradation is proposed herein. The biobased monomers are produced employing catalytic procedures and less toxic chemicals. More specifically, a bisepoxide with a structure similar to diglycidylether of bisphenol A is sustainably synthesized by reaction and further epoxidation of allyated vanillyl alcohol with 2,2-dimethoxypropane or dimethylcarbonate. A biobased diamine is also produced in a sustainable fashion from terpenes.

Epoxy resins are formulated from these biobased monomers and their thermomechanical properties compared to the ones of classic networks. The degradation of the network is also investigated.

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THERMAL DEGRADATION OF POLYPHTHALALDEHYDE

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Polyphthalaldehyde has garnered interest over the past couple of years due to its triggerable rapid depolymerization both in solution and solid-state.[1] It has been used as a small signal amplification polymer as well as a physically transient substrate for transient electronics.[2] In this work, we investigate the tunable thermal degradation behavior of cyclic polyphthalaldehyde (cPPA). Thermogravimetric analysis reveals that cPPA rapidly depolymerizes and evaporates at temperatures > 120 °C.[3] We explored accelerating the kinetics of thermal depolymerization for cPPA by incorporating a thermal acid generator (TAG). The acid generated by the TAG – in response to temperatures > 70 °C – protonates the acetal backbone of cPPA and initiates the unzipping depolymerization of cPPA. The addition of the TAG lowers the degradation temperature from temperatures >120 °C to temperatures as low as 80 °C. Raman spectroscopy and NMR analysis confirms the depolymerization of cPPA into the starting monomer material, o-phthalaldehyde. The accelerated and tunable degradation of cPPA has direct applications for the rapid transience of electronics.

References

1) DiLauro, A. M., Robbins, J. S., & Phillips, S. T. (2013). Reproducible and Scalable Synthesis of End-Cap-Functionalized Depolymerizable Poly(phthalaldehydes). Macromolecules, 46(8), 2963–2968. http://doi.org/10.1021/ma4001594
2) Kaitz, J. A., Diesendruck, C. E., & Moore, J. S. (2013). End group characterization of poly(phthalaldehyde): surprising discovery of a reversible, cationic macrocyclization mechanism. Journal of the American Chemical Society, 135(34), 12755–61. http://doi.org/10.1021/ja405628g
3) Park, C. W., Kang, S.-K., Hernandez, H. L., Kaitz, J. a., Wie, D. S., Shin, J., … White, S. R. (2015). Thermally Triggered Degradation of Transient Electronic Devices. Advanced Materials, 27(25), 3783–3788. http://doi.org/10.1002/adma.201501180

P157

pH-RESPONSIVE NANO-OBJECTS PREPARED BY POLYMERIZATION INDUCED SELF-ASSEMBLY

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It is well known that diblock copolymers undergo spontaneous self-assembly into various nano-objects when in a solvent selective for only one block. Recently, several groups have developed a method to prepare nano-objects in situ using polymerization-induced self-assembly (PISA).[1] For example, Armes and co-workers demonstrated that nano-objects can be prepared by chain extending a poly(glycerol monomethacrylate) (PGMA) macromolecular chain-transfer agent (CTA) with 2-hydroxypropyl methacrylate (HPMA) by RAFT aqueous dispersion polymerization.[2] Furthermore, preparation of PGMA-PHPMA copolymers using a charged CTA yields pH-responsive nano-objects. Charging the CTA end-group on the PGMA block drives an order-order morphological transition as the stabilizer increases in hydrophilicity. However, this behaviour can be salted out. Herein, we extend this research by developing new pH-responsive nano-objects using PISA by incorporating pH-sensitive monomers in either the stabilizer or core-forming block. The latter allows for the preparation of nanoparticles which undergo order-disorder transitions. Furthermore, synthesis of PGMA-PHPMA diblock copolymers using a dicarboxylic acid-functionalized CTA yields nano-objects that remain pH-responsive in high salt concentrations. Such nano-objects are expected to be useful in bio-medical applications.

References

1) Canning, S. L.; Smith, G. N.; Armes, S. P. Macromolecules 2016, 49, 1985.
2) Blanazs, A.; Ryan, A. J.; Armes, S. P. Macromolecules 2012, 45, 5099.

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THE EFFECT OF GLYCOPOLYMER NANOPARTICLE CORE PROPERTIES AND SURFACE SUGARS, ON: LECTIN BINDING, CELLULAR UPTAKE AND DRUG DELIVERY

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Glycopolymer nanoparticles show promise for a variety of biomedical applications, particularly as targeted delivery agents, whose sugar residues enable them to bind specifically to lectins on biological targets of interest. The influence of glycopolymer nanoparticles outer shell on lectin binding has been extensively studied in literature. However, the effect of particle core properties on lectin binding and cell interactions, remains largely unexplored. We have therefore investigated the effect of particle core glass transition temperature (T_g) on the ability of glycoparticles to bind to lectins, and the subsequent impact this has on cellular uptake and drug delivery. A variety of “soft” and “hard” glycoparticles, with various sugar moeties have been synthesised primarily by RAFT emulsion polymerisation. The aggregation of the particles was examined using an online DLS aggregation technique, with toxicity and cellular uptake determined by SRB assay and confocal microscopy respectively.

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REVERSIBLE NETWORKS FOR UV CURABLE MATERIALS

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Commonly used UV-curable monomers are (meth)acrylates. These monomers polymerize rapidly but display significant stress. In order t osolve this it is thought to incorporate dynamic covalent bonds into the polymer network. These reversible bonds can rearrange upon a stimitus yielding relaxation of the stress in the material

References

1) Chem. Soc, Rev., 2013, 42, 7161-7173
2) Polym. Chem., 2010, 1, 102-106

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TUNEABLE ROBUST HYDROGEL MATERIALS USING NUCLEOPHILIC THIOL-YNE CLICK CHEMISTRY

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Tailoring the characteristics of a material to meet the needs of a biological environment is a key goal in material science.[1] Hydrogels, with their high water content and synthetic flexibility, are promising candidates to achieve this goal.[2] The controlled ability to tune and pre-define these materials allow unique hydrogels to be synthesised for specific requirements *e.g.* a particular biological environment[3] or to elicit a desired cellular response[4] through simple chemistry. Recently, the nucleophilic thiol-yne click reaction has also been demonstrated as an attractive route for the synthesis of tuneable bio-materials.[5-7]

The synthesis robust, tuneable hydrogel materials has been undertaken utlising the nucleophilic thiol-yne click reaction while maintaining a high water content (*ca.* 90%). Remarkably, optimization of the molecular weight and geometry of the poly(ethylene glycol) (PEG) precursors allows access to strong materials (up to 2.4 MPa) with a range of storage moduli. Moreover, these hydrogels can be simply tuned to specific requirements by a simple precursor blending process leading to range of hydrogels with intermediate stiffness without changing the chemistry used and with minimal changes to the hydrogel structure.

References

1) R. Langer and D. A. Tirrell, Nature, 2004, 428, 487-492.
2) A. S. Hoffman, Adv. Drug Deliv. Rev., 2002, 54, 3-12.
3) E. Bellas and C. S. Chen, Curr. Opin. Cell Biol., 2014, 31, 92-97.
4) Y. Geng, P. Dalhaimer, S. Cai, R. Tsai, M. Tewari, T. Minko and D. E. Discher, Nat. Nano., 2007, 2, 249-255.
5) V. X. Truong, M. P. Ablett, S. M. Richardson, J. A. Hoyland and A. P. Dove, J. Am. Chem. Soc., 2015, 137, 1618-1622.
6) X. Y. Cai, J. Z. Li, N. N. Li, J. C. Chen, E.-T. Kang and L. Q. Xu, Biomater. Sci., 2016, 4, 1663-1672.
7) L. J. Macdougall, V. X. Truong and A.P. Dove, ACS Macro. Lett., Submitted.

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DESIGN OF NEW TYPE OF POLYAMPHOLYTES WITH THERMORESPONSIVE BEHAVIOR IN ALCOHOL/WATER SOLVENT MIXTURE

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Functional core-shell nanoparticles with high solubility and high dispersibility have been developed by the combination of reversible addition-fragmentation chain transfer (RAFT) polymerization and in-situ Suzuki coupling reaction. A well-defined amphiphilic block copolymer poly(PEGMA)-*b*-poly(DB3VT) was synthesizsed by RAFT polymerization. Then the micellization of poly(PEGMA)-*b*-poly(DB3VT) and in-situ Suzuki coupling reaction between poly(PEGMA)-*b* -poly(DB3VT) and various diboronic acid monomers were carried out simultaneously in THF/H_2O, which yielded core-shell nanoparticles with cross-linked functional core structures. The obtained nanoparticles showed high solubility for common organic solvents, and good dispersibility was observed by atomic force microscopy analysis. A series of functional nanoparticles, such as semiconducting nanoparticles and luminescent nanoparticles, were successfully synthesized by using various functional diboronic acid monomers in the Suzuki coupling reaction. Furthermore, the size of nanoparticles was tunable by adjusting the Suzuki coupling conditions.

References

1) Debashish Roy, William L. A. Brooks and Brent S. Sumerlin, Chem. Soc. Rev., 2013, 42, 7214-7243.
2) Qilu Zhang and Richard Hoogenboom, Chem. Commun., 2015, 51, 70-73.

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ABSTRACT CANCELLED

P163

UNDERSTANDING THE MECHANISM OF SELF-ASSOCIATION CONTROLLING THE FORMATION OF CYCLIC-PEPTIDE/POLYMER CONJUGATE NANOTUBES

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Peptide nanotubes have gained increasing interest in recent years for a diverse range of biomedical applications. Cyclic peptides with alternating d- and l-amino acids can readily self-assemble into nanotubes

via hydrogen bonding. These systems can then be further modified with a range of polymers resulting in water-soluble nanotubes, thus expanding their potential. However, the length and aggregation mechanism of these systems is not fully understood; and therefore understanding the fundamental mechanisms governing the self-assembly process is crucial in order to critically assess how the constructs will behave in a biological setting. Recently, we have used a combination of FRET analysis, ITC, and scattering techniques to show a concentration-dependence on the self-assembly process; indicative of a cooperative mechanism. By further probing and extrapolating the governing thermodynamic parameters, we can further understand this mechanism and the fundamental processes controlling the self-assembly; providing insights into potentials ways the process can be controlled and manipulated for complex applications.

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ACCESS TO AROMATIC HETEROCYCLIC POLYMERS VIA MULTI-COMPONENT REACTIONS

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Recent developments in the design of new macromolecular structures have led to a renewed interest in the re-investigation of old organic reactions by polymer chemists. Passerini, Ugi or Biginelli Multi-component reactions (MCR) have definitely emerged as very efficient tools to bring new insights in the development of original macromolecular scaffolds.

In order to broaden the scope of this strategy to the synthesis of complex aromatic and heterocyclic polymers, this work evidences the potential of different multi-component reactions for the formation of various heterocycles. Specific attention is devoted to one-pot syntheses of tri(arylimidazole)s, tetra(arylimidazole)s or tri(arylpyridine)s involving 3 or 4 reactants…. On the basis of results obtained from preliminary studies on model molecules, the experimental conditions for different multi-component polycondensations are established. Poly(triarylimidazole)s, poly(tetra(arylimidazole)s and poly(triarylpyridine)s are synthesized by direct formation of the heterocylic structures during the polymer chain growth. Structural characterization (NMR) as well as thermal properties of the new macromolecular structures synthesized will be described.

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UPGRADING CASTOR OIL: FROM HEPTANAL TO NON-ISOCYANATE POLY(AMIDE-HYDROXYURETHANE)S

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Non-isocyanate polyurethanes (NIPUs) emerged as an environmentally friendly approach to polyurethanes that avoids the use of toxic isocyanate raw materials. Intensive research on pathways to NIPUs concluded that the aminolysis of cyclic carbonates is one of the most promising alternatives.[1] Moreover, isocyanates and polyols are currently synthesized from petrochemical resources and renewable plant oils have been investigated for the production of NIPUs using this approach.[2] Undecylenic acid, obtained from the thermal cracking of ricinoleic acid, has also been investigated.[3] However, heptanal, the other product of this process, is practically not used as intermediate in polymer chemistry.

The aim of this work was developing a more environmentally friendly synthetic strategy for PUs by using heptanal as biobased starting material and by avoiding isocyanates. The preparation of a new five-membered disubstituted cyclocarbonate methyl ester precursor through the cycloaddition of CO_2 to a renewable heptanal derivative was carried out. The polymerization through carbonate ring opening and methyl ester amidation afforded a poly(amide hydroxyurethane) containing pendant aliphatic chains. The self-assembling of this amphiphilic structure into polymeric nanoparticles was investigated.

References

1) L. Maissonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, Chem. Rev., 2015, 115, 12407-12439; A. Corneille, R. Auvergne, O. Fogovsky, B. Boutevin, S. Caillol, Eur. Polym. J., 2017, 87, 535-552; B. Nohra, L. Candy, J.F. Blanco, C. Guerin, Y. Raoul, Z. Moulongui, Macromolecules, 2013, 46, 3771-3792; H. Blattman, M. Fleischer Macromol. Rapid Commun., 2014, 35, 1238-1254
2) M. Bähr, R. Mülhaupt, Green Chem. 2010, 14, 483-489; L. Poussard, J. Mariage, B. Grignard, C. Detrembleur, C. . Jérôme, C. Calberg, B. Heinrichs, J. De Winter, P. Gerbaux, J.-M. Raquez, L. Bonnaud, P. Dubois, Macromolecules, 2016, 49, 2162-2171; I. Javni, D.P. Hong, Z.S. Petrovic, J. Appl. Polym. Sci. 2013, 128, 566-571
3) O. Lamarzelle, P.-L. Durand, A.-L. Wirotius, G. Chollet, E. Grau, H. Cramail, Polym. Chem. 2016, 7, 1439-1451

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AUTOMATED SYNTHESIS OF SEQUENCE-DEFINED, MULTIFUNCTIONAL PRECISION POLYMERS

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Chemists have made great progress in synthesizing functionalized polymer architectures with defined structure–property relationships, yet these structures do not reach the same potential as biopolymers. In the last decade, the control of the primary structure of polymers has received higher priority, in hopes of creating an even stronger correlation between structure and properties.[1]

We synthesize sequence-defined oligomers, based on a thiolactone strategy with a protecting-group-free, two-step iterative protocol on solid phase. First, a thiolactone is opened using an amino alcohol and an acrylic. Next, the incorporated alcohol reacts with a thiolactone isocyanate. This last reaction reinstates a thiolactone, which allows for the procedure to start again, while the acrylic and amino alcohol allow to vary the sidechain and backbone. The protocol was translated to an automated approach to easily make sequences in parallel.[2]

These structures can be used as new data carriers. Reliable storage of digital data has been recognized as a major challenge of the 21st century.[3] We wrote and have read a sentence with different oligomers to proof that data can be easily stored on polymers.

References

1) J.-F. Lutz; J.-M. Lehn; E. W. Meijer; K. Matyjaszewski Nature Reviews Materials 2016, 1, 16024.
2) S. Martens; J. Van den Begin; A. Madder; F. E. Du Prez; P. Espeel J. Am. Chem. Soc. 2016, 138, 14182.
3) H. Colquhoun; J.-F. Lutz Nat. Chem. 2014, 6, 455.

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FUNCTIONAL EMULSION-TEMPLATED POROUS POLYMERS BY MACROMOLECULAR SURFACTANT ANCHORING STRATEGIES

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Macroporous polymer monoliths with interconnected structures have attracted considerable interest in the fields of supported catalysis, chromatography, water purification, etc. A popular and straightforward synthesis approach for such open-cell polymers is based on the polymerization of high internal phase emulsion (HIPE).[1] Advanced functional polyHIPEs were also produced via different post-modification strategies but the latter often consists in tedious multi-step processes. This communication aims at reporting an efficient one-pot macromolecular surfactant-assisted method for the simultaneous synthesis and chemical functionalization of macroporous polyHIPEs. Briefly, amphiphilic block copolymers prepared by nitroxide-mediated radical polymerization (NMP) [2] or reversible addition-fragmentation chain transfer (RAFT) [3,4] were used as HIPE stabilizers and grafted at the surface of the walls of polyHIPE during the polymerization process. The impact of the controlled radical polymerization mechanism on the porous structure, openness and functionalization of the monoliths will be discussed. This strategy was also implemented with alkyne-terminated copolymers in order to decorate the surface of the polyHIPE's cavities with "clickable" moieties which broadens the scope of functional macroporous polymers.

References

1) M. S. Silverstein, "PolyHIPEs: Recent advances in emulsion-templated porous polymers," Prog. Polym. Sci., vol. 39, no. 1, pp. 199–234, 2014.
2) K. Mathieu, J. De Winter, C. Jérôme, A. Debuigne, "Simultaneous synthesis and chemical functionalization of emulsion-templated porous polymers using nitroxide-terminated macromolecular surfactants," Polymer Chemistry, vol. 8, no. 11, pp. 1850-1861, 2017.
3) K. Mathieu, C. Jérôme, A. Debuigne, "Influence of the Macromolecular Surfactant Features and Reactivity on Morphology and Surface Properties of Emulsion-Templated Porous Polymers," Macromolecules, vol. 48, no. 18, pp. 6489–6498, 2015.
4) K. Mathieu, C. Jérôme, A. Debuigne, "Macro- and near-mesoporous monoliths by medium internal phase emulsion polymerization: A systematic study," Polymer, vol. 99, pp. 157-165, 2016.

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BULK COPOLYMERIZATION OF LACTIDE WITH E-CAPROLACTONE CATALYZED BY AN ORGANOCATALYST: TOWARD A METAL-FREE RANDOM-LIKE COPOLYMER

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Random biodegrable and biocompatible copolymers based on lactide (LA) and e-caprolactone(CL) (P(LA-*ran*-CL)) already received a significant attention in both medical and pharmaceutical fields[1,2]. Besides, they have been recently found suitable as compatibilizing agents for PLLA/PCL blends[3]. Metallic initiator systems successfully enable the ring-opening polymerization (ROP) of LA with CL[4] but suffer from some expensiveness and a certain toxicity level as regards to both humans and animals. In this context, cheap organocatalysts with low toxicity are particularly attractive for the synthesis of P(LA-*ran*-CL) copolymers. To date, the discovery of thermostable organocompounds for the catalysis of L-LA ring-opening (co)polymerization (ROcP) in bulk is one of the most challenging and exciting research subjects in ROP chemistry. Herein, the ROcP of L-LA with CL (50:50) in bulk at 155°C catalyzed by natural acidic molecules is reported.

References

1) D. W. Grijpma, G. J. Zondervan and A. J. Pennings, Polym. Bull., 1991, 25, 327–333
2) S. H. Kim, S. H. Kim and Y. Jung, J. Controlled Release, 2015, 206, 101–107
3) M. Rizzuto, A. Mugica, M. Zubitur, D. Caretti and A. J. Müller, CrystEngComm, 2016, 18, 2014–2023
4) M. Florczak and A. Duda, Angew. Chem. Int. Ed., 2008, 47, 9088–9091

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POLYMERIC COPPER(I)-BISCARBENE MECHANOCATALYSTS FOR THE COPPER(I)-CATALYZED AZIDE/ALKINE “CLICK” REACTION

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In the recent years the topic of mechanochemistry came more and more into focus of scientific research especially as it turned out as a powerful tool for designing autonomous self-healing or stress-sensing materials [1, 2]. Triggering chemical reactions directly by the damage event itself e.g. by *in situ* activation of a latent catalyst would avoid the otherwise required protection of reactive compounds [3]. Thus we designed a series of polymeric bis(*N*-heterocyclic carbene) (NHC) copper(I) mechanocatalysts, which could solely be activated applying external mechanical force by cleaving one of the shielding NHC ligands [4]. The generated monocarbene complex is suitable for the copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC) and can be used for self-healing or stress-sensing applications [3, 4].

The catalytic activity of the mechanocatalysts was investigated in solution via a model CuAAC reaction of benzyl azide and phenylactetylene revealing in the best case almost quantitative conversions. Subjecting the mechanophore into the bulk state to compression triggers a fluorogenic “click” reaction of initially non-fluorescent 3-azido-7-hydroxy-coumarin and phenylactelyene yielding the highly fluorescent 7-hydroxy-3-(4-phenyl-*1H*-[1,2,3]triazole-1-yl)-coumarin and probed thus the potential for stress-sensing applications by the appeared fluorescence.

References

1) Li, J.; Nagamani, C.; Moore, J. S., Acc. Chem. Res. 2015, 48, 2181.
2) Polymer Mechanochemistry; Boulatov, R., Ed.; Springer International Publishing: Heidelberg, 2015; Vol. 369.
3) Gragert, M.; Schunack, M.; Binder, W. H., Macromol. Rapid Commun. 2011, 32, 419.
4) Michael, P.; Binder, W. H., Angew. Chem. Int. Ed. 2015, 54, 13918.

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NONLINEAR SUGAR CENTERED POLYBASES FOR METHOTREXATE DELIVERY

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Methotrexate (MTX) is a cytostatic agent which is frequently used drug for severe psoriasis, i.e. psoriatic arthritis and erythrodermic psoriasis [1]. However, use of MTX in the treatment brings the risk of hematologic complication and bone marrow aplasia [2, 3]. In order to overcome drug treatment side effects, novel drug delivery systems are being explored, for instance polymer-drug conjugates [4]. In our study V-shaped, three and four-arm star shaped amphiphilic copolymers having hydrophilic 2-hydroxy-3-diethylaminopropyl methacrylate units were used in conjugation of MTX via amide bond formation. The physicochemical properties of obtained conjugates were examined in order to find correlation between size, charge, shape or binding constant and the structure of polymeric matrix. Furthermore, the drug release kinetic profiles allowed to evaluate the influence of the arm composition and abovementioned properties on the rate of drug release.

References

1) D. Jullien, J. Eur. Acad. Dermatol. Venereol. 2006, 20 (suppl 2), 10-23.
2) N. Kozak, J. Friedman, A. Schattner, Drugs R. D. 2014, 14, 155-158.
3) J. West, S. Ogston, J. Foerster, PLoS One, 2016; 11: e0153740.
4) A. Mielańczyk, M. Skonieczna, Ł. Mielańczyk, D. Neugebauer, Bioconjug. Chem. 2016, 27, 893-904.

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SYNTHESIS AND CHARACTERIZATION OF WATER SOLUBLE pH- AND THERMOSENSITIVE STAR-SHAPED COPOLYMERS WITH GLUCONOAMIDE CORE via ATRP

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Star-shaped copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) were obtained using gluconolactone based initiator with five bromoester groups via atom transfer radical polymerization (ATRP). The composition and length of chains/arms varied with the initial proportion of monomer pair DMAEMA/HEMA: 50/50, 75/25, 85/15 mol% as well as initial molar ratio of monomer to initiator $[M_0]$:$[I_0]$=300:1 or 500:1, respectively. The properties of star copolymers were compared with linear analogs. Both thermo- and pH-responsive properties of obtained (co)polymers were determined by measuring their phase transition in the phosphate buffer saline (PBS) solution. Those experiments revealed that at pH 5.0 electrostatic repulsion between protonated amino groups increased solubility of copolymers and prevented their aggregation. Otherwise, at slightly basic pH 7.4, the cloud point temperatures (T_{CP}) of corresponding copolymers varied between 61-66°C and depended on both structure and chain composition. Further, linear and star-shaped P(DMAEMA-*co*-HEMA) were used as macroinitiators for insertion-coordination ring opening polymerization (ROP) of ε-caprolactone (CL), resulting comb and star-comb amphiphilic polymers with biodegradable blocks.

