ACS Division of Polymer Chemistry

Graphical Abstracts

A collection of the POLY session and poster graphical abstracts presented at the Spring ACS National Meeting.

August 2021
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Programming Chair
Hayley Brown
DOW
hbrown1@dow.com

Fall 2022 Lead
Robert Mathers
Penn. State Univ.
rtm11@psu.edu

Spring 2022 Lead
Levi Moore
AFRL
levimjmoore@gmail.com

Fall 2021 Program Lead
Sara Orski
NIST
sara.orski@nist.gov

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2020 Mark Scholars Award in Honor of Luis Campos

Craig Hawker, Organizer, Univ of California; Egbert Meijer, Organizer, Eindhoven University of Technology; Egbert Meijer, Presider, Eindhoven University of Technology; Craig Hawker, Presider, Univ of California; Dino Wu, Presider; Will Gutekunst, Presider

Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Tuesday 02:00pm - 04:00pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312

Precision polymer nanoparticles
02:00pm - 02:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Prof Rachel O'Reilly, Presenter

Designing polymeric amphiphiles with high molecular precision: From nanocarriers for controlled drug release to micellar catalysis
02:30pm - 03:00pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Prof. Roey J. Amir, Presenter, Tel Aviv University

Well defined conjugated polymers
03:00pm - 03:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Dwight Seferos, Presenter

Capsules of active liquids templated by pickering emulsions
03:30pm - 04:00pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Katelynn Edgehouse; Yifei Wang; Sarah Lak; Emily Pentzer, Presenter, Case Western Reserve University

Tuesday - 04:30pm - 06:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312

Polyolefin based electrolytes
04:30pm - 05:00pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Geoffrey Coates, Presenter, Cornell Univ

Embracing the challenges of aldehyde polymerization
05:00pm - 05:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Robert B Grubbs, Presenter, Stony Brook University; Chenwei Liu; David Hewitt

Sustainability and circularity in the chemical recycling of polydiketoamines
05:30pm - 06:00pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Brett Helms, Presenter

Manipulating Multiexciton Mechanisms in Molecules and Macromolecules
06:00pm - 06:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Luis Campos, Presenter
Crystallization-driven self-assembly (CDSA) is a novel tool in the solution polymer self-assembly toolbox and has been utilized to create an impressive range of hierarchical block copolymer structures. Unlike in conventional solution self-assembly, where the range of morphologies obtained are determined by varying the relative block composition of each block, in polymers assembled via CDSA, the formation of micelles with low interfacial curvature is favored. However, despite advances in CDSA there are relatively few examples where the aggregate morphology can be readily controlled to form nanostructures whose size can be controlled in 2 dimensions. In this work we present the CDSA of a range of block copolymers which form a range of self-assembled nanostructures including 2D nanostructures. Using these we have further explored the design rules for the synthesis and functionalisation of such 2D nanomaterials and demonstrated their epitaxial growth.
Designing polymeric amphiphiles with high molecular precision: From nanocarriers for controlled drug release to micellar catalysis

Roey J. Amir\textsuperscript{1,2}, amirroey@tauex.tau.ac.il. (1) School of chemistry, Tel Aviv University Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv, Israel (2) ADAMA Center for Novel Delivery Systems in Crop Protection, Tel Aviv University, Tel Aviv, Israel

Polymeric amphiphiles and their assemblies have been widely explored for applications ranging from nanocarriers for controlled drug delivery to nano-containers for green chemistry. Taking advantage of accelerated synthetic approaches for the synthesis of dendritic amphiphiles and their well-defined structures - their degree of amphiphilicity can be tuned with high molecular precision reminiscence of low molecular weight amphiphiles and amphiphilic peptides. Over the past few years, we used highly modular synthetic methodology to study how small changes in the hydrophobic dendron can affect the enzymatic responsiveness of micellar nanocarriers. In this talk, we will share our key findings as well as preliminary data on how the hydrophobicity of such micelles affects their function as micellar catalysts.
Well defined conjugated polymers

Dwight S. Seferos, dseferos@chem.utoronto.ca. Chemistry, University of Toronto, Toronto, Ontario, Canada

Controlled polymerizations are highly sought-after methods for preparing macromolecules since they have the potential to produce large molecules with consistent length, sequence, and end groups. In this vein, much of our work has focused on the implementation of ‘living’ methods to produce new classes of very well-defined conjugated polymers. In particular our group has utilized the Kumada Catalyst Transfer Polymerization, which was pioneered by the Yokozawa and McCullough groups, to prepare new classes of well-defined conjugated polymers including those that incorporate ‘heavy’ atoms such as selenium and tellurium. Very recently we have learned two remarkable things about this exciting polymerization method. In one line of inquiry, I will describe how we are able to arrest the catalytic cycle at the transmetalation step by controlling the temperature. This allows us to ‘stop’ the polymerization and add stoichiometric amounts of monomer one by one. In doing so, we are able to prepare monodisperse polymers of poly-3-hexylthiophene (P3HT) in a homogeneous manner. In a second line of inquiry, I will show that after reductive elimination and oxidative addition the catalyst-polymer complex is remarkably stable. This allows us to isolate pure living chains with the polymerization catalyst intact at the chain ends and still active. While these are both great feats in polymer synthesis, they are limited in monomer/catalysts scope to P3HT and P3HT-like systems. In the final part of this talk, I will discuss a new initiative in our group to use templates to prepare broader classes of well-defined conjugated polymers.
Encapsulation provides an attractive route for overcoming the cumbersome handling of viscous liquids or accommodating solid-liquid phase changing materials. This presentation will highlight recent work from our group in using Pickering emulsions stabilized by 2D particles to template the encapsulation of “active” materials, including ionic liquids (ILs), phase change materials (PCMs), and polyalpha olefins. Based on the nanosheet surfactant functionality, aqueous or water-free emulsions can be prepared, with polymerizations at the interface leading to a composite capsule shell. We will describe the benefits of these tailored materials, as well as current limitations, highlighting application of the capsules for the uptake of gases and solvent remediation.
POLY – 2020 Mark Scholars Award in Honor of Luis Campos