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HIGH-TOUGHNESS SUPRAMOLECULAR HYDROGEL BASED ON HYDROPHOBIC INTERACTIONS

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In this work, we describe the preparation of a high-toughness, supramolecular hydrogel, based exclusively on hydrophobic associations. The system in question consists of a multiblock, segmented copolymer, synthesized by polycondensation reaction between hydrophilic, polyethylene glycol (PEG) and hydrophobic, dimer fatty acid (DFA) building blocks. A series of four copolymers containing different molecular weights of PEG was prepared. The network is formed by self-assembly of hydrophobic DFA units in nanodomains, which act as stable, physical cross-link points. The size and interdomain distances were investigated in detail by small-angle neutron scattering (SANS) measurements. Moreover, viscoelastic and mechanical properties were studied with rheology and tensile testing techniques. It was found that the hydrogel containing PEG 2000 is mechanically very stable and tough, possessing tensile toughness of 4.12 MJ/m^3, despite being completely formed by physical, reversible interactions. Combination of high-toughness, processability and ease of preparation make these hydrogels very attractive for possible industrial applications, where mechanical stability and load bearing features of soft materials are required.

References

1) Biomacromolecules 2012, 13, 3966–3976
2) J. Am. Chem. Soc. 2014, 136, 6969–6977

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SYNTHESIS OF BIO-INSPIRED FUNCTIONAL ADHESIVE COPOLYMERS

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Several recent polymer syntheses have used DOPA and dopamine derivatives as a means of imparting the adhesive properties of mussel foot protein into synthetic polymers. Dopamine methacrylamide is a monomer which has the potential to provide these properties, and the resulting polymers could be modified to become surface active coatings. Acetonide-protected dopamine methacrylamide (ADMA) was used as a monomer in the synthesis of copolymers using free radical and reverse addition-fragmentation chain transfer (RAFT) polymerisation. Various co-monomers were investigated, including methyl methacrylate, stearyl methacrylate and glycidyl methacrylate, which were all found to form copolymers with ADMA. The kinetics of the free radical copolymerisation of ADMA and methyl methacrylate were investigated with a view to predicting the monomer sequence distribution of the synthesised copolymers. These copolymers represent an opportunity to design functional coatings that can be used industrially for various purposes.

P174

THERMORESPONSIVE TRIBLOCK COPOLY(2-OXAZOLINE)S AS POTENTIAL INJECTABLE HYDROGELS

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Poly(2-oxazoline)s are an emerging class of polymers for biomedical applications. Amongst their interesting properties are thermoresponsiveness, with poly(2-ethyl-2-oxazoline) (PEtOx) having a cloud point of ca. 60ºC and poly(2-n-propyl-2-oxazoline) having a cloud point of ca. 25ºC. Advances in our laboratory have led to the synthesis of extremely narrow (approaching Poisson distribution) block copolymers without parasitic homopolymers. This work will discuss the synthesis of poly(n-propyl)(ethyl)(n-propyl) triblock copolymers by one-ended initiation and the thermal effects of changing the hydrophilic EtOx block size. Materials which are liquid solutions at room temperature but soft hydrogels at body temperature have been synthesised, and are interesting as potential injectable hydrogels. This work emphasises the need for relatively high molar mass (> 50 kDa) materials in this application.

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HOW TO RESTORE THE LUBRICATION PROPERTIES OF ARTICULAR CARTILAGE AFTER DEGENERATION WITH POLY-2-METHYL-2-OXAZOLINE BASED GRAFT-COPOLYMERS: AN EX-VIVO STUDY

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Natural or traumatic articular cartilage degeneration is often correlated with an alteration of the lubrication properties of this tissue, due to the progressive loss of glycosaminoglycans (GAGs) and extracellular matrix degradation[1]. The absence of vascularization in the articular cartilage inhibits self-healing processes, making this degeneration irreversible.

Inspired by the structure and properties of the cartilage natural lubricants (GAGs and lubricin), we developed an injectable, fully synthetic and not degradable formulation for both protecting the cartilage tissue and restoring its lubrication properties. This relies on brush-forming graft-copolymers featuring a tissue reactive, aldehyde-bearing polyglutamic acid (PGA) backbone, and poly-2-methyl-2-oxazoline (PMOXA) side grafts. The designed graft-copolymers can readily bind on the degenerated cartilage tissue through Schiff bases and generate a bioinert and highly lubricious brush layer.

A precise tuning of the length, density and chain-topology of the PMOXA grafts allow to reproduce the low coefficient of friction characteristic of the healthy articular cartilage, protect the degraded tissue from protein contamination and prevent further damage.

References

1) Poulet, B.; Staines, K.A. Curr. Opin. Pharmacol. 2016, 28, 8-13

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EFFICIENT AVENUES TOWARDS THE FUNCTIONALIZATION OF UNSATURATED POLYMERS

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Inserting variable functional groups into a polymer backbone offers the possibility to carefully adjust the material properties of the polymer for tailored applications.[1] However, the well-known controlled radical polymerization methods do not allow for the incorporation of all functional groups.[2,3] Moreover, only few methods for the modification of unsaturated polymers have been developed so far. Herein, new strategies for the synthesis of post-functionalized polymers are explored. The first method rests on a metal-free, novel electrophilic cascade reaction to decorate alkene functionalities within a lateral polymer chain with pendent bromine and alkoxyether motifs.[4,5] The introduced pendent bromine groups serve as an intermediate to afford other chemical functionalities, thus opening vast possibilities for polymer post-functionalization. An alternative facile and atom-economical method is introduced for the synthesis of β-acetamido sulfide derivatives based on unsaturated polymers. Thus, a metal-free direct difunctionalization of the alkene functionality with thiols and nitriles was successfully adopted. By employing the aforementioned methods, we demonstrate that it is possible for unsaturated polymers to be readily functionalized, allowing for the adaptation of the material properties of the polymers.

References

1) C. J. Hawker and K. L. Wooley, Science 2005, 309, 1200
2) M. A. Gauthier, M. I. Gibson and H. A. Klok, Angew. Chem. Int. Ed. 2009, 48, 48
3) K. A. Guenay, P. Theato and H. A. Klok, J. Polym. Sci. Part A Polym. Chem. 2013, 51, 1
4) C. M. Geiselhart, J. T. Offenloch, H. Mutlu and C. Barner-Kowollik, ACS Macro Lett. 2016, 5, 1146
5) J. T. Offenloch, J. Willenbacher, P. Tzvetkova, C. Heiler, H. Mutlu and C. Barner-Kowollik, Chem. Commun. 2017, 53, 775

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SPATIALLY RESOLVED SURFACE PATTERNING OF METALLOPOLYMERS

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We present the synthesis and fabrication of metallopolymers and their spatially resolved surface immobilization on a silicon surface *via* a combination of light-triggered ligation chemistry, reversible deactivation radical polymerization, and post-modification steps. Such multifunctional materials are potent candidates for heterogeneous catalyst designs including the fabrication of continuous flow reactors.

In a previous study$^{(1)}$, we demonstrated the spatially resolved surface patterning of metal complexes on a functional silicon surface utilizing the reaction between a phenacyl sulfide and maleimide functional metal complexes (Au, Pd). Mono-, as well as bifunctional metal complex surfaces could be obtained.

The current contribution extends this concept, exchanging the single metal complexes through a metallopolymer prepared *via* the RAFT process. Spatially resolved surface attachment of the polymer is realized *via* NITEC chemistry employing a maleimide terminal polymer and a silicon surface functionalized with a suitable tetrazole. ToF-SIMS and XPS analysis show the effective and mild photo ligation chemistry and the successful spatially resolved immobilization of the polymer onto the surface.

References

1) Lang, C.; Bestgen, S.; Welle, A.; Müller, R.; Roesky, P. W.; Barner-Kowollik, C. Chem. Eur. J. 2015, 21, 14728-14731.

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MULTINOMIAL DESCRIPTION OF POLYCONDENSATION MIXTURES

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The portions of individual oligo- and polymeric species in polycondensates can be approximated a priori from the stoichiometry of all employed condensation building blocks and from the degree of conversion. We herein show how a combination of bi- and multinomial distribution with the enumeration of possible oligomeric species offers insight into i) residual monomer content, ii) portions of individual oligomers and iii) overall composition of complex oligo- and polymeric mixtures. Theoretical distribution estimates have been confirmed by analytical methods such as ^{1}H nuclear magnetic resonance spectroscopy and gel permeation chromatography on polyester model systems.

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SYNTHESIS OF FUNCTIONAL CORE-SHELL NANOPARTICLES BASED ON RAFT POLYMERIZATION

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Functional core-shell nanoparticles with high solubility and high dispersibility have been developed by the combination of reversible addition-fragmentation chain transfer (RAFT) polymerization and in-situ Suzuki coupling reaction. A well-defined amphiphilic block copolymer poly(PEGMA)-*b*-poly(DB3VT) was synthesizsed by RAFT polymerization. Then the micellization of poly(PEGMA)-*b*-poly(DB3VT) and in-situ Suzuki coupling reaction between poly(PEGMA)-*b*-poly(DB3VT) and various diboronic acid monomers were carried out simultaneously in THF/H_2O, which yielded core-shell nanoparticles with cross-linked functional core structures. The obtained nanoparticles showed high solubility for common organic solvents, and good dispersibility was observed by atomic force microscopy analysis. A series of functional nanoparticles, such as semiconducting nanoparticles and luminescent nanoparticles, were successfully synthesized by using various functional diboronic acid monomers in the Suzuki coupling reaction. Furthermore, the size of nanoparticles was tunable by adjusting the Suzuki coupling conditions.

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POLYMER SELF-ASSEMBLIES FOR FUNCTIONAL MEMBRANES DEVELOPMENT

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One of the challenges in functional membranes development is the production of the mechanically strong materials with a percolating network of polar channels giving rise to ion or proton conductivity. This study is devoted to the development of the new approach for the production of micro-structured block-copolymer films (membranes) based on the one-stage synthesis of block-copolymer self-assemblies by means of polymerization induced self-assembly (PISA) technique and further use of these dispersions as “building blocks” for the creation of micro-structured materials of larger scale. The main peculiarity of the process is that water-soluble surface-active oligomers act both as a surfactants stabilizing emulsions and as reversible addition – fragmentation chain transfer (RAFT) agents.

The results of the synthesis of different amphiphilic block-copolymers, which are self-organized in core-shell particles are presented. The obtained particles were used for film formation. The films structure and their properties were investigated.

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SELF-ASSEMBLY OF STATISTICAL AMPHIPHILIC COPOLYMERS AND THE EFFECTS ON THEIR RHEOLOGICAL PROPERTIES

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A range of poly(butyl methacrylate-stat-methacrylic acid) [P(BMA-st-MAA)] copolymers of various compositions and molecular weights from 5-30 kDa are prepared using reversible addition-fragmentation chain transfer (RAFT) solution polymerization in isopropanol (IPA). These amphiphilic copolymers self-assemble on the addition of water to form spherical micelles as confirmed by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Interestingly, the resulting spherical micelle radii are composition-dependent, but independent of molecular weight. SAXS analysis suggests that these charged particles (pH > pKa) arrange in a structural order at low concentrations. Furthermore, SAXS was utilized to monitor the micellar assembly on the gradual addition of water to the original 50 wt% polymer-IPA solution. Rheological studies indicate a high-viscosity intermediate during this process at polymer concentrations of 25-30 wt%, which is due to a large scale interpenetrated polymer network formed by spherical micelles, as suggested by the SAXS data. This research demonstrates a straightforward route to self-assembled spherical particles at high copolymer concentrations simply by tuning the solvent mixture, where the micelle radius can be tuned for particular polymer compositions.

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THE UNDERLYING MECHANISMS FOR SELF-HEALING OF POLY(DISULFIDE)S

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Recently, self-healing polymers based on disulfide compounds have gained attention due to the versatile chemistry of disulfide bonds and easy implementation into materials. In literature, however, both metathesis[1] and a radical-mediated mechanism[2] have been used to describe the mechanism of disulfide exchange for self-healing of poly(disulfide)s. Since this ambiguity is an issue when describing the mechanisms of disulfide exchange and when trying to understand self-healing, it is necessary to clarify this matter.

In this work, spectroscopic techniques were used to (kinetically) study the underlying mechanism of the disulfide exchange inducing self-healing in polydisulfide materials. Comparing a model exchange reaction of 4-aminophenyl disulfide and diphenyl disulfide with modified reactions in the presence of radical sources or traps proved that the exchange occurred via a radical-mediated mechanism. These results agreed with the theoretical predictions of Matxain *et al.* stating that disulfides exchange through formation of S-based radicals.[3] Moreover, investigating the effect of catalysts on the model exchange reaction showed that catalysts enhance disulfide exchange through the formation of S-based anions in addition to the radical-mediated mechanism.[4]

References

1) Caraballo, R.; Rahm, M.; Vongvilai, P.; Brinck, T.; Ramstrom, O., Phosphine-catalyzed disulfide metathesis. Chem. Commun. 2008, (48), 6603-6605
2) Fairbanks, B. D.; Singh, S. P.; Bowman, C. N.; Anseth, K. S., Photodegradable, Photoadaptable Hydrogels via Radical-Mediated Disulfide Fragmentation Reaction. Macromolecules 2011, 44 (8), 2444-2450
3) Matxain, J. M., Asua, J. M. & Ruipérez, F. Design of new disulfide-based organic compounds for the improvement of self-healing materials. Phys. Chem. Chem. Phys. 18, 1758–1770 (2016)
4) Nevejans, S., Ballard, N., Miranda, J. I., Reck, B. & Asua, J. M. The underlying mechanisms for self-healing of poly(disulfide)s. Phys. Chem. Chem. Phys. 18, 27577–27583 (2016)

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OCCLUSION OF SULFATE-BASED DIBLOCK COPOLYMER NANOPARTICLES WITHIN CALCITE: EFFECT OF VARYING THE SURFACE DENSITY OF ANIONIC STABILIZER CHAINS

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Polymerization-induced self-assembly (PISA) offers a highly versatile and efficient route to a wide range of organic nanoparticles. We for the first time demonstrate that poly(ammonium 2-sulfatoethyl methacrylate)-poly(benzyl methacrylate) [PSEM-PBzMA] diblock copolymer nanoparticles can be prepared with either high or low PSEM stabilizer surface densities using either RAFT dispersion polymerization in a 2:1 v/v ethanol/water mixture or RAFT aqueous emulsion polymerization, respectively. We then use these model nanoparticles to gain new insight into a key topic in materials chemistry – the occlusion of organic additives into inorganic crystals. Substantial differences are observed for the extent of occlusion of these two types of anionic nanoparticles into calcite ($CaCO_3$), which serves as a suitable host crystal. A low PSEM stabilizer surface density leads to uniform nanoparticle occlusion within calcite at up to 7.5 % w/w (16 % v/v), while minimal occlusion occurs when using nanoparticles with a high PSEM stabilizer surface density. This counter-intuitive observation suggests an optimum anionic surface density is required for efficient occlusion, which provides a hitherto unexpected design rule for the incorporation of nanoparticles within crystals.

References

1) Ning, Y.; Fielding, L. A.; Ratcliffe, L. P. D.; Wang, Y-W; Meldrum, F. C.; Armes, S. P. Occlusion of sulfate-based diblock copolymer nanoparticles within calcite: effect of varying the surface density of anionic stabilizer chains, Journal of the American Chemical Society 2016, 138, 11734-11742.

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SYNTHESIS AND THERMAL PROPERTIES OF DIFUNCTIONAL BENZOXAZINE MONOMERS WITH ATTACHED OXAZINE RING AT P-, M-, AND O-POSITION

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Benzoxazines are relatively new class of thermosetting resins belongs to addition type phenolic family, and can undergo thermally activated ring opening polymerization to yield a crosslinked network consists of phenolic-Mannich bridges as repeating unit. The tremendous molecular design flexibility allows them to be used in wide range of applications, as the desired properties can be easily introduced into the final polybenzoxazine by changing suitably functionalized starting phenol or amine.[1] Recently, we have focused on developing benzoxazine monomers solely containing oxazine moieties instead of opting for other functional groups, in order to explore their potential in overcoming the drawbacks (high curing temperature, weight loss during ring-opening polymerization etc.) associated with these resins.[2] In the present work, we have designed difunctional benzoxazine monomers with attached oxazine ring at *p*-, *m*- and *o*- position and investigated their role on ring-opening polymerization and thermal stability of corresponding polybenzoxazines. We found that regioisomerism had a great influence on lowering their curing temperature and was favourable in the order of *m*-> *o*-> *p*-. A curing mechanism responsible for this trend will be discussed.

References

1) Ishida, H.; Agag, T. Handbook of Benzoxazine Resins, Elsevier, 2011.
2) Sini, N. K.; Endo, T. Macromolecules, 2016, 49, 8466-8478.

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CONTROLLING MOLECULAR WEIGHT AND POLYMER ARCHITECTURE DURING THE PASSERINI THREE COMPONENT STEP-GROWTH POLYMERIZATION

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The use of multicomponent reactions represents a current trend in macromolecular chemistry, allowing many straightforward and unprecedented synthetic approaches to highly defined macromolecules.[1-5] In this contribution, we could demonstrate, for the first time, that the Passerini reaction allows for molecular weight control during step-growth polymerization, which is very rarely achieved using classic polyaddition or polycondensation approaches. Apart from molecular weight control, our results demonstrate an easy tuning of side-groups, block copolymer synthesis, the preparation of star-shaped polymers, and, last but not least, high end-group fidelity.

The approach relies on the use of a monocarboxylic acid as an irreversible and selective chain transfer agent (ICTA) in combination with a bifunctional monomer and an isocyanide to achieve control over the molecular weight. The thus resulting carboxylic acid end-group subsequently allows for the synthesis of block copolymers. Moreover, the use of a tricarboxylic acid as core unit results in the formation of star-shaped homo- and copolymers.

In summary, we thus report a new and very versatile strategy to achieve control over polymer architectures in a straightforward fashion.

References

1) O. Kreye, T. Tóth and M. A. R. Meier, J. Am. Chem. Soc., 2011, 133, 1790.
2) A. Sehlinger and M. A. R. Meier, Adv. Polym. Sci. 2015, 269, 61.
3) A. Sehlinger, R. Schneider and M. A. R. Meier, Eur. Polym. J., 2014, 50, 150.
4) L.-J. Zhang, X.-X. Deng, F.-S. Du, and Z.-C. Li, Macromolecules 2013, 46, 9554.
5) A. Lv, X.-X. Deng, L. Li, Z.-L. Li, Y.-Z. Wang, F.-S. Du and Z.-C. Li, Polym. Chem., 2013, 13, 3659.

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ENZYME IMMOBILIZATION IN MICROFLUIDIC REACTORS FOR SERIAL ENZYMATIC CONVERSIONS

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Miniaturizing chemical reactors is of great interest due to a reduced consumption of chemicals and costs.[1] By immobilizing biocatalysts into accordingly designed microfluidic reactors, specific conversions with high turnover rates may be carried out under mild conditions.[2]

The incorporation of enzyme-loaded hydrogel dots in a microfluidic device and the execution of enzymatic (cascade) reactions under flow-through conditions have already successfully been demonstrated.[3,4]

This study focuses on the design, simulation, and production of multi-chamber microfluidic reactors for advanced (multi-) enzymatic reactions which shall be carried out serially. By applying micro-valves at the interface of the reaction chambers, operations such as dilution, separation, and mixing of the educt-containing fluid shall be reached.

Furthermore, the enzymes will be encapsulated into polymersomes by self-assembly and photo-crosslinking of functionalized block copolymers [5] prior to the entrapment in the hydrogel matrix. The biocatalysts are thereby protected from deactivation and enzyme leakage is restricted due to the larger dimensions of the polymersomes and thus improved fixation within the hydrogel. Additionally, stimuli-responsiveness may allow a controlled enzymatic conversion under acidic conditions.

References

1) W. G. Koh, M. Pishko, Sens Actuator B Chem 2005, 106, 335.
2) F. Kazenwadel, M. Franzreb, B. E. Rapp, Anal. Methods 2015, 7, 4030.
3) J. Heo, R. M. Crooks, Anal. Chem. 2005, 77, 6843.
4) D. Simon, B. Voit, D. Appelhans, Manuscript in preparation.
5) D. Gräfe, J. Gaitzsch, D. Appelhans, B. Voit, Nanoscale 2014, 6, 10752.

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INTRACELLULAR UNFOLDING NANOPARTICLES FOR THE DELIVERY OF IMMUNE-STIMULATORY CUES TOWARDS ANTICANCER IMMUNITY

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Engineering the tumor stroma and its draining lymph nodes is an attractive strategy to mount anti-cancer immunity. Here, a multifunctional core-crosslinked nanogel platform was designed that targets lymph nodes and unfolds after cellular uptake into soluble polymers.[1] It is based on amphiphilic reactive ester block copolymers synthesized via RAFT polymerization,[2] where the solvophobic block self-assembles in aprotic polar solvents and allows crosslinking by pH-degradable ketal moieties as well as further post-modification with immune stimulatory cues. Using functional RAFT chain transfer agents provides access to orthogonally addressable polymer end groups that facilitate nanoparticle surface engineering with targeting ligands or antigens, e.g. via Michael-type thiol-vinylsulfone ligation or copper-free click chemistry.[3,4] Nanoparticle degradation was proved by the ligation of the Cy3/Cy5 FRET pair on separate polymer strands and monitoring the loss of FRET signal over time in vitro on dendritic cells and in vivo in the draining lymph nodes. Immune-activation and anti-tumor effects were evaluation in murine models and showed significant tumor growth retardation while avoiding exerted systemic inflammatory toxicity.

References

1) Lutz Nuhn, Nane Vanparijs, Ans De Beuckelaer, Lien Lybaert, Glenn Verstraete, Kim Deswarte, Stefan Lienenklaus, Nikunj M. Shukla, Alex C. D. Salyer, Bart N. Lambrecht, Johan Grooten, Sunil A. David, Stefaan De Koker, Bruno G. De Geest – "pH-Degradable Imidazoquinoline-ligated Nanogels for Lymph Node-focused Immune Activation", PNAS 2016, 113, 8098-8103.
2) Lutz Nuhn, Markus Hirsch, Bettina Krieg, Kaloian Koynov, Karl Fischer, Manfred Schmidt, Mark Helm, Rudolf Zentel – "Cationic Nanohydrogel Particles as Potential siRNA Carriers for Cellular Delivery", ACS Nano 2012, 6, 2198-2214.
3) Nane Vanparijs and Lutz Nuhn, Samantha J. Paluck, Maria Kokkinopoulou, Ingo Lieberwirth, Heather D. Maynard, Bruno G. De Geest – "Core/shell protein-reactive nnanogels via a combination of RAFT polymerization and vinyl sulfone postmodification", Nanomedicine (Lond.) 2016, 11, 2631-2645.
4) Lutz Nuhn, Leonard Kaps, Mustafa Diken, Detlef Schuppan, Rudolf Zentel – "Reductive Decationizable Block Copolymers for Stimuli-Responsive mRNA Delivery", Macromolecular Rapid Communications, 2016, 37, 924-933.

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PECTIN-BASED WOUND DRESSING GELS WITH CONTROLLED PROTEIN RELEASE

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Strategies to control the delivery of proteins are critically important in the design of advanced wound dressings. The objective of this work is to prepare and characterize calcium pectinate films as protein delivery systems to the tissue side. For this purpose, protein loaded hydrogel films have been prepared focusing on two different drug loading systems; swelling and mixing. Different concentrations of protein (25, 50, 75 and 100 mg/g-film) and various pH (4.3 and 6.4) were studied to obtain an effective drug loading and release performance for the films, where Bovine Serum Albumin, $CaCl_2$ and glycerol were used as model protein, cross-linker and plasticizer, respectively. The release studies were performed by UV-spectrophotometer at pH 7.4. To explain the drug loading and release mechanism of the films, FTIR and swelling studies were also conducted. Optimum conditions were achieved at 50 mg protein /g-film and pH 6.4 conditions.

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PYRENE BEARING NOVEL POLYESTERS AND THEIR NONCOVALENT INTERACTIONS WITH MULTIWALLED CARBON NANOTUBES

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Carbon nanotubes have speedily turned into an interdisciplinary field because of showing their superior structural, mechanical, electrical features. These features increase the usage of carbon nanotubes (CNTs) in many areas such as censoring, nerve cell stimuli, drug delivery, and cancer therapy. However, major limitation for application of CNTs is their poor solubility, dispersion, processibility and self-aggregation. Hence, functionalization of CNTs is necessary. Some methods have been reported such as non-covalent functionalization (π-π stacking interactions[2]) and covalent functionalization.

In this study, a series of polyesters containing electron deficient internal alkyne units derived from acetylene dicarboxylic acid in the main backbone were synthesized. Polyesters was employed as a polymeric platform in copper free cycloaddition reaction like, Huisgen type 1,3-dipolar in the presence of pyren-1-ylmethyl 3-azidopropanoate. The 1,3-dipolar cycloaddition reactions were performed at 40 °C in 1,4-dioxane for 16 h with high efficiencies[1].

Polyesters (pyrene-PE) that possess pyrene in their backbone used as a surface modifier to enhance the dispersion stability of MWCNTs in common organic solvents.

References

1) M. Cetin, C. Esen, O. Daglar, S. Luleburgaz, G. Hizal, H. Durmaz, U. Tunca, Polym. Chem., 2016, 7, 7094
2) H. Durmaz, A. Dag, U. Tunca, G. Hizal, J. Polym. Sci. Part A: Polym.Chem. 2012, 50, 2406–2414

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PH-CONTROLLED SUPRAMOLECULAR POLYMERIZATION OF PEPTIDE-POLYMER CONJUGATES

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Here we present a pH-switchable supramolecular system in aqueous media using a covalent water soluble polymer as a shielding block to an aggregating peptide block.[1]

A telechelic polysarcosine polymer was prepared using NCA-Polymerization and was functionalized with an alternating phenylalanine histidine peptide sequence at both ends. The peptide sequences were synthesized using SPPS and introduced using a peptide with a primary amine group as the NCA initiator and a complementary peptide sequence with a carboxylic acid group as a quencher.

The molecules were characterized by NMR and GPC measurements. The aggregation of the peptide-polymer conjugates with different polysarcosine chain lengths was monitored using TEM and CD spectroscopy.

The assembly of the system is dictated by the hydrophobicity of the phenylalanines, the intra- and intermolecular hydrogen bonding and interaction of the peptide backbone resulting in antiparallel beta sheet formation. The protonation of the imidazoles in the histidine side chains at acidic pH values results in the disassembly of the system due to the repulsive charges.

References

1) P. Besenius, J. Polym. Sci. Part A: Polym. Chem. 2017, 55, 34–78.

P191

SYNTHESIS OF CROSS-LINKED P(HEMA) PARTICLES IN SUPERCRITICAL CARBON DIOXIDE FOR PROTEIN DELIVERY

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This project aims to develop a novel one-pot strategy to obtain well-defined cross-linked particles able to carry peptides/proteins in their core, as along with targeting and/or imaging agents on their surface. In addition to this objective, polymerisations will be carried out in supercritical carbon dioxide ($scCO_2$), which confers environmentally benign features to the process[1].

Here, we investigate the feasibility of free radical dispersion polymerizations of 2-hydroxyethyl methacrylate (HEMA) in $scCO_2$. In order to ensure the successful dispersion in $scCO_2$ novel diblock CO_2 -philic surfactants are employed. These diblock surfactants[2,3] are formed from two different segments, a CO_2-phobic block which has an affinity to the growing particles and a second CO_2-philic block that ensures surfactant solubility.

References

1) C. Lepilleur and E. J. Beckman, 1997, 9297, 745–756.
2) Z. Ma and P. Lacroix-desmazes, 2004, 45, 6789–6797.
3) N. A. Birkin, N. J. Arrowsmith, E. J. Park, A. P. Richez and S. M. Howdle, Polym. Chem., 2011, 2, 1293.

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TRITYL-SUBSTITUTED ALKOXYAMINES AS POTENTIAL NMP CONTROLLERS AND SPIN-LABELS

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Trityl-nitroxide biradicals gain many new applications recently. In our report, the first preparation of trityl radical attached to alkoxyamines (TA) based on the SG1 and TEMPO nitroxyl fragments is described. The corresponding kd values were measures by ESR. It is clearly shown that the trityl radical moiety has no influence in kd wherever its position, i.e., on the alkyl fragment or on the nitroxyl fragment. The EPR features of the trityl-TEMPO and trityl-SG1 biradicals were also investigated.

The non-alteration of the kinetic properties of the alkoxyamines opens a lot of opportunities of application in Polymer Sciences, Material Sciences, and Theranostic. For example, one might envisioned the presence of trityl as end-group to track the distribution of polymer-drug entities, or it might be used to dope the magnetic properties of materials.

Moreover, the potential of TA to control NMP was checked with the polymerization of styrene that proceeded in controlled regime with “living” polymer obtained. Thus, the presence of trityl moiety has no significant effect on the NMP mechanism.

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A FACILE SELF-ASSEMBLING AMPHIPHILIC POLYPEPTIDE SYSTEM CROSS LINKED FOR CONTROLLED DRUG RELEASE

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The restrictions associated with prevailing therapeutics highlight the requirement for precise and controlled drug delivery systems. To address this need, we devised a self-assembling micellar system based on amphiphilic polypeptides which can be loaded with drugs and can be cross linked to form a drug delivering hydrogel as a general carrier model for the switchable and controlled release of dual drugs. Here, two different di-block polypeptides, poly (L-lysine-*b* -L-phenylalanine) and poly (L-glutamic acid-*b* -L-phenylalanine) (PGA-PPA), were synthesized to form distinct self-assembling micelles that were loaded with curcumin and amphotericin B, respectively, as model drugs. The drug-loaded micellar mixture was crosslinked utilizing the pendant amino groups of the L-lysine side chains via genipin to yield a micelle-hydrogel composite with PGA-PPA micelles trapped in the interlinked hydrogel system. This composite allowed the control of multiphasic drug release and could be effectively tuned to moderate the pace and amount of drug release and be easily regulated to switch the drug release kinetics over a range of simple factors such as change in pH, cross-linking density, and composition.

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CROSS-LINKED CATIONIC DIBLOCK COPOLYMER WORMS AS SUPERFLOCCULANTS OF MICROMETER-SIZED SILICA PARTICLES

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A series of linear cationic diblock copolymer nanoparticles are prepared by polymerisation-induced self-assembly (PISA) via reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerisation of 2-hydroxypropyl methacrylate (HPMA). A detailed phase diagram was constructed to isolate a pure, cationic worm phase. Aqueous electrophoresis studies indicated that zeta potentials of +35 mV could be achieved for such cationic worms over a wide pH range. Core cross-linked worms were prepared via statistical copolymerization of glycidyl methacrylate (GlyMA) with HPMA using a slightly modified PISA formulation, followed by reaction with 3-aminopropyl triethoxysilane. TEM and DLS studies confirmed that such core cross-linked cationic worms remained colloidally stable when challenged with either excess methanol or a cationic surfactant. Importantly, these cross-linked cationic worms are more effective bridging flocculants for 1.0 µm silica particles at pH 9 than the corresponding linear cationic worms (and also various high molecular weight commercial polymeric flocculants). SEM studies confirmed that the cross-linked worms remained intact after their adsorption onto the silica particles, whereas the much more delicate linear worms underwent fragmentation. Similar results were obtained with 4 µm silica particles.

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POLYMERIC STABILISATION OF POLY(VINYL ACETATE) MICROSPHERES IN HETEROGENEOUS FREE-RADICAL POLYMERISATION

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Sterically stabilised heterogeneous polymerisations of vinyl acetate have been carried out to synthesise poly(vinyl acetate) (PVAc) microparticles. Poly(vinyl alcohol) and poly(vinyl pyrrolidone) have been used as steric stabilisers in the emulsion and suspension polymerisations of PVAc in water producing particles of sub-micron and larger than 50 μm respectively. In order to access an intermediate size range, a methacrylic acid based statistical copolymer has been synthesised to utilise as a polymeric stabiliser. Alkylation reactions with benzyl bromide have been carried out on the statistical copolymers to remove acid functionality and enable accurate analysis of copolymer composition by ^{1}H NMR, GPC and ATIR. A range of copolymer compositions have been synthesised and the most successful has been used in the suspension polymerisation of vinyl acetate producing solid particles with sizes between 0.5 and 15 μm. By performing polymerisations at a range of concentrations and agitation speeds, particle size and uniformity could be tuned, with higher stirring speeds and stabiliser concentrations of 2-2.5 wt % producing uniform, spherical particles of approximately 5 μm.

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CHEMOSELECTIVE SYNTHESIS OF READABLE SEQUENCE-CODED POLYURETHANES

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Polyurethanes constitute a class of plastic materials used on a large scale by industry for a wide range of applications. However, they usually have a non-uniform primary structure, as they are produced by step-growth polymerisation. Here we report a facile protective-group-free approach to prepare sequence-defined polyurethanes. This method relies on the use of two chemoselective steps. In a first step, a hydroxy group was reacted with N,N'-disuccinimidyl carbonate to afford an active carbonate. In a second step, this carbonate was reacted with an amino alcohol to afford selectively a hydroxyl-fucntional carbamate. The iterative repetition of these two steps on a Wang resin modified with a hydroxy carboxylic acid linker led to the synthesis of a sequence-defined polyurethane. Different sequence-coded polymers have been synthetized using two different amino alcohols, defined as 0 and 1 bit. Thanks to the carboxylic function from the linker cleavage and the selective fragmentation of the C-O carbamate bound, the sequence of this new type of polymers can be easily read by tandem mass spectrometry in negative mode.

References

1) Carothers, W.H. (1931). Polymerization. Chem. Rev. 8, 353–426.
2) Gunay, U. S., Petit, B. E., Karamessini, D., Al Ouahabi, A., Amalian, J.-H., Chendo, C., Bouquey, M., Gigmes, D., Charles, L., and Lutz, J.-F., (2016). Chemoselective synthesis of uniform sequence-coded polyurethanes and their use as molecular tags. Chem. 1, 114-126
3) Ghosh, A.K., Doung, T.T., McKee, S.P., and Thompson, W.J. (1992). N,N'-dissuccinimidyl carbonate: a useful reagent for alkoxycarbonylation of amines. Tetrahedron Lett. 33, 2781–2784.

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URETHANE-CONTAINING POLYMER NETWORKS AS NEW GENERATION MENISCAL IMPLANTS: THE KEY TO SUCCESS?

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Meniscal tissue engineering is challenged by the complexity of meniscal tissue, its demanding biomechanical properties and degradation profile and its patient-specific design. In this research, an acrylate end-capped urethane-based poly(ethylene glycol) (AUP) is evaluated for its potential in the development of a tissue engineering meniscus scaffold. AUP combines the flexibility and strength of (poly)urethanes with the biocompatibility and hydrophilicity of poly(ethylene glycol). Patient-specific 3D meniscus scaffolds were successfully fabricated after careful optimization of two different processing techniques: direct rapid prototyping (RP) and an indirect RP method based on fused deposition modelling. The structural properties of the AUP scaffolds were assessed via micro-computed tomography (μ-CT), showing the realization of a regular, porous, interconnective network of the 3D hydrogel scaffold structure, which is important in the tissue engineering context. Next, preliminary cell culture studies were performed. Cell viability, proliferation and adhesion were observed through *in vitro* biological assays indicating a good cell biomaterial interactivity. In conclusion, AUP can be regarded as a promising material for meniscal tissue engineering.

References

1) H. N. Chia and B. M. Wu, “Recent advances in 3D printing of biomaterials,” J. Biol. Eng., vol. 9, no. 1, p. 4, 2015.
2) P. Dubruel, S. Van Vlierberghe, A. Houben, H. Van den Bergen, P. Roose, and D. Bontinck, “Novel urethane based materials, derivatives, methods of their preparation and uses.” Patent WO2017/005613, 2017.
3) A. Houben, P. Roose, H. Van den Bergen, H. Declercq, J. Van Hoorick, P. Gruber, A. Ovsianikov, D. Bontinck, S. Van Vlierberghe, P. Dubruel, “Flexible Oligomer Spacers as the Key to Solid-State Photopolymerization of Hydrogel Precursors”, Mater. Today Chem., (Accepted), 2017.
4) A. Houben, N.Pien, X. Lu, F. Bisi, J. Van Hoorick, M. Boone, P. Roose, H. Van den Bergen, D. Bontinck, T. Bowden, P. Dubruel, S. Van Vlierberghe, “Indirect Solid Freeform Fabrication of an Initiator-Free Photocrosslinkable Hydrogel Precursor for the Creation of Porous Scaffolds,” Macromol. Biosci., pp. 1–12, 2016.

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MULTIFUNCTIONAL SELF-ASSEMBLED NANOPARTICLES: FROM ELABORATION TO POTENTIAL APPLICATIONS

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One of the most important scientific in polymer chemistry is the elaboration of polymer nanoparticles with well-defined functionality and architectures. The multifunctional nanoparticles targeted in our work are tunable, stimuli-responsive, degradable, highly functional, and respectful of environment. The originality of such nanostructures relies on a reactive azlactone-based polymer and on a terpyridine ligand in precise location, providing a versatile platform of nanoparticles. The azlactone-based polymer gives the opportunity to: (i) introduce reversible cross-links between the reactive functionalized polymer chains and, to (ii) transform the reactive functionalized polymer into a stimuli-responsive polymer through chemical modification using various amines.[1,2] It is thus possible to obtain « smart » nanoparticles including nanogels with adjustable stimuli-sensing properties and with adjustable cross-linking rate without platform modification. Moreover, with terpyridine ligand in precise location-end of nanoparticles- it is possible to form metal-terpyridine complexes in order to obtain nanostructured hydrogel that combine large responsive swelling ratio, rapid response rate and high elasticity.[3] Thanks to this platform of nanoparticles, it is thus possible to envisage some applications in health and environment.

References

1) H. T. Ho, M. Levere, S. Pascual, V. Montembault, N. Casse, A. Caruso, L. Fontaine, Polymer Chemistry, 2013, 4, 675.
2) M. Levere, H. T. Ho, S. Pascual, L. Fontaine, Polymer Chemistry, 2011, 2, 2878.
3) M. Le Bohec, M. Banère, S. Piogé, S. Pascual, L. Benyahia, L. Fontaine, Polymer Chemistry, 2016, 7, 6834.

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ADVANCED CELL-INSTRUCTIVE PHOTO-HYDROGELS FOR LASER-BASED HIGH RESOLUTION 3D PRINTING

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In the present work, the synthesis and characterization of photo-sensitive gelatin[1] and poly(2-alkyl/aryl-2-oxazoline) (PAOx)[2] precursors for subsequent use in two-photon polymerization (2PP)[3] hydrogel development will be discussed. More specific, gelatin (type A and type B) is modified using methacrylic anhydride, resulting in methacrylamide-modified gelatin (gel-MOD). Furthermore, C3-MestOx, a functional PAOx monomer having a methyl ester side-chain, is synthesized *via* the modified Wenker method. To this end, the current research will explore the potential of hydrogel blends consisting of gelatin and PAOx derivatives covering a range of molecular weights and possessing a variable number of different polymerizable functionalities. The resulting material toolbox will enable us to combine natural, cell-interactive and synthetic building blocks into one single hybrid hydrogel with tunable mechanical, biodegradable and cell-interactive properties. The hydrogel constructs will serve as a biomimetic artificial 3D cell culture matrix[4] and will be used as a tool to gain information on the correlation between the hydrogel matrix properties and the cell response and to make tissue engineering in the future more performing.

References

1) Qin, X.-H.; Ovsianikov, A.; Stampfl, J.; Liska, R. et al.; J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 4799.
2) Viegas, T. X.; Bentley, M. D.; Harris, J. M.; Fang, Z. et al.; Bioconjugate Chemistry 2011, 22, 976-986.
3) Torgersen, J.; Ovsianikov, A.; Liska, R.; Stampfl, J. et al.; Adv. Funct. Mater. 2013, 23, 4542.
4) DeForest, C. A.; Anseth, K. S.; Ann. Rev. Chem. Biomol. Eng. 2012, 3, 421.

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CRYSTALLIZATION OF POLY(2-ISOPROPYL-2-OXAZOLINE)-BLOCK-POLY(LACTIDE) IN SOLID STATE AND AQUEOUS SOLUTION

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Crystallization delicately influences the self-organization of linear diblock copolymers (BCPs) both in solid state and in solution. Resolving the effects of molecular weight and composition requires a systematic library of BCPs. We chose a post-polymerization conjugation approach to study a wide compositional range of BCPs and their parent homopolymers. The first block, poly(2-isopropyl-2-oxazoline) (PiPOx), crystallizes in a fully stretched conformation by directional growth. This requires temperatures of 120 - 140°C in solid state and 60 – 65°C in aqueous solution. The second block, consisting of either semi-crystalline poly(L-lactide) (PLLA) or amorphous poly(DL-lactide) (PDLLA), renders the BCPs double-crystalline or crystalline-amorphous, respectively.
A variety of methods were used to investigate the influence of molecular weight and composition on crystallization and structure formation. In solid state, PiPOx dominated the crystallization behavior. In aqueous solution, the PiPOx-PLLA BCPs formed stable spherical particles that underwent an irreversible sphere-to-rod transition at elevated temperatures. No such transition was observed for PiPOx-PDLLA particles, indicating that crystallization of the PLLA core is the driving force.

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POST-POLYMERISATION FUNCTIONALISATION OF POLYETHERS BY OLEFIN CROSS METATHESIS

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Industrial uses of polyethers have expanded to medical applications, ranging from artificial tissues (i.e. implants, sutures and prosthetics), to the encapsulation of drugs; however post-polymerisation functionalisation methods are limited.[1] Olefin cross metathesis (CM) is a powerful carbon-carbon bond forming reaction, and therefore could potentially conjugate polyethers possessing pendent olefin handles, but there are very few examples of CM of polymers with olefinic side chains.[2]

This project will study the synthesis of novel biocompatible polyethers with diverse pendent olefins and their CM reaction with a range of partners. These various polymers are designed to probe the possibility of preventing the occurrence of self metathesis upon functionalisation using Hoveyda-Grubbs' second-generation catalyst. One such polymer, poly(methylallyl glycidyl ether), has been proven to be immune to the undesired self metathesis pathway allowing for retention of the low polymer dispersity (D = 1.15). We are currently working on coupling the polymer range with various bioactive compounds such as the cell signalling peptide, RGD.

References

1) Rinaudo, M. Polym. Int. 2008, 57, 397-430.
2) Mathers R. T.; Coates, G. W. Chem. Commun. 2004, 422-423; Montero de Espinosa, L.; Kempe, K.; Schubert, U. S.; Hoogenboom R.; Meier, M. A. R. Macromol. Rapid Commun. 2012, 33, 2023-2028; Fournier, L.; Robert, C.; Pourchet, S.; Gonzalez, A.; Williams, L.; Prunet J.; Thomas, C. M. Polym. Chem. 2016, 3700-3704; Sinclair, F.; Chen, L.; Greenland, B. W.; Shaver, M. P. Macromolecules 2016, 49, 6826-6834.

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CRYSTALLIZATION BEHAVIOR, MORPHOLOGY AND PROPERTIES OF BIODEGRADABLE POLYMERS

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Biodegradable polymers have recently received more and more attention, as they may not only degrade into carbon dioxide and water after usage but also be prepared from renewable resource. Even though some biodegradable polymers have already been commercially available, the following disadvantages, such as relatively high cost, poor mechanical properties, slow crystallization rate, and slow degradation rate, have limited their further practical application. In our lab, we have been using several methods, including copolymerization, polymer blending, and polymer nanocomposite, to modify the chemical and physical structures and adjust the physical properties of biodegradable polymers. In this lecture, we would like to briefly introduce our recent progress of crystallization behavior, morphology and properties of biodegradable polymers.

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References

1) Weng M, Qiu Z. Macromolecules 2013; 46: 8744–8747.
2) Weng M, Qiu Z. Macromolecules 2014; 47: 8351–8358.
3) Cui Z, Qiu Z. Polymer 2015; 67: 12–19.
4) Zhao Y, Qiu Z. RSC Advances 2015; 5: 49216–49223.
5) Li X, Qiu Z. RSC Advances 2015; 5: 103713–103721.

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PREPARATION OF FLUORINATED METHACRYLATE/CLAY NANOCOMPOSITE VIA IN-SITU RADICAL POLYMERIZATION: CHARACTERIZATION, STRUCTURE, AND PROPERTIES

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Novel fluorinated coating containing well-dispersed silicate nanolayers is successfully produced via *in-situ* free radical polymerization of 2,2,2-trifluoroethyl methacrylate (MATRIF) in the presence of vinylbenzyl-functionalized montmorillonite with different loading. The organic modification of sodium montmorillonite is achieved through an ion exchange reaction with triphenylvinylbenzylphosphonium chloride as surfactant prepared before use by reaction with vinylbenyl chloride and phosphine. Depending on the clay concentration, the nanocomposites with mixed morphologies containing partially exfoliated and intercalated structures were obtained as evidenced by XRD and TEM observations. The FTIR analysis also confirmed the presence of MMT layers and PMATRIF homopolymer in all nanocomposites samples. According to DSC and DMA results, the Tg values of nanocomposites slightly reduced about 2–8 °C compared to the virgin PMATRIF, but an improvement of their thermal stabilities was evidenced by TGA. The incorporation of nanoclay with fluorinated polymers improved the hydrophobicity and surface properties of obtained nanocomposites as well. These nanocomposites with enhanced physical properties appropriate for many applications such as fuel cell, lithium ion batteries, electronic, that fluoropolymers are used or likely to be used.