Polyolefin based electrolytes

Geoffrey W. Coates, gc39@cornell.edu. Cornell University, Ithaca, New York, United States

In this presentation, new advances in the synthesis of hydroxide-stable, mechanically strong, and highly conducting alkaline anion exchange membranes will be presented.
Embracing the challenges of aldehyde polymerization

Robert B. Grubbs, robert.grubbs@stonybrook.edu, Chenwei Liu, David R. Hewitt. Chemistry, Stony Brook University College of Arts and Sciences, Stony Brook, New York, United States

Polymers with acetal linkages in the backbone have great potential as degradable or recyclable materials and can be prepared by chain polymerization of carbonyl compounds. The wide variety of aldehydes and ketones that occur naturally or through sustainable transformations of naturally occurring compounds suggests that they also have promise as sustainable materials. Glyoxylate esters are one such class of monomers that can be polymerized by treatment with bases, but monomer purification is a critical issue and the polymerization mechanism has not been studied in detail. Efforts to control the polymerization of glyoxylate esters from hydroxyl-terminated macroinitiators and to prepare a range of block copolymers with degradable polyglyoxylate blocks, including polymers that form hydrogels, will be discussed, as will attempts to expand these polymerization methods to include other monomers.
Polydiketoenamines (PDKs) are a versatile class of chemically recyclable polymers and can be formulated as thermoplastics, thermosets, elastomers, hydrogels, and composites. I will discuss our recent efforts to understand their prospects as sustainable materials for circular manufacturing. This will include an assessment for how monomers should be designed from bio-based chemical feedstocks to impart useful and valuable properties to PDK resins. I will also describe how monomer design opens doors to mixed-PDK and mixed-material recycling. While it is common to consider the cleavable bonds in polymers as being deterministic in certain aspects of performance and circularity in recycling, it's clear there are other factors beyond the bond that can also be exploited. I will discuss some surprising insights along those lines and showcase how they play out in chemical recycling schemes.
Manipulating Multiexciton Mechanisms in Molecules and Macromolecules

Luis M. Campos, campos96@hotmail.com. Chemistry, Columbia University, New York, New York, United States

Organic molecules and macromolecules (MnMs) that harvest and convert one photon to one exciton have been exploited in chemistry, optoelectronics, and optics. The single light-induced excitons formed in a variety of organic MnMs essentially serve as a source of potential energy to trigger photophysical and photochemical processes with spatiotemporal control. However, conventional mechanisms of exciton generation can be impaired by inherent energetic losses. Therefore, efforts are now geared to develop materials that generate multiple excitons from a single photon to overcome thermodynamic limitations. Singlet fission is a process that has been observed in organic MnMs, where a singlet excited state can lead to two triplet states. This talk will highlight our work focused on understanding how the chemistry of molecular building blocks and their architectural connectivity in macromolecular systems impact the formation and dynamics of triplet pairs from a single incident photon.
2020 Mark Scholars Senior Award in Honor of Karen Winey
Hayley Brown, Organizer, The Dow Chemical Company; Craig Hawker, Organizer, Univ of California; Edwin Thomas, Organizer; Edwin Thomas, Presider, Rice University Brown Sch of Engr Session Type: Oral - Virtual
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Wednesday, 10:30am - 12:15pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47

Nanostructured ionomers for ion transport
10:35am - 11:00am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Karen Winey, Presenter, University of Pennsylvania

Morphology and ion transport in hydrated ion containing polymers
11:00am - 11:25am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Dr. Amalie Frischknecht, Presenter, Sandia National Laboratories

Alignment and Morphology of Nanoplates in Lamellar Diblock Copolymer Thin Films
11:25am - 11:50am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Russell Composto, Presenter, University of Pennsylvania

High melting polyethylene sulfones
11:50am - 12:15pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Dr. Kenneth B. Wagener, Presenter, University of Florida; Julia Pribyl Ham

Wednesday, 02:00pm - 03:50pm USA / Canada - Eastern - August 25, 2021 | Room: A311-A312

Deconstructing the mechanism of nanoparticle reinforcement in polymer nanocomposites
02:05pm - 02:30pm USA / Canada - Eastern - August 25, 2021 | Room: A311-A312
Robert Riggleman, Presenter, University of Pennsylvania; Entao Yang; James Pressly; Bharath Natarajan; Karen Winey, University of Pennsylvania

Single ion conducting block copolymers
02:30pm - 02:55pm USA / Canada - Eastern - August 25, 2021 | Room: A311-A312
Yossef Elabd, Presenter, Texas A&M University