P204

INDUCING AN ORDER-ORDER MORPHOLOGICAL TRANSITION VIA CHEMICAL DEGRADATION OF AMPHIPHILIC DIBLOCK COPOLYMER NANO-OBJECTS

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The disulfide-based cyclic monomer, 3-methylidene-1,9-dioxa-5,12,13 -trithiacyclopentadecane-2,8-dione (MTC), is statistically copolymerised with 2-hydroxypropyl methacrylate (HPMA) to form a range of diblock copolymer nano-objects via reversible addition−fragmentation chain transfer (RAFT) polymerisation. Poly(glycerol monomethacrylate) (PGMA) is employed as the hydrophilic stabiliser block in this aqueous polymerisation-induced self-assembly (PISA) formulation, which affords pure spheres, worms or vesicles depending on the target degree of polymerisation for the core-forming block. When relatively low levels ($<$ 1 mol %) of MTC are incorporated, high monomer conversions ($>$ 99%) are achieved and high blocking efficiencies are observed. The worm-like nanoparticles obtained via PISA can be successfully transformed into spherical nanoparticles by addition of excess tris(2-carboxyethyl)phosphine (TCEP) at pH 8-9. Surprisingly, DLS and TEM studies indicate that the time scale needed for this order-order transition is significantly longer than that required for cleavage of the disulfide bonds located in the worm cores indicated by GPC analysis. This reductive degradation pathway may enable the use of these chemically-degradable nanoparticles in biomedical applications, such as drug delivery systems and responsive biomaterials.

P205

GLYCOSYLATED GOLD NANOPARTICLE BIOSENSORS

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The development of new analytical tools to probe pathogenic infection processes and as point-of care diagnostics is crucial to combat the spread of infectious diseases or to detect biological warfare agents. There is a growing need for biosensors that are fast, label-free, sensitive and inexpensive. Glycosylated gold nanoparticles that change colour due to lectin-mediated aggregation many find wide applicability as biosensors of bacteria and toxins.

Here we present the use of precision polymer-coated gold nanoparticles to negotiate the delicate balance between saline stability and the speed of the colorimetric readout.[1] These simple, monosaccharide conjugated gold nanoparticles are powerful tools for probing protein-carbohydrate interactions. Using a multiplexed assay and linear discriminant analysis differentiation between lectins and toxins such as Ricin or the cholera toxin[1-3] and bacterial phenotypes[4] is demonstrated. We have shown that the colour change in response to the correct glycan-lectin pairing can be determined not only spectrophotometrically but by using the simple combination of a mobile phone camera and image analysis freeware, providing an ultra-low cost route to biosensors.[2]

References

1) S-J. Richards and M. I, Gibson, ACS Macro Lett., 2014, 3, 1004
2) S-J. Richards, L. Otten, M. I. Gibson, J. Mater. Chem. B, 2016, 2016, 4, 3046
3) S. Won, S-J. Richards, M. Walker, M. I. Gibson, Nanoscale Horizons, 2017, DOI: 10.1039/C6NH00202A
4) S.-J. Richards, E. Fullam, G. S. Besra and M. I. Gibson, J. Mater. Chem. B, 2014, 2, 1490

P206

DESIGN OF POLYPHOSPHOESTER-BASED DRUG DELIVERY SYSTEMS BY EFFICENT THIOL-ENE REACTION

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Thanks to their biocompatibility, biodegradability and their structure similar to natural biomacromolecules, polyphosphoesters (PPE) are appealing polymers for biomedical applications. In contrast to polyesters, PPE properties and functionality are easily tuned via the chemical nature of the lateral chains[1-3]. To enhance the drug loading capacity of PPE-based micelles used as carriers for the delivery of poorly soluble drugs, an efficient strategy to increase the lipophilicity of the PPE block of polyethylene oxide (PEO)-*b*-PPE amphiphilic copolymers has been investigated. A PEO-*b*-PPE copolymer bearing pendant vinyl groups along the PPE block was synthesized and then modified by thiol-ene click reaction with thiols bearing either a linear alkyl chain (dodecyl) or a tocopherol moiety[4]. Ketoconazole was used as model hydrophobic drugs. Comparison of the loading contents and release profiles with PEO-*b*-PPE bearing shorter pendant groups is presented evidencing the key role of the structure of the pendant group on the PPE backbone. Finally, the low cytotoxicity of these PEO-*b* -PPE copolymers was also demonstrated. The tocopherol derivative was evidenced as particularly promising for drug delivery systems.

References

1) Clément, B.; Grignard, B.; Koole, L.; Jérôme, C.; Lecomte, P. Macromolecules 2012, 45, 4476–4486.
2) Vanslambrouck, S.; Clément, B.; Riva, R.; Koole, L.; Molin, D. G. M.; Broze, G.; Lecomte, P.; Jérôme, C. RSC Advances 2015, 5, 27330–27337.
3) Yilmaz, Z. E.; Vanslambrouck, S.; Cajot, S.; Thiry, J.; Debuigne, A.; Lecomte, P.; Jérôme, C.; Riva, R. RSC Advances 2016, 6, 42081-42088.
4) Vanslambrouck, S.; Clément, B.; Riva, R.; Ucakar, B.; Préat, V.; Gagliardi, M.; Molin, D. G. M.; Koole, L.; Lecomte, P.; Jérôme, C. Polymer Chemistry 2017, submitted.

P207

FUNCTIONALIZATION OF CELLULOSE NANOCRYSTALS WITH PEGMA-METAL-CHELATING COPOLYMERS

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Nanomedicines in the form of colloidal nanoparticles (NPs) can serve as powerful vehicles for the delivery of cytotoxic agents to tumours. Cellulose nanocrystals (CNCs) are glucose based, rod-like nanoparticles that are dispersible in water, non-toxic, and biodegradable. In a proof-of-concept experiment, our group showed that a CNC sample functionalized with a block copolymer formed colloidal dispersions in physiological media that were non-toxic and able to penetrate into multicellular tumour spheroids. Our most recent work builds on these results with the objective of optimizing the structure of the polymer as well as the number of polymers per CNC nanocarrier to minimize interaction with serum proteins and maximize tumour penetration. In this new design, stealth is provided by poly(oligoethylene glycol methacrylate) (PEGMA) copolymerized with aminopropylmethacrylamide (AMPA) which provides amine groups for attachment of metal chelators for eventual applications in radioimmunotherapy. Chemistry based on copper-catalyzed alkyne-azide click chemistry has also been successfully implemented in order to control and increase the number of polymers per CNC over our initial studies.

P208

ENCAPSULATION OF SELF-HEALING AGENTS VIA EMULSION/SOLVENT EVAPORATION AND 3D PRINTING TECHNIQUES

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The encapsulation of self-healing agents still represents a challenge in terms of defined capsule sizes and stability as well as shell thickness and materials. Especially nanometer-sized capsules with narrow particle size distributions and different core / shell combinations build up by biodegradable polyesters and filled with a variety of hydrophobic liquids acting as self-healing agents[1-3] need further development. Thus, for the encapsulation of hydrophobic liquids a combination of emulsion / solvent evaporation method [1] and 3D printing techniques is used.

Due to the growing industry of 3D printers, this technique appears realistic for producing entire capsule-based self-healing materials in a large macroscopic scale and within one single step.[4,5] The strategy as such is based on low melting thermoplastics, extracted as a strand, to build up the capsule shell which is also the macroscopic specimen. Therefore, small indentations are created during printing which are filled with the liquid healing agents and are closed with the next layer. Consequently, after several repetitions a completely finished macrosized polymer specimen filled with self-healing agents is generated.

References

1) Rana et al., Macromol. Rapid Commun. 2016, 37, 1715-1722.
2) M. Gragert et al., Macromol. Rapid Commun. 2011, 32, 419-425.
3) Wolfgang H. Binder, Self-Healing Polymers: From Principles to Applications 2013, Wiley-VCH, Weinheim.
4) M. K. Gupta et al., Nano Lett. 2015, 15, 5321-5329.
5) S. A. Khaled et al., Int. J. Pharm. 2015, 494, 643-650.

P209

MODULATION OF HYDROGEN-BOND STRENGTH IN A SQUARAMIDE-BASED SUPRAMOLECULAR POLYMER

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Supramolecular polymers have gained special interest over the past years due to their expected potential applications in areas such as regenerative medicine, tissue engineering and electronics.[1] Recently, we reported the synthesis of a squaramide-based bolaamphiphile (SBB) in which two squaramides were incorporated in the hydrophobic core of the SBB, which was flanked by two oligo(ethylene glycol) chains providing water solubility. They self-assembled into high-aspect-ratio fibrils, due to their hydrophobic character and synergistic coupling of hydrogen-bonding and aromaticity.[2] Here, we modulate the hydrogen-bonding strength of the monomer by incorporation of thiosquaramides within the identical bolaamphiphile structure. A decrease in the persistence and overall length of the thio-SBB was observed by cryoTEM and SAXS. Spectroscopic studies were performed in order to understand the changes in electronic and geometric properties at the molecular scale on the SBBs upon self-assembly in terms of hydrogen-bond interaction and aromatic character. By computational techniques, we found that while squaramides benefit from a reinforcement of the hydrogen-bond interactions by an increase in the aromatic character of the ring, thiosquaramides benefit to a lesser extent.

References

1) T. Aida, E. W. Meijer, S. I. Stupp, Science 2012, 335, 813-817
2) Saez Talens, V., Englebienne, P., Trinh, T. T., Noteborn, W. E. M., Voets, I. K. and Kieltyka, R. E., Angew. Chem. Int. Ed. 2015, 54, 10502-10506

P210

IONIC STRENGTH EFFECT OF DRUG RELEASE FOR PECTIN BASED HYDROGELS

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Based on classical Flory's theory, osmotic pressure arising from mobile ions is regarded as a swelling force due to ionic charges; in other words, the gel was assumed to be surrounded by Donnan potential barriers[1]. This study aims to investigate the role of ionic strength on swelling and drug release performance of pectin based polyelectrolyte gels. For this purpose, hydrogels were stynhesized with ionotropic gelation method. In this method $CaCl_2$ is usedas crosslinker. Swelling behavior and drug release profile were determined in external buffer solutions at different ionic strength and pH values. Theophylline was used as model drug due to its interactive relations with pectin. In order to explain the drug release and swelling mechanism, FTIR and ICP studies were conducted. Our results suggests that the ionic strength and pH of the buffer solution are strongly effects the swelling and release performance of the calcium pectinate hydrogels.

References

1) Ende M.T., Hariharan D., Peppas N.A. (1995). Factors influencing drug and protein transport and release from ionic hydrogels, 25(2-3), 127-137.

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NOVEL SELF-ASSEMBLIES VIA DOUBLE-HYDROPHILIC BLOCK COPOLYMERS IN AQUEOUS SOLUTION

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Self-assembly of block copolymers has a long tradition in polymer science. Especially amphiphilic block copolymers have been utilized often in the formation of micellar or vesicular structures in aqueous solution.[1] In contrast to amphiphilic block copolymers, the present contribution deals with double-hydrophilic block copolymer based self-assembled structures in aqueous solution without involvement of external stimuli.

The self-assemblies are formed due to the hydrophilic effect, which allows the formation of nano- to micro-scale aggregates in aqueous solution. The structure formation is based on significant differences in hydrophilicity of the individual blocks even though completely water-soluble non-thermo- and non-pH-responsive blocks are employed.[2] With regard to future applications in drug-delivery, biocompatible blocks are utilized, e.g. poly(*N*-vinylpyrrolidone), poly(2-ethyl-2-oxazoline), poly(ethylene oxide) or poly(saccharides).[3,4] As completely hydrophilic structures are formed, significant enhanced membrane permeability compared to traditional amphiphilic systems is expected. Moreover, the stability of the formed assemblies can be improved via crosslinking of the self-assembled structures via various techniques.

In summary, a new concept of block copolymer self-assembly based on completely water-soluble and biocompatible polymers is presented.

References

1) D.E. Discher, A. Eisenberg, Science 2002, 297, 967
2) S. M. Brosnan, H. Schlaad, M. Antonietti, Angew. Chem., Int. Ed. 2015, 54, 9715
3) J. Willersinn, M. Antonietti, B.V.K.J. Schmidt, Macromolecules, 2016, 49 (15), 5331
4) J. Willersinn, A. Bogomolova, M. Brunet Cabré, B.V.K.J. Schmidt, Polym. Chem., 2017, DOI: 10.1039/C6PY02212J

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PRECISION SYNTHESIS AND CHARACTERISATION OF NOVEL FUNCTIONAL POLYMERS

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Among the controlled radical polymerisation techniques, cobalt-mediated radical polymerisation (CMRP) has proven to be a valuable alternative in polymerising unreactive and unconjugated monomers of many different monomer classes under mild conditions, including α-olefins.[1,2,3] In a reversible deactivation mechanism, a cobalt complex reversibly traps the active growing chains and converts them into dormant species, avoiding side reactions and allowing for a controlled polymerisation. A fine control over the architecture is possible and allows to synthesise a large diversity of unprecedented block and alternating copolymers. Furthermore, functionalisation of the α- and ω-chain ends is now also possible.[4] Here, the polymerization of different vinyl monomers using CMRP is described to design highly functional materials under mild experimental conditions. The copolymerisation behaviour of these novel monomers was examined and the structure and thermal properties of the new copolymers were investigated.

References

1) A. Debuigne, Y. Champouret, R. Jérôme, R. Poli and C. Detrembleur, Chem. - A Eur. J., 2008, 14, 4046–4059.
2) A. Kermagoret, A. Debuigne, C. Jerome, C. Detrembleur, Nat. Chem., 2014, 6, 179-187.
3) A. Debuigne, C. Jerome, C. Detrembleur, Polymer 2017, DOI: 10.1016/j.polymer.2017.01.008.
4) J. Demarteau, A. Kermagoret, I. German, D. Cordella, K. Robeyns, J. De Winter, P. Gerbaux, C. Jerome, A. Debuigne and C. Detrembleur, Chem. Commun., 2015, 51, 14334–14337.

P213

USING DEGRADABLE MICROGELS FOR LONG-TERM STORAGE OF VITAMINS FOR ELONGATED SPACE FLIGHT

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On future Mars missions, astronauts have to bring food along with them which has to contain all necessary nutrients. Since unmanned supply rockets will be send to Mars ahead of the manned missions, nutrients must be stored for a long time period (ca. 5 years). Many nutrients, however, break down much faster. Retinol (vitamin A_1), for instance, degrades easily with time and temperature by a transition from trans to cis conformation. Even under ideal storage conditions (i.e. -70 °C, dark and inert atmosphere), a journey to Mars will exceed the stability range.

This work discusses the idea of using microgels based on poly-*N*-vinylcaprolactam as containers for retinol as a model vitamin. A highly crosslinked microgel hinders the transformation of retinol from trans to cis due to steric hindrance. The advantage of microgels is their low weight in lyophilised state, their biodegradability due to nature of the crosslinker, and their non-toxicity.

Results obtained in space industry can be used for everyday life when considering how to store nutrients for an extended period of time under harsh conditions such as deserts.

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OXIDATIVE SELF-ASSEMBLY AND SINGLE CHAIN POLYMER FOLDING: TOWARD ADVANCED STRUCTURAL CONTROL

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In nature, arising from absolute sequence control, proteins fold in solution into highly complex conformations which are, in most cases, responsible for the biological properties of proteins. Recently, an increasing interest has been shown toward the development of synthetic polymer materials with a similar degree of structural organization as protein. Synthesis routes for cyclic, multicyclic polymer chains, by using supramolecular or covalent bonds have already been developped.[1]

Herein, we present a study of single polymer chain folding by using dynamic covalent bridges such as disulfide and diselenide bonds. Free selenol exhibits fast oxidative dimerization to form diselenide bridge that can be orthogonal to disulfide bridge formation. The opportunities of a two steps folding process and the use of these reversible bonds are believed to lead to advanced control of single chain self-assembly.

The design and the synthesis protocols of building blocks containing side reactive functions (selenol and thiol) were established.[2] Sequence-controlled macromolecules exhibiting precisely positioned pendant function groups were synthesized and characterized successfully. Thiol and selenol groups were exploited to induce controlled intramolecular cross-linking via disulfide and diselenide bridges.

References

1) Bernhard V. K. J. Schmidt, Nina Fechler, Jana Falkenhagen and Jean-François Lutz, Nature Chemistry 2011, 3, 234-238
2) Olga Shishkan, Mirela Zamfir, Marc Andre Gauthier, Hans G. Börner and Jean-François Lutz, Chem. Commun. 2014, 50, 1570

P215

NEW FULLY BIOBASED MATERIALS FROM EUGENOL DERIVATIVES OBTAINED BY THIOL-EPOXY CLICK REACTION

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A triglycidyl derivative of eugenol, obtained by a four step synthetic procedure that includes O-allylation, Claisen rearrangement, allylation of phenol produced and final epoxydation with oxone was studied as epoxy resin in thiol-epoxy curing systems. As thiols we selected the commercial pentaerytritol tetrakis (3-mercaptopropionate) (PETMP), an hexathiol derived from squalene (6SH-SQ) and a trithiol derived from eugenol (3SH-EU).

The curing was studied by DSC and the enthalpy released when using 6SH-SQ as thiol was lower than the expected, which was attributed to its high multifunctionality and compact structure. Therefore, a linear renewable diepoxide (1,6-hexanedioldiglycidylether) was added to reduce the topological constrains of 6SH-SQ. 4-(N,N-dimethylamino)pyridine (DMAP) was used as the base that increases the nucleophilicity of the thiols.

The materials obtained are rigid at room temperature with T_gs higher than 60°C and higher than other thermosets prepared from eugenol derivatives.

The materials obtained showed initial degradation temperatures at about 300°C and good thermomechanical characteristics.

The new thiol-epoxy materials synthesized show better thermomechanical performance that the ones previously prepared obtained by photocuring of thiol-ene formulations based on triallyl eugenol derivatives.

References

1) Rémi Auvergne, Sylvain Caillol, Ghislain David, Bernard Boutevin, Jean-Pierre Pascault. Biobased thermosetting epoxy: present and future. Chem. Rev. 2014, 114, 1082–1115
2) Dailyn Guzmán, Xavier Ramis, Xavier Fernández-Francos, Àngels Serra. New catalysts for diglycidyl ether of bisphenol A curing based on thiol-epoxy click reaction. Eur. Polym. J. 59, 377-386, 2014.
3) Tsubasa Yoshimura, Toshiaki Shimasaki, Naozumi Teramoto, Mitsuhiro Shibata. Bio-based polymer networks by thiol–ene photopolymerizations of allyl-etherified eugenol derivatives. Eur. Polym. J. 2015, 67, 397–408.

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POLY(IONIC LIQUID)S AS ADVANCED MATERIALS FOR NEW DESIGN OF ELECTROCHEMICAL DEVICES

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Poly(ionic liquids) (PILs) are a new class of polyelectrolytes which combines the unique properties of ionic liquids and polymers that recently has attracted considerable attention [1]. PILs are considered as perspective substituents of volatile, toxic and flammable liquid electrolytes.

By varying the macromolecular architecture, nature of cations and anions we succeeded in preparation of PILs with high ionic conductivity (10^{-5} S/cm at 25^{o}C) and target mechanical properties. Such polyelectrolytes were further implemented for assembly of truly all-solid state Li batteries, electrochromic devices, supercapacitors and artificial muscles.

The advantages for a) “smart windows” are the fast switching times (3÷5 s), the high coloration efficiency (430 cm^2/C) and optical contrast (28.5 %); b) for $LiFePO_4$/PIL/Li batteries are the lithium transference number approaching unity, the possibility to operate at room temperature, the high delivering capacities (150 mAh/g) at high rates (C/2); c) for supercapacitors are the simplicity of assembly, the relatively high capacities (5 F/g) and real energies (0.5 Wh/kg) at 25^{o} C; d) for actuators the possibility of bending at low potential (2 V) both in open air and under vacuum at 25^{o}C.

References

1) Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Electrochim Acta 2015, 175, 18–34.

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SEQUENCE-CONTROLLED METHACRYLIC MULTIBLOCK COPOLYMERS VIA SULFUR-FREE RAFT (SF RAFT) EMULSION POLYMERIZATION

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There has been significant interest in synthesis of multiblock copolymers in the solution phase over the past few years. However, most reports utilise either transition metals (usually copper) or sulphur containing catalysts/chain transfer agents and often require multiple purification steps to isolate a pure end product. Recently our group has been exploring a technique in which emulsion polymerisation is combined with sulphur free Reversible Addition Fragmentation chain Transfer (SF RAFT) to form well define multi-block copolymers. Multiblocks derived from SF RAFT polymerisation, are easy to scale up, do not require specialised equipment or purification, higher degree of control over structural and physicochemical properties is obtained compared to homogenous polymerisation in the case of methacrylates and end group fidelity can be prepared.

Synthesis has focused on a wide range of methacrylic macromonomers by investigating the effect of various quantities of catalytic chain transfer agent on the physical and chemical properties of obtained macromonomers. Subsequently, macromonomer with ideal properties were utilised to facilitate the block formation of polymethacrylates, with the ultimate objective of achieving well defined sequence controlled macromolecules.

References

1) N. G. Engelis, A. Anastasaki, G. Nurumbetov, N. P. Truong, V. Nikolaou, A. Shegiwal, M. R. Whittaker, T. P. Davis and D. M. Haddleton, Nat. Chem., 2016, 1–19.

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MUSSEL-INSPIRED CATECHOLIC PRIMERS FOR RIGID AND DUCTILE DENTAL RESIN COMPOSITES

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In the construction of dental restorative material, surface priming is essential for improving mechanical performance for practical applications. We present catechol functionalized primers for resin composite inspired by interfacial mussel foot proteins. The catecholic primers with different chain end group were designed and coated on the surface using simple process. The surface binding ability and possible crosslinking of the bifunctional primer were evaluated by the knife shear test. Compression tests of dental resin composite using primed glass filler demonstrated the enhanced mechanical properties such as toughness and elastic modulus owing to the bidentate hydrogen bonding of catechol moieties. Furthermore, the superior biocompatibility of the priming surface was confirmed via cell attachment test, thus providing applicability of catecholic primers as dental materials.

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RIGID POLYESTERS, POLYCARBONATES AND POLYURETHANES FROM RENEWABLE KETAL MONOMERS

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Research in the area of polymers obtained from polycondensations is shifting from the use of crude oil based monomers to renewable monomers. An important feature asked from renewable polymeric structures, is a higher rigidity while maintaining processability. In this context, much research is devoted to renewable alternatives for terephtalic acid in polyesters, bisphenol A in polycarbonates and diisocyanates in polyurethanes.

In this work, rigid new diols were synthesized from glycerol, which is a renewable and cheap bulk chemical. The rigidity of the new monomers was realized by reacting glycerol with various diketones to form cyclic ketal containing diols. Initially, the diols were used in the polyurethane synthesis to obtain high T_g and fully amorphous polymer materials. Next, polycarbonates were synthesized with diphenyl carbonate. Thus, more renewable and less toxic diols, providing alternatives to bisphenol A, are presented. These new diols were also combined with several diesters in order to obtain renewable polyesters with good thermal properties. Initially, a procedure for the different polymerizations was explored. Subsequently, extensive chemical, thermal and mechanical analysis was performed on the synthesized polymers.

References

1) Gandini A., Lacerda T.M. Progress in Polymer Science. 2015;48:1-39.
2) Leoneti A.B., Aragão-Leoneti V., de Oliveira S.V.W.B. Renewable Energy. 2012;45:138-145.

P220

INTEGRATION OF ENZYMATIC CASCADE REACTIONS IN MICROFLUIDIC PROCESSES – COMBINING BIOCHEMISTRY WITH MICROFLUIDICS

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Hydrogels are one of the most promising carriers for enzyme immobilization to ensure the reusability and long-term stability of enzymes in chemical synthesis.[1] This multiply adaptable and mechanically stable molecular scaffold could be integrated in microfluidic systems to generate enzyme-loaded microfluidic reactors.[2,3]

This study demonstrates the usage of two multi-enzymatic cascade reactions (1: lactase, glucose oxidase, horseradish peroxidase; 2: phospholipase D, choline oxidase, horseradish peroxidase) immobilized in micro-scaled hydrogel dots structured by photolithography and covalently bound to a glass surface. The long-term stability of immobilized enzymatic cascade reactions was proven by constant activity measurement and storage in PBS-buffer over a period of at least 21 days. Additionally the immobilization of several enzymes in the same polymeric network conducted to the known substrate-channeling effect and thus increased activity.[4]

The enzyme-loaded hydrogel structures have been successfully integrated in microfluidic channels and were tested under the mechanical stress of a through flow process. In this setup the desired stabilizing effect and reusability can be indicated by slightly decreasing enzyme activity within several cycles of at least 15 hours usage.

References

1) R. Wohlgemuth, Current Opinion in Biotechnology 2010, 21, 713–724.
2) R. A. Sheldon, S. van Pelt, Chemical Society Reviews 2013, 42, 6223–6235.
3) C. Mateo, J. M. Palomo, G. Fernandez-Lorente, J. M. Guisan, R. Fernandez-Lafuente, Enzyme and Microbial Technology 2007, 40, 1451–1463.
4) Y.-H. P. Zhang, Biotechnology Advances 2011, 29, 715–725.

P221

ABA BLOCK COPOLYMERS SYNTHESIZED BY RAFT EMULSION POLYMERIZATION

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The synthesis of polymers with well-defined architecture is of ongoing high interest for many application areas and has experienced tremendous expansion with the development of reverse deactivation radical polymerizations (RDRP)[1–3]. Among all the RDRP, reversible addition fragmentation chain transfer (RAFT)[4] has shown to be a versatile and robust technique, allowing the polymerization of both polar and nonpolar monomers in a wide range of reactions conditions, including bulk, solution and aqueous dispersions[5,6]. Aqueous dispersed systems are generally favoured because of low environmental impact, good heat transfer and low viscosity.

In this contribution, we present the synthesis of high molecular weight ABA block copolymers of styrene and 2-ethylhexyl acrylate (EHA) containing hard and soft domains by means of RAFT emulsion polymerization using a bifunctional symmetric RAFT agent. Miniemulsion polymerization was first used for the A-block hard domains formation, followed by EHA fed to build the soft domains. Variations were done on chemical composition, and molecular weights together with studying the polymerization kinetics, MWD's and the morphology of resulting copolymers. Finally, the thermal and mechanical properties of the block copolymers were characterized.

References

1) Zetterlund, P. B.; Thickett, S. C.; Perrier, S.; Bourgeat-Lami, E.; Lansalot, M. Controlled/Living Radical Polymerization in Dispersed Systems: An Update. Chem. Rev. 2015, 115 (18), 9745–9800.
2) Qiu, J.; Charleux, B.; Matyjaszewski, K. Controlled/living Radical Polymerization in Aqueous Media: Homogeneous and Heterogeneous Systems. Prog. Polym. Sci. 2001, 26 (10), 2083–2134.
3) Braunecker, W. A.; Matyjaszewski, K. Controlled/living Radical Polymerization: Features, Developments, and Perspectives. Prog. Polym. Sci. 2007, 32 (1), 93–146.
4) Hill, M. R.; Carmean, R. N.; Sumerlin, B. S. Expanding the Scope of RAFT Polymerization: Recent Advances and New Horizons. Macromolecules 2015, 48 (16), 5459–5469.
5) Jennings, J.; He, G.; Howdle, S. M.; Zetterlund, P. B. Block Copolymer Synthesis by Controlled/living Radical Polymerisation in Heterogeneous Systems. Chem. Soc. Rev. 2016, 5055–5084.
6) McLeary, J. B.; Klumperman, B. RAFT Mediated Polymerisation in Heterogeneous Media. Soft Matter 2006, 2, 45.

P222

SOFT AND CONDUCTING POLYANILINE CRYOGELS SUPPORTED WITH POLY(VINYL ALCOHOL)

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Single-step preparation of new type of soft macroporous conducting cryogels is reported. Polyaniline/poly(vinyl alcohol) cryogel was prepared by the oxidation of aniline hydrochloride in frozen reaction mixtures containing a supporting polymer, poly(vinyl alcohol). Resulting hydrogels are macroporous and macroscopically homogeneous. The conducting polyaniline phase was fibrillary. The conductivity of cryogel was 0.004 S/cm in water and 0.105 S/cm in 0.1 M sulfuric acid. Due to the contribution of electronic transport, the conductivity of cryogel was always higher than the ionic conductivity of aqueous phase used for its penetration. Viscoelastic and mechanical properties have been assessed and demonstrated good mechanical integrity and feasibility of potential applications.

P223

MODULAR SYNTHESIS OF POLY(AMPHOLYTES) FOR CONTROLLING ICE GROWTH AND CELL STORAGE

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Antifreeze (glyco) proteins (AF(G)Ps) are highly active ice recrystallisation inhibitors (IRI), however issues with their synthesis and extraction limit their commercial use as cryoprotectants. One class of synthetic materials which display IRI activity are poly(ampholytes), which have been found to be effective synthetic analogues to these AF(G)Ps. However, previous work used statistical copolymers with broad dispersity. Here we exploit maleic anhydride co-polymers to obtain regio-regular polymers, which can be modified post-polymerisation to install ampholytic (mixed charge) functionality. These polymers are critically compared to those obtained by statistical copolymerization of mixed-charge monomers and are found to have increased ice recrystallisation inhibition activity. The modular synthesis also enables sequential modification of the hydrophobicity of the polymer to tune activity. These polymers will find use for the cryo storage of cells and tissue for regenerative medicine.

References

1) Stubbs C., Lipecki J., Gibson M.I., Biomacromolecules 2017, 18, 295-302

P224

PHASE CHANGING POLY (ETHYLENE GLYCOL) (PEG) BASED POLYMERIC IONIC LIQUIDS (PIL) WITH CO2 CAPTURE ABILITIES

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Polymeric ionic liquids (PILs) combine the properties of ionic liquids and polymers into a single material and have recently shown good potential in separation of CO_2, an area of critical importance due to the concerns over greenhouse gases emissions leading to global warming. In an effort to develop materials which will help environmental concerns, a series of dicationic PEG based PILs were synthesized. Further, the minimization of growing energy demand can be helped by incorporating PEG in the PIL structure. With the use of acrylate of PEG, the dicationic PIL was prepared having ammonium cationic centre. The prepared PIL was made to undergo metathesis to prepare hydrophobic PILs having ability for CO_2 capture. These materials exhibited solid-liquid phase transition and the enthalpy was measured using differential scanning calorimetry. The CO_2 capture studies were performed on a fabricated setup with varying pressure range from 1-15 bar. The findings regarding the prepared materials, having potential dual applications in the fields of thermal energy storage and CO_2 capture, will be presented in the conference.

P225

SUSTAINABLE FUNCTIONALIZATION METHODS FOR CARBOHYDRATES

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The ever increasing depency of mankind on crude oil highlights the concern of its finite availability along with its environmental impact.[1] Biomass constitutes very promising and advantageous alternative and renewable resource, offering broad range of suitable organic structures. The focus of our efforts is to develop new methods and procedures that convert renewable resources to useful products in an as sustainable fashion as possible.[2] We thus established several sustainable methods for efficient carbohydrate modification, especially employing cellulose and starch due to the their high abundance along with their distinctive properties. In our recent work, starch and plant oils were directly combined without any pre-treatment or derivatization for the synthesis of polymeric materials with desirable properties.[3] Moreover, succinic anhydride was employed for the efficient functionalization of cellulose and starch using a CO_2-based switchable ionic liquid and leading to high degrees of substitution. Passerini and Ugi reactions were subsequently applied to the succinylated cellulose, resulting in full conversion. Moreover, functional cellulose carbonates have been obtained by using diallyl carbonate as sustainable alkylating reagent, which can be further functionalized by thiol-ene addition.

References

1) The New Plastic Economy: Rethinking the future of plastics, World Economic Forum, 2016.
2) A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Soyler, M. A. R. Meier, Chem. Eur. J. 2016, 22, 11510–11521.
3) Z. Soyler, M. A. R. Meier, ChemSusChem 2017, 10, 182–188.

P226

A STUDY ON THE GAS PERMEATION BEHAVIOUR OF A MICROPOROUS SPIROBISINDANE-BASED POLYMER (PIM-1)

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Polymers of intrinsic microporosity (PIMs) are a class of high free volume glassy polymers with rigid contorted macromolecular backbones and interconnected free volume. These properties allow for formation of microporous films with promising performance for energy-efficient gas separations. In this study, PIM-1, the archetypal representative of solution-processable PIMs, was synthesized by step-growth polymerization and was used to prepare free-standing PIM-1 membranes. To explain the current discrepancies between literature data for the gas separation performance of PIM-1 membranes, the effect of PIM-1 molecular weight, film thickness, methanol treatment and measurement method was studied in separation of O_2/N_2, H_2/N_2, H_2/CH_4 and CO_2/CH_4 gas pairs. The results suggested that although permeability is a characteristic of the polymer, thicker films of PIM-1 showed higher permeability with almost similar or higher selectivity for all gas pairs. Also, it was found that the molecular weight of PIM-1 did not have a strong effect on the performance of the resulting membrane. Finally, two of the current methods for measuring the permeability and selectivity of the membranes were studied and the differences were addressed.

P227

THIOLACTONE-BASED MULTICOMPONENT REACTIONS IN MICROFLUIDICS: PREPARATION OF FUNCTIONAL PARTICLES

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Thiolactone chemistry is proven to be a powerful tool to prepare and functionalise macromolecules because of its single-pot multicomponent character. Indeed, using a combination of amine and acrylate, aminolysis followed by a thia-Michael addition allows for the click-like double modification of a thiolactone-bearing substrate. In this work, a polyacrylamide copolymer bearing thiolactone moieties was prepared and efficiently crosslinked by adding an amine and a diacrylate, both in aqueous and organic media. This strategy was then applied for the preparation of uniform particles that were generated by a simple T-microfluidics setup. The discrete phase consisted of an aqueous solution of the thiolactone-bearing copolymer and diacrylate, while toluene containing surfactant and amine was selected as the continuous phase. In the next phase, the particles will be functionalised by using an appropriate (functional) amine.

P228

ORGANIC BULK HETEROJUNCTION SOLAR CELLS BASED ON THIENOTHIOPHENE AND BENZOTHIADIAZOLE CONTAINING CONJUGATED POLYMERS

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For the last few decades, conjugated polymers were found to be organic semiconductors that can be used as alternatives in inorganic semiconductors for a variety of electronic applications.1,2,3 With this regard, the focus of this study is to develop low band gap polymer by combining electron-rich (donor) and electron-deficient (acceptor) moieties as repeating units, in order to design internal donor– acceptor (D–A) structures for organic photovoltaic (OPV) devices. For this purpose, thieno[3,2-b]thiophene(TT) and benzo[c][1,2,5]thiadiazole containing monomers were independently synthesized, then polymerized via Stille cross-coupling reaction. Oxidation and reduction behavior of the polymer was studied by using cyclic voltammetry. The optical band gap of the polymer was calculated by using UV-VIS-NIR spectroscopy as 1.08 eV from onset of the maximum absorption band at 980 nm. Two broad absorption peaks in the visible region located at around 400 nm and 700 nm resulted in blue-green color in its neutral state and upon oxidation, the color shifted to grey. After optimization of the thickness and morphology of polymer:PCBM, device construction and current/voltage measurements will be conducted in a nitrogen-filled glovebox system.

References

1) Jeffries-El, M.; Kobilka, B. M.; Hale, B. J. Macromolecules 2014, 47 (21), 7253–7271.
2) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Chem. Rev. 2015, 115 (23), 12666–12731.
3) Chiu, C.-Y.; Wang, H.; Brunetti, F. G.; Wudl, F.; Hawker, C. J. Angew. Chem. Int. Ed. Engl. 2014, 53 (15), 3996–4000.

P229

VINYLCYCLOPROPANES: A PROMISING ALTERNATIVE TO METHACRYLATES FOR THE DEVELOPMENT OF LOW SHRINKAGE DENTAL COMPOSITES

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Dental composites are made up of an organic matrix and silanized inorganic fillers. The organic matrix typically contains a mixture of different dimethacrylates and additives (photoinitiator system, stabilizer, etc.)[1]. Polymerization shrinkage is one of the mayor drawbacks of such materials. The resulting shrinkage stress can lead to marginal leakage between the restoration and the tooth, increasing the risk of marginal staining and of secondary caries formation. Cyclic monomers which, are able to undergo radical ring-opening polymerization are great alternatives to methacrylates for the development of low shrinkage materials. Vinylcyclopropanes (VCPs) are particularly attractive for dental materials because they are stable in composite formulations[2]. Until now, VCPs could not be applied in dental composites because of their low reactivity in comparison to methacrylates. It has been recently reported that the use of bis(4-methoxybenzoyl)diethylgermane as a photoinitiator results in a significant increase of the VCP polymerization rate[3]. In this work, the synthesis of new crosslinking vinylcyclopropanes and their evaluation in restorative composites containing bis(4-methoxybenzoyl)diethylgermane is described. Materials exhibiting good mechanical properties and significantly lower polymerization shrinkage than methacrylate-based formulations were obtained.

References

1) N. Moszner, T. Hirt, J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 4369-4402
2) N. Moszner, F. Zeuner, T. Voelkel, V. Rheinberger, Macromol. Chem. Phys. 1999, 200, 2173-2187
3) Y. Catel, U. Fischer, N. Moszner, Macromol. Chem. Phys. 2016 DOI: 10.1002/macp.201600463

P230

INDUSTRIAL DEVELOPMENTS OF POLYMERIC ADDITIVES TO FUNCTIONALIZE TEXTILES SUBSTRATES AND COMPOSITE MATERIALS

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Devan Chemicals develops speciality chemicals for the worldwide textile industry, focusing its activity on the development of high added-value products for niche markets and applications.

In this context Devan, with an open innovation mindset, is currently working on the development of different kinds of industrial polymeric additives for the manufacture of smart textiles and self-healing materials.

Amongst the developed additives are microcapsules containing “phase changing” or “probiotic” ingredients that are sold in the bedding industry; microcapsules have also been developed containing highly reactive components for self-healing materials. We will demonstrate how to functionalize microcapsules through our patented reactive technology, which allows a permanent fixation of microcapsules onto fibres and other surfaces to provide a good compatibility/bondability with the surrounding matrices.

In addition, we will show our latest developments in masterbatch polymeric additives that can bring additional performance to standard fibres with functionalities such as: antimicrobial, soft touch or flame retardant properties. The use of functional master batches instead of topical treatments (traditional approach) has several advantages such as: durability to washing cycles, flexibility in dosing levels and energy consumption.

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RENEWABLE POLYMERS FROM PINENE METABOLITES FOR MATERIAL APPLICATIONS

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Polymeric materials are an integral part in virtually all aspects of life in modern society, e.g., in medicine, transportation, food, and clothing. The vast majority of today's polymers are synthetic and stem from fossil-fuel sources. Fossil fuels are not only finite but also have a big impact on the environment. There is hence a great demand for suitable polymers from renewable sources. The forest and paper industry offers several interesting options for such polymers. Most commonly known are cellulose, hemicellulose, and lignin, but there are also small compounds available from the industry's side streams with potential as building blocks in novel polymers for various applications. One such type of compounds are pinenes, the main component of turpentine. Pinenes are microbially degraded into a wide range of interesting compounds. We here present the synthesis and characterization of novel polymers based on such renewable metabolites of pinenes. We believe these underutilized compounds have great value as components of renewable polymers for a wide range of material applications.

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NOVEL SEGMENTED POLYHYDROXYURETHANES: CONTROL OF NANOPHASE SEPARATION IN LINEAR NON-ISOCYANATE POLYURETHANES TO ACHIEVE PROPERTIES UNLIKE AND LIKE THOSE OF LINEAR SEGMENTED POLYURETHANES

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Polyhydroxyurethane (PHU) is a potential replacement for polyurethane (PU), which is synthesized by reacting alcohols with isocyanates. Because isocyanates are facing increasing regulation, there is a need to investigate the synthesis and structure-property relationships of non-isocyanate-based polyurethane (NIPU). PHU is a NIPU which is synthesized via cyclic carbonate aminolysis, resulting in polymers which contain urethane linkages with adjacent hydroxyl groups. With segmented PUs in the form of multiblock linear copolymers, urethane linkages are confined to hard-segment domains dispersed in a soft-segment matrix, leading to thermoplastic elastomers. Here, I will describe how the the hydroxyl group and resulting intersegmental hydrogen bonding with certain soft segments can lead to complete loss of nanophase separation in PHU. With other soft segments which moderate the intersegmental hydrogen bonding, the resulting PHUs exhibit nanophase separation but with broad interphases and thus exhibit behavior that makes them well designed as broad-temperature-range damping materials. Finally, with other soft segments which eliminate intersegmental hydrogen bonding, the resulting PHUs are thermoplastic elastomers, the properties of which can be tuned to be competitive with PU thermoplastic elastomers.

References

1) E.K. Leitsch, G. Beniah, K. Liu, T. Lan, W.H. Heath, K.A. Scheidt, J.M. Torkelson, "Non-Isocyanate Thermoplastic Polyhydroxyurethane Elastomers via Cyclic Carbonate Aminolysis: Critical Role of Hydroxyl Groups in Controlling Nanophase Separation," ACS Macro Letters 5, 424-429 (2016).
2) G. Beniah, K. Liu, W.H. Heath, M.D. Miller, K.A. Scheidt, J.M. Torkelson, "Novel Thermoplastic Polyhydroxyurethane Elastomers as Effective Damping Materials over Broad Temperature Ranges," European Polymer Journal 84, 770-783 (2016).
3) G. Beniah, B.E. Uno, T. Lan, J. Jeon, W.H. Heath, K.A. Scheidt, and J.M. Torkelson, "Tuning Nanophase Separation Behavior in Segmented Polyhydroxyurethane via Judicious Choice of Soft Segment", Polymer 110, 218-227 (2017).

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POLYANILINE FILM WITH ENHANCED THERMAL STABILITY OBTAINED VIA INTERACTION WITH PHOSPHONATE ON THE SURFACE

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Interaction between blue non-conducting film of polyaniline base with dibutyl phosphonate yields a green conducting polyaniline film. The character of interaction was studied by evolution of the infrared spectra of the film recorded during heating up to 200 °C. The experiments demonstrate that dibutyl phosphite, and not its phosphonate tautomeric form in which no proton available, interacts with polyaniline base. Such interaction prevents dibutyl phosphite from the oxidation into dibutyl phosphate which occurs in the case of heating of neat dibutyl phosphite, in which phosphonate form predominates. The thermal stability and the changes in molecular structure have been assessed by UV-visible, FTIR and Raman spectra. The model of the interaction based on the quantum-chemical optimization of the idealized structure is proposed.

References

1) I. Šeděnková, M. Trchová, J. Dybal, J. Stejskal. Polym. Degrad. Stab. 134, 357–365 (2016).

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CLICK REACTION STRATEGY IN THE PREPARATION OF NANOPOROUS MATERIALS

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Mesoporous materials decorated with 4-phenyltriazoles were obtained after the segregation-hydrolysis of the block copolymer poly(4-methyl-(4'-benzyltriazole) styrene-*co*-styrene)-*b*-poly(lactic acid)). The synthesis starts with the preparation of the PLA macroinitiator via Ring Opening Polymerization (ROP) with microwave energy and a bifunctional initiator. Block copolymerization of this macroinitiator was carried out via Atomic Transfer Radical Polymerization (ATRP) with styrene and 4-methylazide styrene using different molar ratio of the functional co-monomer. The azide group was transformed with Click chemistry using phenylacetylene to obtain the triazole group along the styrenic block. The functionalized copolymers were characterized by ^{1}H, ^{13}C Nuclear Magnetic Resonance (NMR) and phase segregated with a stainless steel die through a thermal sheer stress process, followed by an alkaline hydrolysis to remove the PLA block. The resulting material showed cylindrical cavities that contain triazole groups in the PS matrix, which was characterized with Scanning Electron Microscopy (SEM).

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CHARGE DENSITY IN POLYMER CONJUGATES - STRIKING THE BALANCE BETWEEN TRANSFECTION EFFICIENCY AND TOXICITY

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The controlled delivery of genetic material into cells using non-viral vectors, *e.g.* polymers, is more topical than ever.[1] Regarding its polymeric structures, cationic charges are recommended for strong and reversible complexation of nucleic acids and high transfection efficiencies, unfortunately accompanied with cytotoxic side-effects.[2] This creates the need of strategies for overcoming this obstacle. We present two strategies of the balancing between cytotoxicity and complexation properties:

(i) We used a copolymerization with biocompatible monomers or architecture. For this purpose poly(2-oxazoline) derivatives were utilized in two approaches, as statistical poly(2-oxazoline) copolymer used for brain-targeting of plasmid DNA[3] and as more complex oligo(2-ethyl-2-oxazoline)s in methacrylate-based graft-copolymers for reduction of cytotoxicity.

(ii) We further tested the encapsulation of membrane active methacrylate-based polymers forming “Trojan horse systems”. Thereby, the cell membrane can be preserved from strong interactions and thus from toxic side effects.[4]

References

1) D. W. Pack, A. S. Hoffman, S. Pun, P. S. Stayton, Nat. Rev. Drug Discov. 2005, 4, 581-593.
2) S. Hong, P. R. Leroueil, E. K. Janus, J. L. Peters, M.-M. Kober, M. T. Islam, B. G. Orr, J. R. Baker, M. M. Banaszak Holl, Bioconjug. Chem. 2006, 17, 728-734.
3) C. Englert, A.-K. Trützschler, M. Raasch, T. Bus, P. Borchers, A. S. Mosig, A. Traeger, U. S. Schubert, J. Control. Release 2016, 241, 1-14.
4) M. Bauer, C. Lautenschlaeger, K. Kempe, L. Tauhardt, U. S. Schubert, D. Fischer, Macromol. Biosci. 2012, 12, 986-998.