Structure and properties of polymer grafted nanoparticle monolayers from coarse-grained simulations
02:55pm - 03:20pm USA / Canada - Eastern - August 25, 2021 | Room: A311-A312
Lisa M. Hall, Presenter, Ohio State University

Grain boundaries in double network phases: Sharp twins and broad aperiodic
03:20pm - 03:45pm USA / Canada - Eastern - August 25, 2021 | Room: A311-A312
Edwin Thomas, Presenter, Rice University Brown Sch of Engr; Xueyan Feng
Nanostructured ionomers for ion transport

Karen I. Winey, winey@seas.upenn.edu. University of Pennsylvania, Philadelphia, Pennsylvania, United States

Polymer chemistry can now provide remarkable control over polymer microstructures, including the placement of associating functional groups in ionomers. We have studied various precise and nearly-precise polymer architectures focusing on connecting the self-assembled morphologies and transport properties. This talk will highlight a set of segmented ionomers containing polar units with one neutralized sulfonate groups separated by a precise number ($n = 10 - 48$) of methylene groups (PESn-X). These PESn-X ionomers exhibit exceptional long-range order and order-order transitions reminiscent of block copolymers and we have constructed phase diagrams for comparison with theoretical predictions of multiblock copolymers. The PES12-Li polymer exhibits a disordered morphology above 120°C and we applied the RPA theory for multiblock copolymers to extract the chi parameter. With respect to ion conductivity, the most promising of the ordered structures is the double gyroid structure that exhibits higher ionic conductivity than the isotropic layered or hexagonal morphologies. Finally, we are exploring additives to further increase the ionic conductivity in these and other precise ionomers.
Morphology and ion transport in hydrated ion containing polymers

Amalie L. Frischknecht, alfrisc@sandia.gov. Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico, United States

Hydrated ion-containing polymer membranes are used as electrolytes in a variety of applications, including in fuel cells and in alkaline batteries. Achieving high conductivity typically requires the hydrophobic backbone of the polymers to be nano-phase separated from the hydrophilic domains so that the ions (protons or hydroxide ions) have well-defined water channels for efficient transport. The ion transport thus depends strongly on the hydration level and the detailed morphology of the hydrophilic domains. It is often difficult to determine the morphology of these domains experimentally. Here I will present results from atomistic molecular dynamics (MD) simulations that reveal the domain morphology in three different ion-containing polymers, two with sulfonate groups and one with ethyl-ammonium groups. In all cases, increasing water content leads to an increase in the characteristic spacing between hydrophilic domains. However, this swelling can be obscured in X-ray scattering due to a loss of scattering contrast between the hydrophobic and hydrophilic domains. The MD simulations reveal that the systems are still nano-phase separated, even when X-ray scattering appears to indicate otherwise. Calculated and measured scattering profiles are in good qualitative agreement. Ion diffusivities calculated from the MD simulations follow the experimentally-measured trends in conductivity and are consistent with changes in the nanoscale morphology with changing water content. I will discuss implications of the results for the future design of ion-conducting polymers.

Isodensities of hydrophilic domains (blue) from MD simulations of three different ion-containing polymers.
Alignment and Morphology of Nanoplates in Lamellar Diblock Copolymer Thin Films

Russell J. Composto, composto@seas.upenn.edu. Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

The ability to disperse inorganic nanoparticles (NPs) of various shapes, sizes, and compositions in polymeric matrices enables researchers to continuously engineer new material combinations with different properties. This talk will present studies of alignment of nanoplates in polymer nanocomposite PNC films. Monodisperse gadolinium trifluoride rhombic nanoplates are assembled in lamellar-forming poly(styrene-b-methyl methacrylate) (PS-b-PMMA) block copolymers (BCPs). With microdomains oriented parallel to the substrate, the lamellae serve as guides to direct nanoplate alignment. To direct placement of the NPs, the nanoplate surfaces are functionalized with phosphoric acid functionalized polyethylene glycol brush to create favorable interactions between the NPs and PMMA. Three characteristic behaviors are observed as a function of nanoplate volume fraction. At low volume fraction, the nanoplates sequester to the PMMA domain and ordered lamellae successfully direct in-plane NP alignment. Here, the nanoplates further assemble into strings separated by small equilibrium interparticle distances. At intermediate volume fraction, the PNCs phase separate into regions of ordered lamellae and regions of disordered BCP with unaligned nanoplates. While at the highest volume fraction, the nanoplates jam in a kinetically trapped state and are isotropically dispersed throughout entirely disordered lamellae. Simulations investigate the effect of brush and block copolymer molecular weights on the alignment, spacing and dispersion of nanoplates. Overall, the studies herein seek to understand the alignment and morphological effects of nanoplates in lamellar BCP thin films by identifying and understanding the thermodynamic contributions of the system.

![Graph showing Potential of Mean Force versus nanoplate separation](image)

Potential of Mean Force versus nanoplate separation
High melting polyethylene sulfones

Kenneth B. Wagener¹, wagener@chem.ufl.edu, Julia Pribyl Ham². (1) Chemistry, University of Florida, Gainesville, Florida, United States (2) Chemistry, US Naval Academy, Annapolis, Maryland, United States

Metathesis chemistry has been explored for more than 60 years, the first report by Eleuterio/DuPont appearing in 1957. The creation of well-defined catalysts led to structure-controlled ROMP and ADMET polymer chemistry, most of it done in solution. We have eliminated solvents in ADMET chemistry now, specifically in preparing polyethylene polysulfones. This bulk synthesis requires high temperatures (up to 175 C) in order to polymerize above the melting point of the polymer. The polymer chemistry is scalable. The presentation describes methodology to create high melting/fast recrystallizing polyethylene sulfones in bulk.
Deconstructing the mechanism of nanoparticle reinforcement in polymer nanocomposites

Robert Riggleman¹, rrig@seas.upenn.edu, Entao Yang¹, James Pressly¹, Bharath Natarajan², Karen I. Winey¹. (1) University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) ExxonMobil Corp, Annandale, New Jersey, United States

Polymer nanocomposites have emerged as an exciting class of materials in a variety of applications ranging from optical coatings to membranes for chemical separations to structural materials. In these applications, the mechanical properties of the resulting composite are going to be of paramount importance. While some qualitative rules have emerged to understand the mechanism for nanoparticle reinforcement in polymer nanocomposites, a precise breakdown of the contributing factors to nanoparticle reinforcement remains elusive. In this talk, I will describe our recent that breaks the reinforcement mechanism down into its separate fundamental contributions. First, we use a machine learning derived quantity “softness” to understand how nanoparticles modulate the packing near the nanoparticle surface, and the nature of the changes in the packing near the particle surface depend on the polymer-nanoparticle interactions. Second, we show that there is an additional contribution to the dynamics that depends on the distance to the nanoparticle surface. We argue that this second contribution is due to a long-range elastic effect that increases the barrier for rearrangement of a monomer near the nanoparticle surface.
Single ion conducting block copolymers

Yossef A. Elabd, elabd@tamu.edu. Texas A&M University, College Station, Texas, United States

Single ion conducting block copolymers can possess the orthogonal properties of high ion conduction and high mechanical strength within robust thin films and therefore have been explored for their use in batteries and fuel cells. Additionally, the morphology type, periodicity, and phase separation strength of the self-assembled nanostructures that form within single ion conducting block copolymers and their subsequent impact on ion conduction have been a subject of great interest. In this work, the ion transport properties and morphology of a variety of single ion conducting diblock copolymers and multiblock polymers synthesized in our laboratory will be presented. Specifically, a fundamental understanding of transport-morphology relationships in these materials as a function of various chemistries and chain architectures will be examined. The application of these materials as solid-state separators for lithium-ion batteries and membranes for both proton exchange membrane fuel cells and alkaline exchange membrane fuel cells will also be discussed.
Inorganic nanoparticles with polymers grafted to their surface, known as polymer-grafted nanoparticles (PGNs), are a means to create functional materials with a controllable nanoscale structure. For instance, a thin film of PGNs on a surface can self assemble into a hexagonally packed structure with mechanically robust and precise spacing, leading to interesting optical properties, improved dielectric breakdown strength, or other desirable features. The type of ordering, interparticle spacing, and other structural details, as well as the resulting material properties, depend on parameters that can be controlled during PGN synthesis, including particle size, the type of polymer used, graft length, and grafting density. We use coarse-grained molecular dynamics simulations to show how these factors interact to determine the interparticle spacing, polymer conformations, and amount of polymer entanglements between nearby particles, and how this relates to the film’s mechanical properties. We consider moderate to high graft densities such that particles can form a stable, well ordered monolayer on a slightly attractive surface. We find that decreasing graft density leads to greater interpenetration of canopies on adjacent particles, a greater number of interparticle entanglements per chain, and thus greater mechanical toughness, both for PGN monolayer melts on a surface and for freestanding glassy films. Furthermore, simulations of crazing of these monolayers show a qualitatively similar behavior to experiments; relative to homopolymers of the same length, the craze structure of PGN films is more uniform and the films are significantly tougher, which we attribute to the entanglement structure and polymer attachment to the nanoparticles. We hope that by relating synthetic parameters to entanglements and to mechanical properties, we can provide insights to improve the rational design of robust, well ordered materials.

Heat maps of interparticle entanglements

10σ

20σ
Grain boundaries in double network phases: Sharp twins and broad aperiodic

Edwin L. Thomas, elt@tamu.edu, Xueyan Feng. Materials Science and Engineering, Texas A&M University System, College Station, Texas, United States

Soft matter crystals (e.g. self-assembled block copolymers (BCPs)) display many of the same types of defects as occur in hard matter but with unique features. BCP assemblies have unit cells with length scales of ~10 to 100 nm and are comprised of tens of thousands of molecules, each molecule in turn, having ~tens of thousands of atoms. In the case of network phases such as the double diamond (DD) and double gyroid (DG), the microphase separated domains are continuously connected in 3D. We employ slice and view scanning electron microscopy (SVSEM) to construct high resolution 3D tomograms of various types of grain boundary defects in polystyrene-polydimethyl siloxane (PS-PDMS) diblock copolymers. Depending on the choice of solvent, both the DD and DG phase can form with the two networks comprised of the ~40 v/v PDMS component. A common type of low energy, sharp grain boundary observed in hard crystals is a coherent twin boundary, where the structure exhibits mirror symmetry across the boundary plane. Using SVSEM we identified twin boundaries in both the DD and DG phases. In the DD, the twin is a (222). In the DG phase, twins appear on the (422) plane and create an interesting chirality transition of the respective pairs of networks upon crossing the boundary plane. In addition to such sharp, coherent boundaries, we also encounter wide aperiodic boundary regions (~100 nm to 10,000 nm wide) comprised of a disordered single network structure with a broad distribution of network strut directions and lengths, a genus over double that of the two interpenetrating ordered networks of the crystal and with a surface to volume ratio very similar to that of the crystal.
ACS Macro Letters/Biomacromolecules/Macromolecules Young Investigator Award