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STEPWISE FOLDING DIFFERENT DOMAINS OF A SEQUENCE CONTROLLED SINGLE POLYMER CHAIN

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Sequence regulated multiblock copolymers are a new class of materials, the properties and functionality of which can be controlled on demand. The highly specialized activity of biopolymers, e.g. proteins, is determined by the control of their precise tertiary three-dimensional (3D) structure, which arises from the controlled folding of a single polypeptide chain. The controlled folding process is inarguably crucial for the specified functions of the proteins as the incorrect folding of proteins is the origin of a wide variety of pathological conditions and cause of prevalent diseases. The delicate controlled folding process of proteins is governed by the sophisticated sequence of amino-acid. It has been a major yet challenging goal for polymer chemists to produce functional materials to mimic the tertiary structure of natural biopolymers by folding into 3D structure through intramolecular interactions of specialized sequences. In order to mimic the precision of the controlled folding process of biopolymers, controlling the sequence of the polymer chain becomes the first significant issue to address. By introducing specified functionality into precisely defined domains of the polymer chain the folding can be controlled.

References

1) Junliang Zhang, Guillaume Gody, Matthias Hartlieb, Sylvain Catrouillet, Jonathan Moffat, Sébastien Perrier. Macromolecules 2016, 49 (23), 8933-8942.

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PHOTO- AND THERMOREVERSIBLE ANTHRACENE-BASED THIOL-ENE NETWORKS

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Using reversible anthracene chemistry, which relies on photochemical dimerization and photochemical or thermal dissociation, reversible thiol-ene networks are made.

Firstly a range of anthracene derivatives were made, having different substituents.[1] The main effect variation effect was found in the thermal stability of the dimers. The most promising derivative was used in combination with poly(dimethylsiloxane-co-propylmercaptomethylsiloxane) or a novel aliphatic trithiol synthesized from 1,2,4-trivinylcyclohexane in a simple two-step procedure.[2]

Networks were analyzed using DSC, DMTA, polarization microscopy, XRD and (photo-)rheology. Both networks show weak endothermic transitions between 50 and 60°C, which proved to originate from melting of a crystalline anthracene-dimer phase (trithiol network) or a liquid crystalline phase (PDMS network) based on X-ray diffraction and polarization microscopy. Using rheology, both types of networks were shown to cleanly decompose into multi-functional anthracene monomers at temperatures above 180°C. Irradiation of these anthracene monomers resulted in the formation of networks having similar physical properties as the original materials.

These thermoset materials can be applied as coatings, allowing an easy removal of the coating at the end of lifetime, as well as self-healing and stress-relaxation.

References

1) Van Damme, J.; Vlaminck, L.; Van Assche, G.; Van Mele, B.; van den Berg, O.; Du Prez, F. Synthesis and evaluation of 9-substituted anthracenes with potential in reversible polymer systems. Tetrahedron 2016, 72 (29), 4303-4311
2) Van Damme, J.; van den Berg, O.; Brancart, J.; Vlaminck, L.; Huyck, C.; Van Assche, G.; Van Mele, B.; Du Prez, F. Anthracene-Based Thiol–Ene Networks with Thermo-Degradable and Photo-Reversible Properties. Macromolecules 2017

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THE INFLUENCE OF THE END-GROUP ON THE CHIRAL SELF-ASSEMBLY OF ALL-CONJUGATED BLOCK COPOLYMERS

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The self-assembly of all-conjugated block copolymers is an effective way to obtain well-ordered structures at the nanoscale. Although these polymers possess an end-group, and a lot of research has been done on their self-assembly, the influence of the end-group has never been considered. It has been demonstrated that the nature of the block as the degree of polymerization (DP) plays a crucial role in the solubility of the different blocks in a conjugated block copolymer. We hypothesize that also the end-group is of importance: more bulky groups will increase the solubility and thus will have an influence on the self-assembly. In our hypothesis, if the blocks of the polymer are each other's enantiomers, the end-group determines when one block becomes dominant in the chiral expression. The ratio of the lengths of the blocks at which this happens is determined by the size of the end-group.

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AMIDATION OF METHYL ESTER SIDE CHAIN BEARING POLY(2-OXAZOLINE)S WITH TYRAMINE: A QUEST FOR A SELECTIVE AND QUANTITATIVE APPROACH

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Poly(2-Alkyl/Aryl-2-oxazoline)s are a class of biocompatible polymers with a pseudopolypeptide structure which have received a growing interest over the past decade. This growing interest can mainly be attributed due to their greater chemical versatility compared to other biocompatible polymers such as poly(ethylene glycol) (PEG) and poly(*N* -vinylpyrrolidone) (PVP). This high degree of chemical versatility is facilitated by the high end-group fidelity of the polymerization, allowing the introduction of functionalities as an initiator or as a terminator; and the wide variety of synthesized monomers allowing the introduction of functionalities via several post-polymerization modification procedures. However, one of the biggest challenges of post-polymerization procedures is to be quantitative in nature. Recently, we reported the quantitative conversion of methyl ester side chain bearing poly(2-alkyl/aryl-2-oxazoline)s via direct amidation with a range of amines. While this approach is robust, it can be challenging to introduce certain amines. Here we report several other amidation approaches of methyl ester side chain bearing poly(2-alkyl/aryl-2-oxazoline)s, via hydrolysis and activation allowing the introduction of more complex/expensive amines such as tyramine.

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HEALABLE SHAPE-MEMORY POLYURETHANES USING REVERSIBLE TAD CHEMISTRY

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Throughout the years, self-healing has become a broad and important research field within polymer chemistry. However, the majority of existing polymer systems focus on the repair of damage on the submicron scale, which leads to inadequate healing when a large-volume damage site is created. The deficiency of these polymer systems to heal damage on the macro scale is a consequence of mainly two issues, being the limited volume of healing agents and the inability to reunite the crack edges.

A polymer system for the healing of polyurethanes upon heating, using a combination of shape-memory and reversible furan-maleimide chemistry to reunite and repair crack edges, was proposed by Rivero *et al.*[1]. Although good mechanical properties were obtained after multiple healing cycles, the time needed for healing (>12h at 50°C) is susceptible for improvement. In this project, shape-memory polyurethanes are equipped with ultrafast triazolinedione (TAD) chemistry[2] in order to significantly reduce the healing time. In addition, mechanochemistry experiments are presented to confirm mechanical breaking of the reversible TAD-indole bond, which is vital for efficient healing.

References

1) Rivero, G., Nguyen, L. T. T., Hillewaere, X. K. D., Du Prez, F. E. One-pot thermo-remendable shape memory polyurethanes. Macromolecules 47, 2010–2018 (2014).
2) Billiet, S., De Bruycker, K., Driessen, F., Goossens, H., Van Speybroeck, V., Winne, J. M., Du Prez, F. E. Triazolinediones enable ultrafast and reversible click chemistry for the design of dynamic polymer systems. Nature Chemistry 6, 815–821 (2014).

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TRANSIENTLY THERMORESPONSIVE TETRAHYDROPYRAN/FURANYLATED -POLYACRYLAMIDES FOR THE FORMULATION OF AMPHOTERICIN B AS A VACCINE ADJUVANT

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Interactive polymers that change their solubility in response to physiologically relevant stimuli are attractive for biomedical applications. A new class of transiently thermoresponsive polyacrylamides was synthesized that in native state have a phase transition temperature below room and physiological temperature, but gradually transform into fully soluble polymers in response to a side chain hydrolysis reaction triggered by acidic pH values relevant for the endosomal intracellular milieu. These polymers were synthesized from 2-hydroxyethyl acrylamide modified with tetrahydropyran or tetrahydrofuran through an acetal linkage yielding acid-degradable properties. RAFT polymerization was used to synthesize well defined homo- and block copolymers. The latter were used for the self-assembly of micellar nanoparticles that could encapsulate hydrophobic compounds. Micelles were used for the formulation of Amphotericin B, a poorly water-soluble anti-bacterial compound that was recently discovered to possess agonist capacities for the Toll like receptors (TLR) 2 and 4. In view of its potential as vaccine adjuvant we showed that encapsulation of Amphotericin B into these micelles strongly reduced its cytotoxic effects, but in the meantime allowed for potent TLR triggering.

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A GENERIC PLATFORM FOR THE VISUALIZATION OF ALL MONOMER SEQUENCES IN INDIVIDUAL COPOLYMER CHAINS

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One of the key challenges for future polymer synthesis is the detailed characterization of individual macrospecies, including the position of all monomer units and functionalities [1]. In this contribution, it is demonstrated that advanced modeling techniques in combination with detailed experimental procedures allow the overcome this challenge. These techniques are further used to identify the most suited protocols for the synthesis of advanced macromolecular architectures, accounting for the possible impact of diffusional limitations and side reactions. Examples are included both for radical and cationic processes [2-5]. The presented modeling platform is generic and can lead to a significant progress in the field of macromolecular engineering.

References

1) D.R. D'hooge, P.H.M. Van Steenberge, M.-F. Reyniers, G.B. Marin Prog. Polym. Sci. 2016, 58, 59
2) P.H.M. Van Steenberge, D. R. D'hooge, Y. Wang, M. Zhong, M.-F. Reyniers, D. Konkolowicz, K. Matyjaszewski, G.B. Marin Macromolecules 2012, 45, 8519
3) P. Derboven, D. R. D'hooge, M. Stamenovic, P. Espeel, M.-F. Reyniers, F.E. Du Prez, G.B. Marin Macromolecules 2013, 7, 362-379
4) P.H.M. Van Steenberge, B. Verbraeken, M.F. Reyniers, R. Hoogenboom, D.R. D'hooge Macromolecules 2015, 48, 7765
5) S. K. Fierens, S. Telitel, P.H.M. Van Steenberge, M.F. Reyniers, G.B. Marin, J. F Lutz, D. R. D'hooge Macromolecules 2016, 49, 9336

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EFFICIENT MACROMOLECULAR COUPLING USING TRIAZOLINEDIONES : PERMANENT OR DYNAMIC LINKING

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Precision polymer structures with raising complexity lead to improved and innovative characteristics for pioneering applications. Nowadays, synthetic chemists in the polymer community continuously get inspired by the click philosophy for the synthesis of complex macromolecules[1,2]. In this respect, our research group revisited a powerful additive-free reaction, based on the reactivity of a 1,2,4-triazoline-3,5-dione (TAD) component, that can form irreversible or dynamic covalent bonds by selecting the suitable reaction partner[3]. In this present work, the potential of the irreversible and reversible TAD reactions for effective synthesis of macromolecular structures, with the focus on block copolymers, will be introduced. In the first part, the irreversible TAD-chemistry is explored as an efficient strategy for the equimolar ligation of polymer segments. Block copolymers can be formed in seconds at room temperature through the additive-free coupling of polymers, containing matching end-groups (TAD/diene)[4]. In the second part, the reversibility between TAD and diversely substituted indole components is introduced in a macromolecular context for the synthesis of dynamic polymer structures such as trans-clickable block copolymers.

References

1) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew. Chem.-Int. Edit. 2001, 40(11), 2004.
2) Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. Angew. Chem. Int. Ed. 2011, 50, (1), 60-62.
3) Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Speybroeck, V.; Winne, J. M.; Du Prez, F. E. Nat.Chem. 2014, 6, (9), 815-821.
4) Vandewalle, S.; Billiet, S., Driessen, F.; Du Prez, F. E. ACS Macro Lett. 2016, 5, 766-771.

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POLYMERS IN COMPLEMENT ACTIVATION-RELATED PSEUDO-ALLERGY: A SINGLE MOLECULE STUDY

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Complement activation of antibodies allows the human body to deal with harmful substances but at the same time it also promotes inflammation. In recent publications, the ability of certain polymers to trigger complement activation has been noted. With the usage of polymers as carriers for therapeutics, the issue of complement activation-related pseudo-allergy due to these polymers becomes more and more relevant. However, to this date a thorough investigation of this phenomenon is still missing. In this work we present a single molecule level method to investigate the kinetics and equilibrium thermodynamics of an antibody – polymer system both in the presence of antigen and in the absence of antigen. This method is based on total internal reflection fluorescence microscopy and determines binding times and rates of labeled antibodies on a polymer functionalized substrate. Using these binding times, we can determine binding and unbinding rate constants for the system, which will lead to insight in the thermodynamics of the investigated system.

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SURFACE REACTIVE NANOSTRUCTURED NANOPARTICLES FROM BIFUNCTIONAL DIBLOCK COPOLYMERS

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Block copolymers (BCPs) represent an important class of synthetic systems owing to their ability to self-assemble into nanostructures in both bulk and solution.[1] In view of designing nanoparticles with well-defined patterned chemical surface, we explored two important aspects: (i) the block-specific introduction of efficient reactive moieties, while retaining properties of the backbone polymer and (ii) the preparation conditions of nanoparticles with specific nanostructured surfaces. For the first aspect, one option is on based post polymerization approach. We particularly explored the suitability of a block copolymer platform containing two pentafluorophenyl moieties of distinct reactivities, namely pentafluorostyrene (PFS) and pentafluorophenyl methacrylate (PFPMA) towards thiol- and amine-based coupling, respectively.[2] Despite an incomplete orthogonality in thiol-coupling conditions, a library of bifunctional BCPs could be obtained following an appropriate functionalization sequence. Self-organization precipitation [3] and annealing steps were further employed to produce nanoparticles with surface patterns displaying functional anchors.

References

1) Block Copolymers in Nanoscience M. Lazzari, G. Liu, S. Lecommandoux, eds., Wiley-VCH, 2006; F. H. Schacher, P. A. Rupar, I. Manners, Angew. Chem. Int. Ed. 2012, 51, 7898–7921.
2) D. Varadharajan, G. Delaittre, Polym. Chem. 2016, 7, 7488–7499.
3) T. Higuchi, A. Tajima, K. Motoyoshi, H. Yabu, M. Shimomura, Angew. Chem. Int. Ed. 2009, 48, 5125 –5128

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INVESTIGATION OF ANTIBACTERIAL ACTIVITY OF SILVER NANOPARTICLES-LOADED POLY(N-BUTYL ACRYLATE-BLOCK-N-ISOPROPYL ACRYLAMIDE), NANOCOMPOSITE FILMS

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Thermo-responsive hydrogel Poly(N-isopropyl acrylamide),P(NIPAM), has a wide spectral range of biomedical applications, ranging from controlled drug delivery, tissue engineering, highly responsive scaffolds and wound dressings[1]. To improve the hydrogel properties and to insert multiple functionalities, NIPAM has been copolymerized with different comonomers [2]. In this study, poly(n-butyl acrylate-block-n-isopropyl acrylamide),P(BA-b-NIPAM), amphiphilic block copolymers were prepared via atom transfer radical polymerization (ATRP). The hydrophobic poly(n-butyl acrylate) was prepared as a macroinitiator (PBA-MI) and then hydrophilic NIPAM monomer is copolymerized as a second block by ATRP.

Amphiphilic block copolymers were characterized by FTIR, ^{1}H-NMR spectroscopy and GPC analysis. The DSC result confirmed phase separated morphology of the block copolymers and two separate Tg's. Silver nanoparticles, AgNP, were loaded into copolymers by using N,N-dimethylformamide (DMF) for the reduction of Ag^+ ions, while also acting as a solvent. The antibacterial activity of composite copolymer films was measured by zone of inhibition method against Gram-negative and Gram-positive bacteria.

References

1) Schwall C.T., Banerjee I.A., Materials, 2009(2), 577–612.
2) Y. Dong, Y. Ma, T. Zhai, F. Shen, Y. Zeng, H. Fu, J. Yao, Macromol. Rapid Commun., 2007(28), 2339-2345.

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CATION-π AND STERIC/INDCUTIVE INTERACTIONS FOR TAILORING SPONTANEOUS GRADIENT FORMATION IN POLY(2-OXAZOLINE)S

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In recent years 2-oxazolines have received considerable attention in the field of asymmetric catalysis, as ligands and as monomers for living cationic ring opening polymerization (CROP) leading to poly(2-alkyl/aryl-2-oxazoline)s (PAOx).[1] The living nature of CROP leads to good control over dispersity, very high end group fidelity, and by variation of the monomer structures a broad range of designs and polymer properties are easily accessible. This makes 2-oxazolines very interesting materials for, amongst others, biomedical applications.[2]

Gradient copolymers are comparatively unexplored polymer architectures to block copolymers, despite exhibiting interesting properties, such as broad glass transition temperature,improved interfacial stabilization compared to block copolymers,… In a copolymerization of 2-oxazolines a spontaneous gradient is formed in general due to differences in reactivity. By utilizing the recently discovered cation-π interaction and the deacceleration of the polymerization by substitution of the alpha-position (methyl>ethyl>*i*-prop) we were able to fine-tune the steepness of the gradient to our desire.

References

1) B. Verbraeken, B.D. Monnery, K. Lava, R. Hoogenboom, Eur. Polym. J., 2017, 88, 451.
2) O. Sedlacek, B. D. Monnery, S.K. Filippov, R. Hoogenboom, M. Hruby, Macromol. Rapid Commun., 2012, 33, 1648.

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GREEN SYNTHESIS TOWARDS POLY(2-OXAZOLINE)S FOR ORAL DRUG FORMULATION

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Recently the biocompatible ‘stealth’ polymer poly(2-alkyl-2-oxazoline)s (PAOx, POx, POz), has received considerable attention for biomedical applications such as polymer-drug conjugates, solid dispersions (SD) and sustained release formulations (SRF).(1,2,3,4) In this regard it is important to move to greener methods for the production of PAOx, especially with respect to monomer residues and greener solvents. PAOx (co)polymers are obtained *via* the living cationic ring-opening polymerization (CROP) of 2-oxazolines. Generally the CROP of 2-oxazolines leads towards good reproducibility in terms of control over molecular weight, molar mass distribution (*i.e.* low dispersity) as well as high end-group fidelity.(5) Different polymer structures and related properties - *i.e.* hydrophilicity, glass transition temperature, side-chain functionalities, *etc.* - are introduced through side-chain variation of the 2-oxazoline monomers. In this way a tunable PAOx (co)polymer platform is created. In this work first optimization towards a greener synthesis was performed, by using ethyl acetate or anisole as polymerization solvent, for the production of defined high molecular weight PAOx. Furthermore an evaluation on the use of defined PAOx versus Aquazol® for SD/SRF will be discussed.

References

1) Hoogenboom, R. Angew. Chemie Int. Ed. 48, 7978–7994 (2009)
2) Hoogenboom, R. et al. Polymers. 3, 467–488 (2011)
3) Hoogenboom, R. et al., U. S. Des. Monomers Polym. 8,659–671 (2005)
4) Claeys, B. et al. Macromol. Rapid Commun. 33, 1701–1707 (2012)
5) Monnery, B. D. & Hoogenboom, R. EP14177587 (2014)

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KUMADA CATALYST TRANSFER CONDENSATIVE POLYMERIZATION: FILLING IN THE BLANKS

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Since the discovery of the Kumada catalyst transfer condensative polymerization (KCTCP) of 2-bromo-5-chloromagnesio-3-hexylthiophene with Ni(dppp)Cl_2 (1,2), a lot of studies were performed to unravel the mechanism. To reach the full potential of this polymerization some crucial information about the influence of side chain branching on the polymerization characteristics, termination reactions and resting state of the active chain ends is still needed.

First, the influence of side chain branching on the KCTCP of 3-alkylthiophenes is studied with a new, severely branched precursor monomer, 2-bromo-5-iodo-3-(2-octyldodecyl)thiophene. The controlled character of its polymerization and the maximal degree of polymerization were investigated and rate studies for both poly(3-hexylthiophene) (P3HT) and poly(3-(2-octyldodecyl)thiophene) (P3ODT) were performed. In a second study, the termination reactions and the resting state of the active chain ends were examined. It was found that the nature of the occurring termination reactions was the dissociation of the nickel catalyst from the growing polymer chain implying that an equilibrium exists between this oxidatively inserted catalyst and the catalyst complexated to the polymer backbone. Based on these new insights, multi-block copolymers were synthesized.

References

1) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. Macromolecules 2004, 37 (4), 1169–1171.
2) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D.; Lovu, M. C.; Laird, D. W.; McCullough, R. D. Macromolecules 2004, 37 (10), 3526–3528.

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DYNAMIC SUPRAMOLECULAR POLYMER NETWORKS WITH ENHANCED PROPERTIES

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The dynamic nature of supramolecular networks makes them an interesting platform for adaptive materials.[1,2] However, the dissociative character of these physical networks negatively affects their mechanical properties. To counter this, we want to introduce associative behaviour to supramolecular polymer networks. The obtained materials are expected to combine the low melt-viscosity of dissociative supramolecular networks with the enhanced strength of associative networks into reprocessable polymer networks (RPN), in this case supramolecularly cross-linked rubbers.[3,4] Our system that will be developed to study and evaluate the proposed RPN are based on strong complementary quadruple hydrogen bonding.[5,6] In this study, the synthesis of the 2-ureido-4-pyrimidone as well as the diamidonaphthyridine has first been optimized. Next, the coupling of both H-bonding units to 1,2-polybutadiene is performed, *via* thiol-ene coupling reactions, to obtain the desired building blocks for the RPN. Finally, complete characterization of both functionalized polymers will be done to visualize initial bonding characteristics and mechanical properties.

References

1) Yang, L.; Tan, X.; Wang, Z.; Zhang, X. Chem. Rev. 2015, 150313093718000.
2) Voorhaar, L.; Hoogenboom, R. Chem. Soc. Rev. 2016, 45, 4013.
3) Agnaou, R.; Capelot, M.; Tencé-Girault, S.; Tournilhac, F.; Leibler, L. J. Am. Chem. Soc. 2014, 136, 11268.
4) Denissen, W.; Winne, J. M.; Du Prez, F. E. Chem. Sci. 2016, 7, 30.
5) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. J. Am. Chem. Soc. 1998, 120, 6761.
6) Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. J. Am. Chem. Soc. 2005, 127, 810.

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TAD-CHEMISTRY AND ADMET-POLYMERS: A SUSTAINABLE ALLIANCE

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Acyclic diene metathesis (ADMET) has been known since the nineties, but its impact on the field of green chemistry, was certainly not anticipated. However, post-functionalisation methods are still limited. Some functionalisation methods have been described, but harsh reaction conditions, long reaction times and low yields show the limited industrial potential of these methods.[1-3] A robust, additive-free and atom efficient procedure for the post-functionalisation is thus needed.

We propose the use of triazolinediones as a functionalisation method for ADMET polymers. 1,2,4-Triazoline-3,5-dione (TAD) exhibits a high reactivity toward both conjugated dienes and isolated alkenes in a Diels-Alder or an Alder-ene reaction, respectively.[4-5] In this work, we demonstrated the quick and quantitative post-functionalisation of bio-based ADMET polymers with several polymer backbones and a variety of TAD compounds. It was shown that the glass transition temperature of the polymers could be tuned by the degree of functionalisation. In a last step, the functionalized polymers were cross-linked by a bivalent TAD compound to obtain functionalized thermoset materials.[6] The efficiency of the functionalisation was demonstrated on tailor-made polyphosphonates and vanillin-based ADMET polymers.

References

1) J. A. van Hensbergen, T. W. Gaines, K. B. Wagener, R. P. Burford, A. B. Lowe, Polym. Chem. 2014, 5, 6225-6235.
2) F. N. Führer, H. Schlaad, Macromol. Chem. Phys. 2014, 215, 2268-2273.
3) M. Unverferth, M. A. Meier, Polymer 2014, 55, 5571-5575.
4) S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne, F. E. Du Prez, Nat. Chem. 2014, 6, 815-821.
5) K. De Bruycker, S. Billiet, H. A. Houck, S. Chattopadhyay, J. M. Winne, F. E. Du Prez, Chem. Rev. 2016.
6) L. Vlaminck, K. De Bruycker, O. Türünç, F. Du Prez, Polym. Chem. 2016, 7, 5655-5663.

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HYPERBRANCHED THERMALLY CURABLE ALL-AROMATIC HIGH PERFORMANCE POLYMERS AND THEIR PROPERTIES

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Hyperbranched polymers (HBPs), a term coined by Kim and Webster, have received much attention due to their unique properties like excellent solubility, low solution viscosity, functionality and ease of synthesis. Even with high molecular weights (>50.000 g/mol) and a fully aromatic backbone they remain soluble in common organic solvents like THF, NMP, DMAc or DMF. Although questions about their globular structure remain unanswered, the potential of this class of polymers is recognized and some excellent reviews have appeared [1a-c]. Dendritic polymers already find many applications, and hyperbranched polymers become increasingly popular as their synthesis and purification is less tedious. The main concern with hyperbranched polymers is their lack of chain entanglements, which makes it hard to explore their use in structural applications.

To address this issue, we are exploring the use of thermally crosslinkable functionalities. We will present the synthetic design strategy towards reactive HBPs and discuss their rheological and thermo-mechanical properties.

This research forms part of the research programme of the Dutch Polymer Institute (DPI), project #718.

References

1a) B. Voit, J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 2505-2525
1b) B. Voit, J. Polym. Sci. Part A: Polym. Chem. 2005, 43, 2679-2699
1c) M. Jikei; M. Kakimoto, Prog. Polym. Sci. 2001, 26, 1233-1285

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DETECTION OF ANTIBIOTICS BY COMBINING A FIBER-OPTIC ARRAY WITH MICROPHERES COATED MOLECULARLY IMPRINTED POLYMERS

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The widespread use of antibiotics in livestock farming leads to trace residues in food products and wastewater, potentially entailing antimicrobial resistance in food-borne pathogens. The determination of antibiotics in aqueous environments and foodstuff is thus of major concern.[1]

We have been developing optical sensors based on molecularly imprinted polymers (MIPs) due to the low production costs, stability, format adaptability and the possibility to imprint and thus their ability to recognize a wide variety of target analytes.[2],[3] As a fluorescently responding moiety in the polymer matrix a tailor-made fluorescent indicator cross-linker for direct transfer of the binding event into an optical signal was used. If such a cross-linker is integrated into a thin MIP-shell on microspheres such core/shell particles can be readily used in advanced multiplexing sensory fiber-optic microarrays.[4]

Here, we propose such a fiber-optic microarray based on fluorescent MIP microspheres for antibiotics. The binding behavior and the selectivity of a microarray using these silica core/MIP shell beads were examined and compared with a non-imprinted polymer (NIP).

References

1) L. Cantas, S. Q. A. Shah, L. M. Cavaco, C. M. Manaia, F. Walsh, M. Popowska, H. Garelick, H. Buergmann, H. Sorum, Frontiers in Microbiology 2013, 4.
2) W. Wan, M. Biyikal, R. Wagner, B. Sellergren, K. Rurack, Angewandte Chemie-International Edition 2013, 52, 7023-7027.
3) K. Haupt, K. Mosbach, Chemical Reviews 2000, 100, 2495-2504.
4) S. Carrasco, E. Benito-Pena, D. R. Walt, M. C. Moreno-Bondi, Chemical Science 2015, 6, 3139-3147.

P254

MODIFIED PROTEINS AS MULTIFUNCTIONAL BIOPOLYMERS FOR NANOMATERIALS

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Nature's polymers, such as polysaccharides and proteins show a remarkable versatility as multifunctional materials for a variety of applications. They can be easily modified with the toolkit of bioorganic chemistry and are particularly attractive because of their degradability and biocompatibility.

We present a recently developed, universal approach for the preparation of a new class of protein-based nanoparticles for the delivery of therapeutics. It features a new concept for the formation of particles based on the assembly of surface-modified proteins. Our method allows the use of solvent evaporation techniques for the formation of stable nanoparticles without denaturation or crosslinking of the proteins. We obtain empty and drug-loaded nanoparticles with a size of around 100 nm that are stable in different physiological environments and can successfully deliver the encapsulated payloads. Additionally, we transferred this particle preparation to various proteins in different sizes, showing that this method can be universally applied to any protein of choice.[1,2]

This opens up the potential for multifunctional nanosystems, where the function and structure of the particle material itself might be as important as the therapeutic payload.

References

1) M. Fach, L. Radi, P. R. Wich, J. Am. Chem. Soc. 2016, 138 (45), 14820–14823.
2) L. Radi, M. Fach, M. Montigny, E. Berger-Nicoletti, W. Tremel, P. R. Wich, Med. Chem. Commun. 2016, 7, 1738–1744.

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PHOTOSWITCHES FOR BIOLOGICAL AND MACROMOLECULAR APPLICATIONS - HEMITHIOINDIGO PROPERTY TUNING

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Hemithioindigos (HTIs) are an emerging class of photoswitches with significant advantages for applications in biology, medicine, and material sciences due to their absorption in the visible-light region and high thermal bistability.[1]

HTIs consist of a thioindigo and a stilbene part, connecting a central double bond, which can be isomerized from the thermodynamically stable *Z* to the metastable *E* state with visible light (> 400 nm). The *E* /*Z* isomerization can be induced by irradiation at longer wavelengths (> 500 nm) or thermally.

We aim at a fully conscious property design of this chromophore - ultimately enabling us to tailor HTIs to a specific application. Recently we found that even the type of light induced motions can be controlled.[2] Special requirements e.g. photochromism, reversible photoisomerization, high thermal bistability, and efficient *Z*/*E* photoisomerization resistance are now predictable.[3] Easy synthesis of HTIs with different substituents at the thioindigo[4] or stilbene part makes it simple to tailor them to new applications e.g. optical devices and smart polymers where we can combine optical and mechanical properties.

References

1) S. Wiedbrauk, H. Dube, Tetrahedron Lett. 2015, 56, 4266-4274.
2) S. Wiedbrauk, B. Maerz, E. Samoylova, A. Reiner, F. Trommer, P. Mayer, W. Zinth, H. Dube, J. Am. Chem. Soc. 2016, 138, 12219-12227.
3) B. Maerz, S. Wiedbrauk, S. Oesterling, E. Samoylova, A. Nenov, P. Mayer, R. de Vivie-Riedle, W. Zinth, H. Dube H. Chem. Eur. J. 2014, 20, 13984–13992.
4) F. Kink, M. Polo Collado, S. Wiedbrauk, P. Mayer, H. Dube, Chem. Eur. J. 2017, accepted.

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GM-1 MIMETIC POLYMERS FOR THE NEUTRALIZATION OF TOXINS

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The use of multivalent glycopolymers to target Toxins (lectins) is of interest due to the high avidity afforded by the cluster glycoside effect. Most glycopolymers, however, simply present a single monosaccharide rather than the actual branched glycan found on e.g. cell surfaces, due to the challenges of carbohydrate synthesis. In this work, we are developing glycopolymers with an architecture which matches the native branching of the GM-1 glycolipid; the target of the Cholera Toxin, responsible for >100,000 deaths annually. This is achieved by using a new tandem-post polymerisation modification approach, installing an allosteric binding unit next to the carbohydrate. We show, using both inhibitory assays and bilayer interferometry, that this approach enables us to enhance avidity and function, wihtout needing multi-step carbohydrate synthesis.

References

1) Richards, S. J., Jones et al. (2012) Angew. Chemie - Int. Ed. 51, 7812–7816.
2) Jones, M. W., Otten et al. (2014) Chem. Sci. 5, 1611.
3) Reinicke, S., Espeel, P., Stamenović, M. M., and Du Prez, F. E. (2013) ACS Macro Lett. 2, 539–543.
4) Espeel, P., and Du Prez, F. E. (2015) Eur. Polym. J. 62, 247–272.

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SPONTANEOUS MOISTURE-DRIVEN HEALING OF UREA-BASED POLYURETHANE

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Innovative and simple molecular designs with low activation energy are crucial to meet the present-day commercial and industrial challenges faced by the self-healing polymers. Up to now, the majority of the proposed self-healing polymers and principles relies on high heating cost, pH changes, or electro-magnetic irradiations and requires external activations to promote the self-healing mechanisms.

In the present work, we report on the efficient, spontaneous, and repetitive healing of a simple urea-based polyurethane film when exposed to atmospheric humidity. The repairs rely on the spontaneous formation of supramolecularly-driven water-urea clusters that bridge the crack and finally induce the complete gap closure. We illustrate this approach with a non-hygroscopic urea-based polyurethane by repetitive scratch-healing tests at different degrees of humidity. Furthermore, the water-urea interaction is supported by density functional theory (DFT) calculations coupled to FTIR experimental results. As a simple, rapid, and spontaneous way to heal a polymer, the new route presented herein is of high interest for anti-corrosive coatings, under-water sealants or technologies requiring soft hydrophobic and healable materials.

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POLY(ETHYLENE ALKYL PHOSPHONATE) COPOLYMERS WITH LCST AND UCST

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Thermal response plays a major role in the development of new smart materials as small temperature differences can induce sharp property changes. Generally, thermal response is divided in two categories: LCST (lower critical solution temperature) polymers show a hydrophilic-hydrophobic transition upon temperature increase, whereas UCST (upper critical solution temperature) polymers show the opposite effect. We present two series of random and degradable poly(alkylene alkyl phosphonate) copolymers with high solubility in water as well as finely tunable thermal responsiveness showing, depending on the pendant groups, either LCST or UCST behavior. The organocatalytic anionic ring-opening copolymerization of 2-alkyl-2-oxo-1,3,2-dioxaphospholanes provided polymers with excellent control over molecular weight and copolymer composition. The polymers from series one show LCST type thermal response which could be precisely adjusted in a range from full solubility down to 6 °C.[1] Polymers from series two, bearing pendant carboxylic acid groups, show UCST behavior. Block copolymers of these UCST poly(phosphonate)s with PEG as non-responsive water-soluble part can self-assemble reversibly into well-defined aggregates upon a temperature stimulus.[2]

References

1) T. Wolf and F. R. Wurm, submitted
2) T. Wolf, T. Rheinberger and F. R. Wurm, submitted

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BASE-TO-BASE ORGANOCATALYTIC APPROACH FOR ONE-POT CONSTRUCTION OF POLY(ETHYLENE OXIDE)-BASED MACROMOLECULAR STRUCTURES

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Block copolymers constituted by poly(ethylene oxide) (PEO) and aliphatic polyesters represent an important class of polymeric materials that have received extensive attention for their attractive physicochemical properties and potential biomedical applications[1]. To meet the rising demand for "greener" and metal-free polymeric materials, a base-to-base organocatalytic approach has been developed for one-pot synthesis of poly(ethylene oxide)-block-polyesters and poly(ethylene oxide)-based polyurethanes[2]. Ethylene oxide is first polymerized from a diol in the presence of a phosphazene superbase; then a thiourea is added to be deprotonated by the strongly basic alkoxide, which attenuates the basicity of the catalytic system and thus allows for controlled polymerization of the subsequently added cyclic ester from the polyether chain end or for step-growth polymerization of an added diisocyanate with the macrodiol which is free from anionic homopolymerization of the diisocyanate. The approach shows several advantages, e.g., a wide applicability toward different "second monmers" including (but not limited to) ε-caprolactone, L-lactide, and diisocyanate, and a low amount of "second catalyst" required as the deprotonated thiourea itself serves as the mildly or weakly basic organocatalyst.

References

1) Liggins, R. T.; Burt, H. M. Adv. Drug Delivery Rev. 2002, 54, 191.
2) Xia, Y.; Chen, Y.; Song, Q.; Hu, S.; Zhao, J.; Zhang, G. Macromolecules 2016, 49, 6817.

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SYNTHESIS AND PROPERTIES OF SILOXANE-BASED MULTI-BLOCK COPOLYMERS WITH ALL-AROMATIC MESOGENIC UNITS

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Two series of multi-block copolymers from all-aromatic liquid crystal (LC) or amorphous (AM) telechelic ester-based maleimide-functionalized oligomers and telechelic thiol-terminated poly(dimethylsiloxane) (PDMS) were synthesized and characterized. The LC and AM precursors are based on poly(p-phenylene terephthalate) with (AM) or without a phenyl substituent (LC) on the hydroquinone unit. Phenyl substitution increases the solubility and lowers the melting temperature and ability to crystallize. In addition, the soluble bismaleimide (all-aromatic) precursors are now compatible with thiol-ene solution-based click chemistry. The multi-block copolymers build from mesogenic (LC) units show micro-phase separation and liquid crystallinity even with a PDMS content as high as 65%. No lyotropic behavior was observed in polymer solutions. The multi-block copolymers build from mesogenic (AM) units display excellent stress-strain behavior and they can be used in shape memory applications.

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CONTROLLED SYNTHESIS OF POLYPEPTIDE BY PHOSGENE-FREE SYSTEM

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Polypeptides have been widely employed to prepare a wide variety of the functional biomaterials for the use of drug delivery system (DDS) and tissue engineering, because of their biocompatibility and biodegradability. One of the most efficient routes for the synthesis of polypeptides has been the ring-opening polymerization of α-amino acid N-carboxyanhydrides (NCAs), because the polymerization gives polypeptides with well-defined structures involving molecular weights and terminal structures. However, the synthesis of NCAs usually requires the use of a highly toxic phosgene or its derivatives.In addition, sensitive nature of NCAs to moisture and heat makes the production, and the utilization of NCAs difficult to achieve a well-controlled polymerization. We have developed an alternative approach to lead a well-defined polypeptide through polycondensation of N-phenoxycarbonyl derivative of α-amino acid, activated urethane derivative, along with the elimination of phenol and CO_2.[1-3] In the approach for synthesis of silk-mimicking polypeptide materials utilizing our synthetic strategy, we will present the preparation and the mechanical property of multi-block copolymer, composed of oligo-L-alaine segment, acting as an effective hard segment, and the polybutadienes of soft segment.

References

1) Yamada, S.; Sudo, A.; ; Goto M.; Endo, T. RSC Advances 2014, 4, 29890
2) Yamada, S.; Ikkyu, K.; Iso, K.; Goto, M.; Endo, T. Polymer. Chemistry. 2015, 6, 1838
3) Yamada, S.; Goto, M.; Endo, T. Polymer 2016, 93, 174

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SURFACE PROPERTY OF CELL MEMBRANE-INSPIRED PHOSPHOLIPID POLYMER BRUSH

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The cell membrane is considered to be of cardinal importance in almost all cellular systems. In well-known fluid mosaic model [1], the proteins are distributed in or on phospholipid bilayer and the choline containing phospholipids are commonly located in the outer leaflet. Cell membrane-inspired phospholipid polymers, which is mainly composed of 2-methacryloyloxyethyl phosphorylcholine (MPC) are widely used in medical devices to facilitate the biocompatibility and suppress unfavourable protein adsorption [2]. MPC polymer brush which has artificial cell membrane structure could be used as a promising biointerface.

In this study surface-initiated Cu(0) mediated controlled radical polymerization, a facile and novel method to prepare covalently linked polymer brush on the silica wafer using a copper plate as the catalyst at the ambient environment[3], was used. The relationship among film thickness and reaction solution concentration and reaction time was investigated via surface topography analysis (surface profilometer and AFM). The graft density was calculated with the help of thickness measurement of ellipsometry in dry (0% humidity) and wet (100%) conditions. The anti-fouling property was indicated by surface free energy calculation and protein adsorption measurement.

References

[1]) Singer, S.J. and Nicolson G.L. Fluid Mosaic Model of Structure of Cell-Membranes. Science, 1972; 175(4023): 720-731.
[2]) Iwasaki Y., Ishihara K. Cell membrane-inspired phospholipid polymers for developing medical devices with excellent biointerfaces. Sci Technol Adv Mat. 2012;13(6): 064101
[3]) Zhang T., Du Y.H., Muller F., Amin I., Jordan R. Surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) using a copper plate. Polym Chem-Uk. 2015;6(14):2726-33.

P263

THE ROLE OF CONFORMATIONAL ENTROPTY IN MACROMOLECULAR HYBRIDS OF CONJUGATED POLYMERS AND CARBON NANOTUBES

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Macromolecular hybrids that combine conjugated polymers and carbon nanotubes (CNT) are expected to offer improved functionality for a variety of applications. It is well known that the electronic, optical and thermodynamic properties of conjugated polymers are dominated by the delocalization length of the π-electrons along the chain backbone, known as the *conjugation length*. In derivatives of polythiophenes, poly(3-alkyl) thiophene, (P3ATs) the conjugation length is determined by the interplay between steric interactions among the side chains that interrupt the co-planarity, the structure of the backbone, and the solvent. In my talk I will present our experimental investigation of systems that combine CNT and P3AT and describe the role of chain-flexibility in P3AT- CNT interactions, the effect of dispersed CNT on self-assembly of the host polymer matrix, the mechanism leading to CNT-induced chain stacking and enhanced crystallization of the P3AT chains. Finally, I will show that our improved understanding of the physical behavior of the hybrid system can be utilized for the development of a single-step electrospinning process of CNT-P3AT nano-fibers with improved structural and optical properties.

P264

MOLECULAR DIFFUSIONAL DEGRADATION OF SERIES ALCOHOLS AS COSURFACTANT ON MINIEMULSIONS SYSTEM

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Miniemulsion-polymerizations depend on the quality of discrete monomer droplets that are produced prior to the free radical polymerization. Miniemulsions are aqueous dispersions of kinetically stable droplets with sizes of 50-500 nm (containing oil or water, surfactants and/or cosurfactants/costabilizers). The molecular diffusional degradation behavior (Ostwald ripening) of two-component miniemulsions with styrene and a homologous series aliphatic alcohol cosurfactants was investigated by fitting a semi-empirical equation to two adjustable parameters K1 and K2. The solubility of these alcohols in water was determined from K1 using the Tauer approach. Ostwald ripening was found to decrease in the order $C_{12}OH > C_{16}OH > C_{18}OH$. This is directly related to capability of these alcoholic cosurfactants to enhance the storage stability of miniemulsion products. This was further extended with polar polymers, such as polyethylene glycols, polyinyl alcohol and amphiphilic polymers (pluronics). Using polymeric surfactants as stabilizors results in the formation of a protective shell around droplets and the prevention of dropplets from merging with one another. The morphology of the miniemulsions was observed by TEM whereas FTIR was used to determine the functional groups in the system.

References

1) Antonietti M., Landfester K. Prog. Polym. Sci. 27(2002): p. 689
2) Chern C.S. Principles and Applications of Emulsion Polymerization; New Jersey: Wiley; (2008) Chapter 5
3) Meliana Y., Chern C. S., J. Dispersion Sci. and Tech., Vol. 34, issue 7 (2013): p. 632
4) Tauer K., Polymer 46 (2005):1385
5) Fisk P. R., etc, Ecotoxicology and Environmental Safety 72 (2009) 980-995

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SYNTHESIS OF FUNCTIONALIZED BLOCK COPOLYMERS VIA ATRP FOR MESOPOROUS PREPARATION

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Well-defined block copolymers useful in the preparation of mesoporous polymers were preparated, with chain end-functionalized triazole group. PDMS-w-functionalized macroinitiator were prepared through anionic polymerization of D3 initiated with butyllithium and terminated with dimethyl chlorosilane. Hydrosilylation with but-3-en-1yl 2-bromo-2-methylpropanoate with platinum catalyst produced the macroinitiaor. Several PDMS-w-functionalized macroinitiators with molecular weight close to Mn = 13, 000 g.mol^{-1}, and narrow dispersity lower than Đ= 1.12 and functionalities >98% determinated by NMR were obtained. PDMS-PMMA and PDMS-PS block copolymer were preparedby the use of normal ATRP polymerization with PMDETA and copper (I) chloride. These w-brominated block copolymers were functionalized with NaN3 in DMF, reacted with phenylacetylene with the CuAAC protocol given a triazolgroup at the end of thepolymer chain. These polymers are capables to complexation with cations. Mesoporous materials can be obtained after the phase segregation and removing the sacrifice polymer block (PDMS).

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BLOCK COPOLYMER SYNTHESIS IN ONE SHOT: CONCURRENT METAL-FREE ATRP AND ROP PROCESSES

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A completely metal-free strategy was developed by combining Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP) for the syntheses of block copolymers. These two different metal-free controlled/living polymerizations, which have no effect on each other was concurrently realized in one reaction media. Using a specifically designed bifunctional initiator, possessing primary hydroxyl and tertiary bromide functionalities, vinyl and lactone monomers were simultaneously polymerized under sunlight, by metal-free strategies. Spectral and chromatographic results reveal that the synthetic approach applied produces block copolymers in a controlled manner, free from homopolymers, and with narrow molecular weight distributions.

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REVERSIBLE SINGLE-CHAIN GLYCOPOLYMER FOLDING VIA HOST-QUEST INTERACTION AND THE EFFECT OF FOLDING ON LECTIN BINDING

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The reversible self-assembly interactions of natural biomacromolecules play very important roles in complex biological environments. Hence, the single-chain folding inspired by nature has attracted significant attention in the last decade. Barner-Kowollik and coworkers have reported the formation of reversible single-chain selective point polymer folding using β-cyclodextrin driven host-quest interaction with adamantane in water.[1] Herein, inspired by this report, the reversible single-chain glycopolymer folding structures in α-shape with different sugar moieties were created to investigate the influence of this folded collapse on the binding capability with different lectins. The synthesis of triblock co-glycopolymers bearing β-CD and adamantane for the host-quest interaction and also mannose residues for the lectin interaction was achieved *via* reversible addition-fragmentation chain transfer (RAFT) polymerization. The reversible single-chain folding of glycopolymers was created in a highly diluted aqueous solution and monitored by 2D nuclear overhauser enhancement spectroscopy (NOESY) NMR and dynamic light scattering (DLS). The binding results with different lectins indicated that the single-chain folded structures present higher binding rates, in comparison to the unfolded structures.

References

1) Willenbacher, J.; Schmidt, B. V. K. J.; Schulze-Suenninghausen, D.; Altintas, O.; Luy, B.; Delaittre, G.; Barner-Kowollik, C. Chemical Communications 2014, 50, 7056.