Paulomi Majumder, Organizer, AMERICAN CHEMICAL SOCIETY; Jitesh Soares, Organizer, ACS; Marc Hillmyer, Presider, University of Minnesota; Sebastien Lecommandoux, Presider, Universite de Bordeaux; Stuart Rowan, Presider, University of Chicago
Session Type: Oral - Virtual
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Wednesday, 10:30am - 12:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27

Introductory Remarks
10:30am - 10:35am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27

Hydrothermal synthesis of polyheterocyclics
10:35am - 11:00am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27
Miriam Unterlass, Presenter, Technische Universitat Wien

Innovative polymers for next generation batteries
11:00am - 11:25am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27
David Mecerreyes, Presenter

Protein-based resins for SLA 3D printing
11:25am - 11:50am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27
Alshakim Nelson, Presenter

Organocatalysis directed selective chemical deconstruction of plastics using energy efficient processes
11:50am - 12:20pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27
Haritz Sardon, Presenter, POLYMAT UPV/EHU

Concluding Remarks
12:20pm - 12:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 27

Wednesday, 02:00pm - 04:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38

Introductory Remarks
02:00pm - 02:05pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38

Visualizing bottlebrush polymers and quantifying their rigidity in the melt using super-resolution microscopy
02:05pm - 02:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38
Jonathan Chan; Avram Kordon; Ruimeng Zhang; Muzhou Wang, Presenter

Defect-enhanced mobility in supramolecular polymer networks
02:30pm - 02:55pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38
Sebastian Seiffert, Presenter

Manipulating hierarchy, mechanics, and function in polyurea-peptide hybrids
02:55pm - 03:20pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38
Prof. LaShanda Korley, Presenter

Insights into the representation and search of polymer structure
03:20pm - 03:50pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38
Bradley Olsen, Presenter, MIT; Dr. Tzyy-Shyang Lin, Massachusetts Institute of Technology

Concluding Remarks
03:50pm - 04:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 38
Hydrothermal synthesis of polyheterocyclics

Miriam M. Unterlass\textsuperscript{1,2,3}, miriam.unterlass@uni-konstanz.de. (1) Institute of Materials Chemistry, Technische Universität Wien, Wien, Wien, Austria (2) Institute of Applied Synthetic Chemistry, Technische Universität Wien, Wien, Wien, Austria (3) CeMM Research Center for Molecular Medicine of the Austrian Academy of Sciences, Vienna, Vienna, Austria

Polyheterocyclics are condensation polymers that are mainly composed of aromatic and heterocyclic functions. Examples comprise aromatic polyimides (PIs, Arimides), polyquinoxalines (PQs), or aromatic polybenzimidazoles (PBIs). The composition of polyheterocyclics leads to high thermal stabilities (typically decomposition temperatures $T_D > 500 \, ^\circ\text{C}$), high chemical resistance (typically against the vast majority of organic solvents). Unfortunately, synthesizing organic materials based on aromatics and heterocycles often requires multistep procedures employing harsh reaction conditions. Typical polymerization media are aprotic polar and toxic solvents (e.g. cresols, N-methyl pyrrolidone), and equally toxic polymerization promoters (such as isoquinoline) are additionally necessary.

With this contribution, I discuss an alternative synthetic route to polyheterocyclics: hydrothermal synthesis (HTS). HTS designates the use of liquid water at temperatures above water’s boiling point, more precisely typically in the range of 150-250 °C, as reaction medium. Advantages of HTS compared to conventional routes include (i) that the reaction medium is much greener, and (ii) that the technique is synthetically easier. Most intriguingly however, HTS typically generates superior crystallinity in polyheterocyclics. This in turn leads to intriguing materials properties that we are just beginning to unravel, but also to challenges in characterization and processing.
Innovative polymers for next generation batteries

David Mecerreyes, david.mecerreyes@ehu.es. POLYMAT, Universidad del Pais Vasco, Donostia-San Sebastian, País Vasco, Spain

Lithium ion batteries are part of our modern life being present in daily used objects such as mobile phones, tablets, computers, watches, sport accessories, electric scooters or cars. The next generation batteries would need the development of innovative polymers that help to improve their performance in terms of power density, cyclability, raw materials availability, low weight, printability, flexibility, sustainability or security. In this presentation we will discuss our recent developments in the area of redox active and ionic conducting polymers. This includes the development of innovative binders for electrodes, polymer electrolytes and redox polymers. All these new polymer developments are leading to new battery technologies such as metal-polymer batteries, organic batteries, polymer-air and redox-flow batteries which are expected to complement in the future the actual commercial batteries.
Protein-based resins for SLA 3D printing

Alshakim Nelson, alshakim@uw.edu. University of Washington, Seattle, Washington, United States