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COLOR-CHANGE OF ALTERNATING COPOLYMERS AND THEIR CROSS-LINKED POLYMERS OF PHENYL VINYLETHYLENE CARBONATE AND N-SUBSTITUTED MALEIMIDES IN SOLUTION AND SOLID-STATE BASED ON ACID-BASE SWITCHING

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The radical copolymerization with various monomer feeds of phenyl vinylethylene carbonate (PVEC) and N-phenylmaleimide (PMI) successfully proceeded through the selective vinyl and alternating polymerization, which gave the structure having the maleimide unit in the main-chain and the five-membered cyclic carbonate group in the side-chain. Moreover, these copolymers were cross-linked by aminolysis between hexamethylene diamine (HMDA) and cyclic carbonate moiety in the side-chain to obtain the networked polymers having the hydroxyurethane structure. Interestingly, these copolymers and networked polymers exhibited the sensitive and reversible color-change based on the acid-base switching in not only solution but also solid-state. In particular, the color-change in solid-state occurred immediately by exposing the amine vapor. IR and UV-vis spectra of these polymers clarified that the malemide moiety formed an enolate tautomer in the presence of sufficiently strong basic reagents. Therefore, the color-change of these copolymers occurred due to the tautomerization of the maleimide moiety based on acid-base switching and solvent effect as the trigger.

References

1) Y. Yoshida, T. Endo, Polym. Chem., 2016, 7, 6770-6778.
2) Y. Yoshida, T. Endo, RSC Adv., 2017, 7, 9373-9380.

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STABILIZING OF LIPOSOMAL CONTAINERS BY AMPHIPHILIC N-(2-HYDROXYPROPYL)METHACRYLAMIDE BASED COPOLYMERS

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Liposomes, bilayered lipid vesicles, can be used as containers for drug delivery. The coating of liposomes with hydrophilic polymer is beneficial to enhance their half-life in blood circulation, so-called "stealth liposomes". The majority of liposomes reported so far are coated by polyethylene glycol (PEG). Here, we propose an alternative to PEG based on hydrophilic copolymers of N-(2-hydroxypropyl)methacrylamide (pHPMA). Highly hydrophobic cholesterol molecules were attached to the polymer structure for anchoring the pHPMA into liposomes. Amphiphilic pHPMA was prepared using controlled RAFT (reversible addition-fragmentation transfer) radical polymerization of HPMA and a cholesterol-containing monomer.

Two approaches for coating were used: copolymer was added during ("in situ") or after ("ex post") the formation of liposomes. The influence of polymer concentration and the way of coating was evaluated using the cryo-TEM, DLS and SAXS techniques. Investigation of physico-chemical stability of modified liposomes showed that the presence of HPMA in liposomal membrane prevent the aggregation and fusion of liposomes during 3 weeks. The possibility of encapsulating hydrophilic substances into liposomes was demonstrated using model compounds.

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POLYDIACETYLENES AS SENSORS FOR USE ON THE BODY

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The development of effective antiperspirants and deodorants has been limited by the troublesome analysis of the sweating/perspiring process. The dependence of the activity of sweat glands on numerous factors, such as gender, age, race or even the time of the day, further complicates this task. A rapid method for mapping active sweat glands and assessing the effectiveness of deodorants and antiperspirants or even sensing chemical changes in the body is required to enable development of superior products. Polydiacetylenes (PDAs) hold a lot of promise with this regard due to their chromatic properties resulting from the conjugated system of carbon-carbon double and triple bonds. Depending on the exact chemical structure, PDAs can produce a chromatic response to water and/or odorous sweat components. A derivative of 10,12-pentacosadiynoic acid inkjet-printed on paper was shown to work particularly well. The initially too high sensitivity to water that would result in immediate colour change over the whole surface area was overcome by changing one of the solvents in the monomer solution used for printing. Maps of active sweat pores in human axilla were successfully created.

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DEVELOPEMENT OF SULFIDE-BRIDGED PECTIN BASED DRUG CARRIER HYDROGELS: CROSSLINKER EFFECT

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Pectin, as a natural polysaccharide, creates an oxygen and moisture permeable media; also it has antimicrobial properties increasing pectin's use in medical applications [1].

This study developed and tested thiolated pectin based drug carrier films with different crosslinker molecules and ratios. Furthermore effectiveness of sulfide bridged pectin was analyzed. Theophylline was chosen as model drug in consideration of its interactive relation with pectin. Samples were prepared as egg-box model created by three different methods: conventional (mixing), swelling and absorption.

Besides synthesis method, crosslinker ratio (5, 7, and 10), buffer pH (3.2, 4.6, and 6.4) and film drying condition (28°C, 50°C) are parameters for this study. In order to clarify release mechanism multiple analysis were used such as swelling test, FTIR, SEM, DSC. The efficiency of loading methods in drug release was analyzed by UV-vis spectrophotometer.

By means of thiolated drug loaded films with barbutric acid, much higher elasticity and controlled drug release was obtained. Also, mucoadhesive property was investigated. Moreover, release kinetic results show that thiolated pectin hydrogels are good candidates for controlled drug delivery systems.

References

1) M. Tummalapallia, M. Berthetb, B. Verrierb, B.L. Deopuraa, M.S. Alamc, B.Guptaa, Composite Wound Dressings Of Pectin And Gelatin With Aloe Vera Andcurcumin As Bioactive Agents ,International Journal of Biological Macromolecules, 2016, 82, 104-113.

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EFFECT OF THE COMPOSITION OF THE INDIVIDUAL LAYERS ON THE OVERALL MECHANICAL PERFORMANCE OF THE MULTILAYERED FILMS

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Multilayer co-extruded polymeric films are widely used in many industries such as packaging and hygiene. A typical multilayer film consists of a main layer at the center which has the major effect on the properties of the whole film, skin layers coinciding with the film's upper and lower surfaces and tie layers between the former two. Inorganic additives are also used for both performance and cost related reasons [1-3].

In this study, a 5 layer structure was chosen for the prototype work. The early prototypes were made using olefinic polymers. In the latter ones, styrenic copolymers were also used both individually and as a blend with olefinic ones. Change of the mechanical properties such as tensile force, elongation and recovery upon polymer type was observed. Incorporating additives into individual layers alters their rheology resulting in a change in the mechanical performance of the whole film structure. The additives in the skin layers are especially important to make a dimensionally stable film having a non-blocky surface. Therefore, the effect of skin layer composition on the whole film structure was also investigated.

References

1) Liu, Y. ve Kontopoulou, M. “The structure and physical properties of polypropylene and thermoplastic olefin nanocomposites containing nanosilica”, Polymer, 47, 7731-7739, 2006.
2) Hejazi, I., Seyfi, J., b, Sadeghi, G. M. M. ve Davachi, S. M. “Assessment of rheological and mechanical properties of nanostructured materials based on thermoplastic olefin blend and organoclay”, Materials and Design, 32, 649–655, 2011.
3) Deshmane, C., Yuan, Q. ve Misra, R. D. K. “High strength–toughness combination of melt intercalatednanoclay-reinforced thermoplastic olefins”, Materials Science and Engineering, A 460–461, 277–287, 2007.

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SEQUENTIALLY PERFORMED ORGANOCATALYTIC RING-OPENING AND STEP-GROWTH POLYMERIZATIONS TOWARD POLYURETHANES WITH READILY TUNABLE COMPOSITIONS AND FUNCTIONS

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One-pot facile synthesis of polyether-based polyurethanes (PUs), starting from raw materials as diols, epoxides and diisocyanates, has been realized by sequentially performed ring-opening polymerization (ROP) and step-growth polymerization (SGP) through organocatalytic processes with a "catalyst switch" step.[1] For example, ROP of ethylene oxide and/or 1,2-butylene oxide promoted by an organic superbase from bio-sourced betulin or its mixture with a designated amount of a commonly used diol was first conducted, followed by switching of the catalytic condition by an acidic organocatalyst and addition of a diisocyanate to undergo SGP with the macrodiol, yielding a series of PUs doped with betulin entities in the main chains. It is found that doping of betulin helps enhance the overall thermal stability of the PU. More interestingly, regardless of a relatively high hydrophobicity, films fabricated by poly(ethylene oxide)-based PUs with betulin entities doped in every polyether segment exhibited complete resistance against protein adsorption, while those with lower content of betulin (higher hydrophilicity) cannot. Phase separation behavior associated with such particular macromolecular structures have been shown to be the rationale behind.

References

1) Xia, Y.; Chen, Y.; Song, Q.; Hu, S.; Zhao, J.; Zhang, G. Macromolecules 2016, 49, 6817-6825.

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EFFECT OF DOPANT AND OXIDANT ON THE ELECTROCHEMICAL PROPERTIES OF PANI/GNP COMPOSITES

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Polyaniline/graphene (PANI/GNP) composite is a promising candidate for the supercapacitor electrode material, which is urgently required due to the rapid growth of the hybrid electric vehicles and portable electronics. PANI/GNP (1:1) and (10:1) composites were synthesized via in-situ chemical polymerization. The effect of content of oxidant and dopant, and the species of oxidant on the electrochemical properties of (PANI/GNP) composite were systematically investigated. It was observed that the dopant could strengthen the redox phenomenon, but its effect on the capacitance of PANI/GNP composite depend on the mass ratio of components. For the effect of oxidant, a $FeCl_3$ to aniline mass ratio of 2 is optimal for the electrochemical properties of both PANI/GNP (1:1) and (10:1) composites, and APS was better than $FeCl_3$ in according to the magnitude of specific capacitance. It is noteworthy that PANI contributes more to the capacitance of composites, and graphene plays a more essential role in the rate capability of composites. In this study, PANI/GNP (1:1) with an APS to aniline ratio of 1 presents the best combination of high specific capacitance and good cycling stability.

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POLY(BUTYLENE TEREPHTHALATE)/GLYCEROL-BASED VITRIMERS VIA SOLID-STATE POLYMERIZATION

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A new type of semi-crystalline vitrimer was prepared via the incorporation of glycerol into the amorphous phase of poly(butylene terephthalate) (PBT) by solid-state (co)polymerization (SSP). A near quantitative incorporation of the glycerol was confirmed by NMR spectroscopy. Wide-angle X-ray diffraction, differential scanning calorimetry (DSC) and temperature-modulated DSC showed that the PBT/glycerol-based vitrimers maintain the crystallization characteristics of normal PBT. By changing the cross-link density of the PBT/glycerol-based vitrimers, a wide range of thermal, rheological and mechanical properties were obtained, *e.g.*, the rubbery plateau modulus at 270 °C could be tuned from 0.07 to 3 MPa. The characteristic vitrimer behavior was demonstrated by stress relaxation and oscillatory frequency sweep experiments. In addition, these semi-crystalline vitrimers can be recycled multiple times by compression molding without a substantial loss in dynamic mechanical and thermal properties.

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SYNTHESIS AND PERFORMANCE RESEARCH OF FUNCTIONAL CYCLIC POLYMER WITH COMPLEX TOPOLOGICAL STRUCTURES

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Comparing with their linear precursors, cyclic polymers have no chain ends and express as the ring topology. This unique topology often brings some different properties with respect to the linear ones.[1,2] For the functional polymers, the functions/performance of the cyclic polymers is usually improved in comparison with the linear counterpart. During the past decade, increasing attentions have been paid to the cyclic polymer-related area.[3-5]

Considering the fascinating functions and performance of PCL and PNIPAAM, one of the targets of the project is the preparations of cyclic PCL, cyclic PNIAAM and more complex cyclic-based topological PCL and PNIAAM, by combination of living polymerization techniques with thiol-X “click” chemistry. Then, the functions or performance of these complex cyclic-based topological PCL and PNIAAM will be explored and compared with its counterparts. The implementation of the project would greatly enrich the research on the cyclic polymer, and the effects of topology on functions/properties of polymers would be figured out.

References

1) Tomikawa, Y.; Fukata, H.; Ko, Y. S.; Yamamoto, T.; Tezuka, Y. Macromolecules 2014, 47, 8214-8223.
2) Md. D. Hossain, Zhongfan Jia, and Michael J. Monteiro.Macromolecules 2014, 47, 4955-4970.
3) Satoshi Honda, Takuya Yamamoto, and Yasuyuki Tezuka. J. Am. Chem. Soc. 2010, 132, 10251 -10253.
4) Justin E. Poelma, Kosuke Ono, DaigoMiyajima, Takuzo Aida, Kotaro Satoh and Craig J. Hawker. ACS Nano 2012, 6, 10845-10854.
5) Boyu Zhang, Hong Zhang, Yejia Li, Jessica N. Hoskins, and Scott M. Grayson. ACS.Macro Lett. 2013, 2, 845-848.

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DESIGN OF POLYMER COMPOSITE-MODIFIED BITUMEN FOR ANTI-ICING PURPOSES

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Ionic salts as de-icing agents have been extensively used to eliminate accumulation of ice on asphalt surfaces. However, salt can be easily removed by rain or automobiles and requires frequent application on roads. Besides this economical consideration, salt compromise the mechanical properties of asphalt and have a negative impact on living organisms and the environment when used in large amounts. Bitumen, an asphalt binder, has previously been modified by styrene-butadiene-styrene (SBS) for improved strength and thermomechanical properties. However, an anti-icing function has not been considered in those previous designs. Here, we developed a functional polymer composite consisting of potassium formate (HCOOK) salt pockets dissolved in a hydrophilic gel medium and dispersed in a hydrophobic SBS polymer matrix. Next, we modified bitumen with this polymer composite to obtain functional bitumen with anti-icing properties and demonstrated salt release and significant increase in freezing delay of composite-modified bitumen compared to base bitumen in a temperature controlled chamber. These results demonstrate the potential of this polymer composite-modified bitumen for anti-icing functionality, and for industrially relevant applications.

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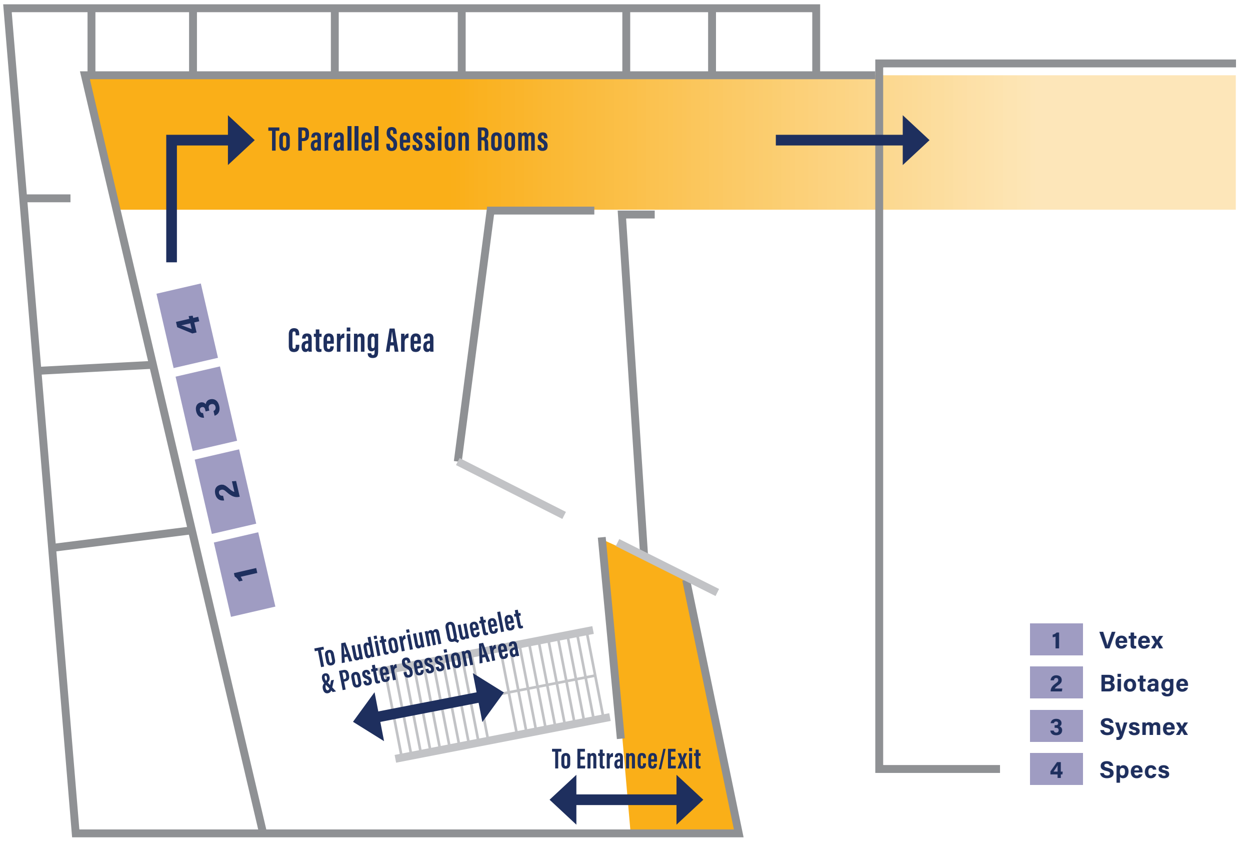
FLOOR PLANS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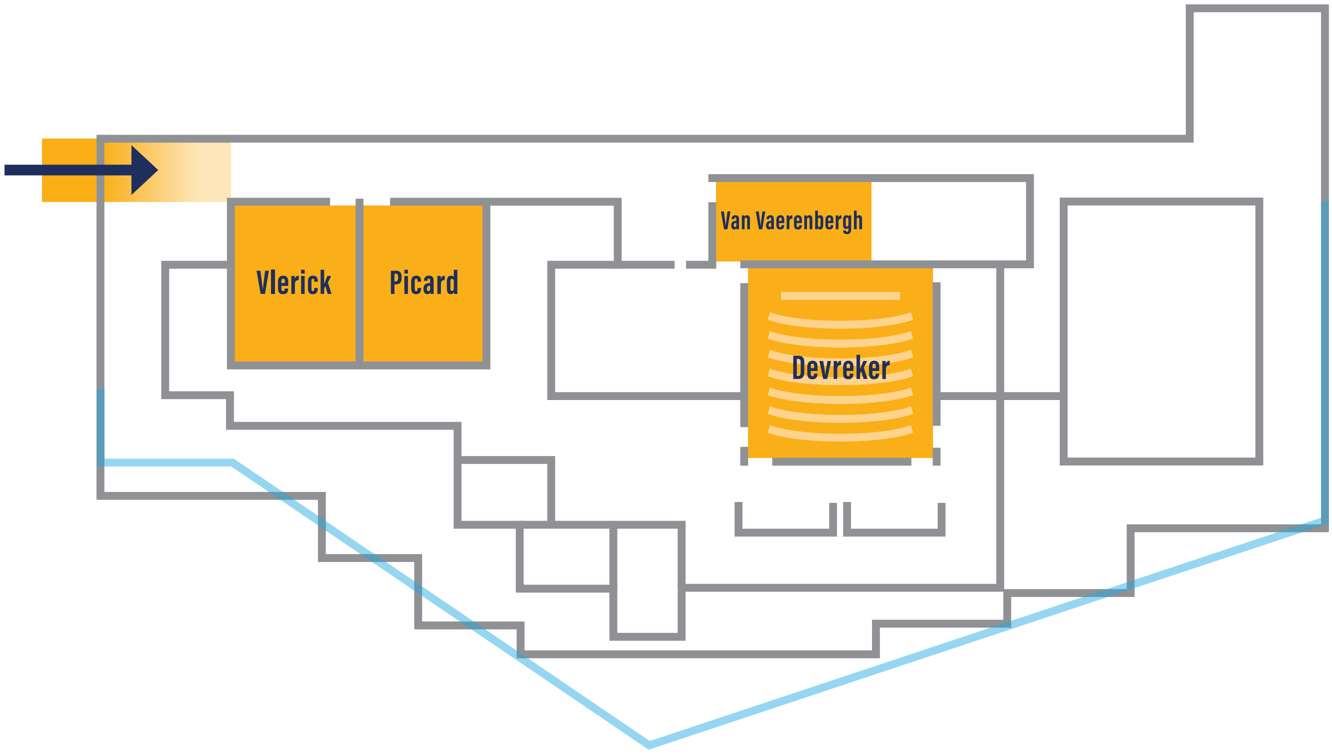
Van Vaerenbergh
Vlerick
Picard
Devreker

SUNDAY 21/5

15:00	Registration
18:00	Welcome reception

MONDAY 22/5

	Devreker	Vlerick	Picard	Van Vaerenbergh
08:00	Registration			
08:50	Introduction			
09:10	PL01			
10:00	Break			
10:10	IL01	IL02	IL03	IL04
10:40	Coffee break			
11:10	IL05	IL06	IL07	IL08
11:40	OC01	OC02	OC03	OC04
12:00	OC05	OC06	OC07	OC08
12:20	lunch			
13:40	PL02			
14:30	Break			
14:35	IL09	IL10	IL11	IL12
15:05	Coffee break			
15:35	IL13	IL14	IL15	IL16
16:05	OC09	OC10	OC11	OC12
16:25	Break			
16:30	OC13	OC14	OC15	OC16
16:50	OC17	OC18	OC19	OC20
17:10	IL17	IL18	IL19	IL20
17:40	Break			
17:45	Poster session 1 (odd numbers)			
19:00	Group picture			
19:15	Beer & fries event			

TUESDAY 23/5

	Devreker	Vlerick	Picard	Van Vaerenbergh
08:40	PL03			
09:30	Break			
09:35	IL21	IL22	IL23	IL24
10:05	Coffee break			
10:25	IL25	IL26	IL27	IL28
10:55	IL29	IL30	IL31	IL32
11:25	Break			
11:30	IL33	IL34	IL35	IL36
12:00	OC21	OC22	OC23	OC24
12:20	lunch			
13:40	IL37	IL38	IL39	IL40
14:10	OC25	OC26	OC27	OC28
14:30	IL41	IL42	IL43	IL44
15:00	Coffee break			
15:20	OC29	OC30	OC31	OC32
15:40	OC33	OC34	OC35	OC36
16:00	Break			
16:05	OC37	OC38	OC39	OC40
16:25	IL45	IL46	IL47	IL48
16:55	Break			
17:00	Poster session 2 (even numbers)			
18:30	Free time			
19:30	Banquet			

WEDNESDAY 24/5

	Devreker	Vlerick	Picard	Van Vaerenbergh
09:00	IL49	IL50	IL51	IL52
09:30	IL53	IL54	IL55	IL56
10:00	IL57	IL58	IL59	IL60
10:30	Coffee break			
10:50	IL61	IL62	IL63	IL64
11:20	OC41	OC42	OC43	OC44
11:40	Break			
11:45	OC45	OC46	OC47	OC48
12:05	OC49	OC50	OC51	OC52
12:25	lunch			
13:50	IL65	IL66	IL67	IL68
14:20	OC53	OC54	OC55	OC56
14:40	Break			
14:45	OC57	OC58	OC59	OC60
15:05	IL69	IL70	IL71	IL72
15:35	Coffee break			
16:00	PL04			
16:50	Closing remarks			
17:15	Busses leaving to soccer tournament			
17:45	Soccer game 'Belgian Polymer team' against 'Rest of the World Polymer team'			
18:45	Free drinks and light dinner			
20:00				

THURSDAY 25/5

10:00	Touristic activity