Bio-sourced and biodegradable polymers for additive manufacturing could enable the rapid fabrication of parts for a broad spectrum of applications ranging from healthcare to aerospace. However, a limited number of these materials are suitable for vat photopolymerization processes. Herein, we report a two-step additive manufacturing process to fabricate protein-based constructs using a commercially available laser-scanning SLA printer. Methacrylated bovine serum albumin (MA-BSA) was synthesized and formulated into aqueous resins that was used to print complex 3D geometrical constructs with a resolution comparable to a commercially available resin. The MA-BSA resins were characterized by rheometry to determine the viscosity and the cure rate, as both of these parameters can ultimately be used to predict the printability of the resin. In the first step of patterning these materials, the MA-BSA resin was 3D printed, and in the second step, the printed construct was thermally cured to denature the globular protein and increase the intermolecular noncovalent interactions. Thus, the final 3D printed part was comprised of both chemical and physical cross-links. Compression studies of hydrated and dehydrated constructs demonstrated a broad range of compressive strengths and Young’s moduli that could be further modulated by adjusting the type and amount of co-monomer. The printed hydrogel constructs demonstrated good cell viability (> 95%) after a 21-day culture period. This strategy was demonstrated with laser-scanning SLA printing, but is expected to be applicable toward other types of vat photopolymerization processes.
Organocatalysis directed selective chemical deconstruction of plastics using energy efficient processes

Haritz Sardon, haritz.sardon@ehu.es. POLYMAT UPV/EHU, Donostia, Gipuzkoa, Spain

Less than 8% of the polymers produced each year are currently recycled and of that small percentage the majority are recycled mechanically by grinding and melt-processing. This leads to a low-quality material that is often rapidly discarded as waste. Aside from mechanical recycling and pyrolysis, chemical recycling of plastic materials has emerged as an alternative recycling method that can potentially retain the inherent value of the plastics as it can be used to produce high purity monomers. Specifically, by chemical depolymerisation virgin like monomers can be attained and/or innovative added-value building blocks can be synthesized to prepare high added value synthons in an upcycling approach. As plastics have traditionally been designed for durability and not for recyclability, their chemical conversion to new products is nowadays considered a grand challenge. While our initial approaches were directed to the design of highly thermally stable ionic salts to guide the chemical recycling at high temperatures (close to 200 °C), the group is now moving towards the selective chemical deconstruction of plastics using energy efficient processes. This not only allows for the selective recycling of one plastic in the presence of other plastics, but also be used to produce high added value organic synthons in high yields in a fully sustainable cycle.
Visualizing bottlebrush polymers and quantifying their rigidity in the melt using super-resolution microscopy

Jonathan Chan, Avram C. Kordon, Ruimeng Zhang, Muzhou Wang, mwang@northwestern.edu. Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, United States

The behavior of single chains is integral to the foundation of polymer science, and yet a clear and convincing image of single chains in a bulk polymer system has not been captured to our knowledge. For bottlebrush polymers, understanding their conformation in the bulk is especially important because their extended backbones may explain their self-assembly and mechanical properties that have been attractive for many applications. In this study, we use single-molecule localization microscopy (SMLM) to image single fluorescently-labeled bottlebrush polymers blended with an unlabeled linear polymer melt. By fitting these images to a wormlike chain model, we are able to accurately and directly measure the persistence length of the backbone for the first time. We synthesize and measure bottlebrush polymers with several side chain lengths and grafting densities. From this data, we extract key scaling relationships that relate molecular architecture to conformation, and we discuss the underlying physics behind these scaling laws.
Supramolecular polymer networks are linked by transient, non-covalent bonds. We focus on such non-covalent linking of monodisperse star-shaped four-arm polymeric building blocks connected by complexation of terpyridine termini to transition metal ions. These networks contain only negligible amounts of inhomogeneities on scales of 10–1000 nm, and at appropriate polymer concentration and linker stoichiometry, their elastic moduli even indicate just little misconnectivity. However, if small amounts of local connectivity defects are intentionally introduced, e.g., by incorporation of a few percent of star polymers in which one of the arms does not carry a terpyridine motif, there is evidence that the mobility of these defective building blocks through the percolated system is significantly accelerated, even on scales from micro- to millimeters. On micrometer scales, even apparent superdiffusivity of the building blocks is evident. An approach to explain these findings assumes that local connectivity defects around such unsaturated network building blocks allow them to migrate through the network with a fast "walking" mechanism. To challenge/support that conceptual picture, we focus on metallo-supramolecular networks based on tetra-arm building blocks that are terminated by motifs undergoing heteroleptic complexation to metal ions, thereby resembling Sakai’s tetra-pEG model-network approach for metallo-supramolecular gels. With such model networks, it is possible to impart controlled types and extents of connectivity defects to study their impact on the passage of the defect centers through the network, along with potential further effects on the network relaxation.
Manipulating hierarchy, mechanics, and function in polyurea-peptide hybrids

LaShanda Korley\textsuperscript{1,2}, lkorley@udel.edu. (1) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (2) Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States

Inspired by natural materials, we have designed a series of polymer-peptide polyurethane/ureas to explore the hierarchical arrangement critical to energy absorption and mechanical enhancement. We have developed chain-extended and non-chain extended peptide-polyurea hybrids with tunable secondary structure, modulating extensibility, toughness, and stiffness. The sheet-dominant hybrid materials were typically tougher and more elastic due to intermolecular H-bonding, while the helical-prevalent systems generally exhibited higher modulus. We have also explored the impact of a molecular design strategy that overlays an architecture comprised of both physical and covalent crosslinks in these hybrids, demonstrating that physical constraints in the network hybrids influences hydrogen bonding and microstructure. Additionally, tailored physical associations within the soft and hard phases were engineered as a function of peptide content, leading to a rheological response dictated by block ordering and highlighting their potential as structural and injectable hydrogels. Recently, we utilized these hybrids to design thermoresponsive, shape memory elastomers with fixity and recovery tuned by secondary structure and associated microstructure. Extending this peptide-hybrid framework to silk-inspired composites and amphiphilic systems also has led to unique architectural features at multiple length scales and manufacturing advances towards actuators and coating technology.
Insights into the representation and search of polymer structure

Bradley D. Olsen, bdolsen@mit.edu, Tzyy-Shyang Lin. chemical engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

What we refer to as “a polymer” is in fact an ensemble of different molecules, where the rules of chemistry govern both the permissible states in the ensemble and their relative probabilities of observation. Within this framework, we can represent the chemical structures of polymers with deterministic notations by defining the ensemble rather than defining an individual molecule. This provides a powerful mapping from stochastic chemistry onto computer-friendly line notations that allow polymer structures to be stored in compact representations. The concept of polymer ensembles leads to a further insight that a polymerization reaction may be considered a language where monomers act as fundamental building blocks (monomers) that can be assembled into large molecules (sentences). The rules of the chemistry used to synthesize the molecules represent the grammar of the language, completing the analogy. This analogy allows developments from applied math for studying formal languages to be directly applied to the characterization of polymerizations, providing, for example, methods for determining if two polymerizations are “equivalent.”

Given these different methods for writing polymer structures, it is now important to be able to search for them. Typically, molecular search relies on comparison of molecular subgraphs, a concept that would be extremely valuable if extended to stochastic polymer graphs. To do this, we recognize that polymer graphs are composed via a structural hierarchy with preferred positions such as monomers, endgroups, and side groups carrying meaning with respect to how the random graphs are constructed that is conveyed through the chemical structure representation. To enable search of these graphs, we have developed a BigSMARTS grammar that is compatible with SMARTS but allows targeted searches on stochastic graphs, and we are developing algorithms to implement this in practical search formats. Taken together, these tools leverage an unconventional perspective on polymerization to allow us to better share, find, and compare our polymer structures.
Circular Economy of Polymers
Dr. Dimitris I Collias, Organizer, Proctor Gamble; Martin James, Organizer, Procter & Gamble Co; John Layman, Organizer; Dr. Dimitris I Collias, Presider, Proctor Gamble
Session Type: Oral - Hybrid
Co-sponsor/Theme: Co-sponsor - Cooperative PMSE: Division of Polymeric Materials Science and Engineering

Sunday, 08:00am - 10:00am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Advanced recycling: A pathway to circularity for critical multilayer flexible packaging
08:00am - 08:30am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Dr. Timi Fadiran, Presenter, Sealed Air Corporation
Smart pyrolysis for re-processing of PC/ABS polymer blends at end of useful life
08:30am - 09:00am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Don Wardius, Presenter; Stefanie Eiden; Rainer Bellinghausen; Andreas Seidel; Erik sluyts; Philippe Rath sack
Withdrawn
Degradable vinyl polymers via photo controlled radical ring opening cascade polymerization
09:30am - 10:00am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Jia Niu, Presenter
Sunday, 10:30am - 12:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Systematic variation of polyolefin sequences to support measurements for materials circularity and end of life concerns
10:30am - 11:00am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Sara Orski, Presenter, NIST
Dynamic crosslinked polymer nanocomposites with boronic ester from commodity thermoplastics enables exceptionally tough adhesion
11:00am - 11:30am USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Dr. Md Anisur Rahman, Presenter, Oak Ridge National Lab; Christopher Bowland; Sungjin Kim; Alexei Sokolov; Aditya Savara; Dr. Tomonori Saito, Oak Ridge National Laboratory
Compatibilization of polymeric interfaces for improved mechanical recycling
11:30am - 12:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Mark Dadmun, Presenter
Sunday, 02:00pm - 04:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Controlled depolymerization and upcycling of PVC
02:00pm - 02:30pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Prof. Jason E. Bara, Presenter, University of Alabama; Ali Alshaikh, Presenter; David McEachern; James Bridges; Kathryn O’Harra; Paul A Rupar, University of Alabama
4D printable naturally derived photopolymers from terpenes and terpenoids: Additive manufacturing and the circular economy
02:30pm - 03:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Andrew Weems, Presenter; Eric Constant; David Merckle; Scott Brooks
Exploring the circularity of ketoenamine-based vitrimers synthesized by thiol-ene photopolymerization
03:00pm - 03:30pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Logan Dugas; William Walker; Rahul Shankar; Keely Hoppmeyer; Travis Thornell; Sarah Morgan, University of Southern Mississippi; Robson Storey; Derek Patton; Prof. Yoan C Simon, Presenter, The University of Southern Mississippi
Growing silk fibroin in advanced materials for food security and precision agriculture
03:30pm - 04:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Hui Sun; Augustine Zvinavashe; Benedetto Marelli, Presenter
**Sunday, 04:30pm - 05:30pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312**

**Design of high performance vitrimers for circular economy**
04:30pm - 05:00pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312
Dr. Md Anisur Rahman, Oak Ridge National Lab; Sungjin Kim; Md Arifuzzaman; Zhengping Zhou; Christopher Bowland; Natasha Ghezawi; Amit Naskar; Alexei Sokolov; Aditya Savara; Dr. Tomonori Saito, Presenter, Oak Ridge National Laboratory

**05:00pm - 05:30pm USA / Canada - Eastern - August 22, 2021 | Room: A311-A312**
Xiaoqian Wang; Rong Tong, Presenter

**POSTER – IN PERSON**
07:00pm - 09:00pm USA / Canada - Eastern - August 22, 2021 | Room: B2 - EXHIBIT HALL

**Seaweed based materials to replace single use plastic at scale**
Jose Andrade, Presenter; Devin Virassamy; Sea Briganti; Victoria Piunova

**Monday, 04:30pm - 06:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44**

**APK Newcycling® : Heading for 'un-recyclable' plastic packaging**
04:30pm - 05:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44
Klaus Wohnig; Hagen Hanel, Presenter

**Decontamination of pyrolysis oil allow its use for new polymer production**
05:00pm - 05:30pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44
Bettina Sigelkow; Nina Karpynec, Presenter; Dr. Vinicius Celinski, Presenter, Clariant

**Economical and practical routes for the chemical recycling of PET**
05:30pm - 06:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44
Dr. Muhammad Rabnawaz, Ph.D., Presenter, Michigan State University

**Radical ring opening polymerization as a powerful tool to prepare degradable materials**
07:00pm - 07:30pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 03
Noémie GIL, Presenter; Didier Siri; Didier Gigmes; Catherine Lefay; Yohann Guillaneuf

**Polyhydroxyurethane-graft-poly(ε-caprolactone) copolymers: Designing complex polymer architectures through sustainable routes**
07:30pm - 08:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 03
Charalampos Pronoitis, Presenter, KTH Royal Institute of Technology; Minna Hakkarainen; Dr. Karin Odelius

**Degradable and thermally stable spiro polycycloacetals from renewable resources**
08:00pm - 08:30pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 03
Minjie Shen; Srikanth Vijjamarri; Hongda Cao; Fahimeh Khakzad; Yanchun Tang; Karla Solis; Megan Robertson, Presenter, University of Houston

**Effects of alkyl and phenyl substituents in ethylene glycol or 1,3-propanediol in binary copolyesters with 2,5-furandicarboxylic acid**
08:30pm - 09:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 03
Massoud Miri, Presenter, Rochester Institute of Technology; Derek Lohmann; Daniel Honeycutt; Daniel Verrico; Alex North; Sara Cobb; William Charbonneau; Red Smith-Sweetser
Multilayer flexible packaging optimizes materials while meeting the performance needs of critical products for food and medical applications. Individual layers in multilayer flexible packaging perform specific, necessary functions (e.g. oxygen barrier for shelf life extension) and enable the reduction of total amount of material used. The flexible packaging industry must continue to reduce waste and global carbon footprint. However, product waste impact is typically much greater than the packaging used to protect it. Shifting to monolayer solutions will lead to increased resource use and potential for product waste.

Advanced recycling solutions, such as pyrolysis and gasification, present a pathway to circularity for critical multilayer flexible packaging. First, these solutions offer high quality recycle content that can be used in critical applications such as food and medical packaging, allowing the flexible packaging industry to meet recycle content goals. Second, advanced recycling offers potential end of life solutions for hard-to-recycle multilayer flexible packaging. Design modifications of multilayer flexible packaging and dilution within the post-consumer waste stream should allow for these critical products to meet advanced recycling specifications.

In this work, the behavior and impact of multilayer products in a pyrolysis process are explored. The acceptability of flexible multilayers in pyrolysis and dilution of flexible multilayers in polyolefin rich streams are investigated. This work is critical to establishing advanced recycling specifications for post-consumer waste to drive a circular economy for flexible packaging.
Smart pyrolysis for re-processing of PC/ABS polymer blends at end of useful life

Don S. Wardius¹, dwardius@alum.mit.edu, Stefanie Eiden², Rainer Bellinghausen², Andreas Seidel², Erik sluys³, Philippe Rathsack⁴. (1) Alliances and Partnerships, Covestro LLC, Pittsburgh, Pennsylvania, United States (2) Covestro Deutschland AG, Leverkusen, Nordrhein-Westfalen, Germany (3) Covestro NV, Antwerp, Belgium (4) Technische Universität Bergakademie Freiberg, Freiberg, Sachsen, Germany

Given the global challenge of anthropogenic carbon in the earth’s atmosphere, there is increasing attention to intelligently managing carbon. Covestro is promoting the development of a circular economy of all materials, including plastics, even encompassing the most complex and elaborate value chains. Polycarbonate / acrylonitrile-butadiene-styrene polymer blends (PC/ABS) find application as an engineering thermoplastic used in electronics and industrial goods, automotive / transportation components, and building and construction / furnishings as a versatile material with an attractive value proposition for durable applications. While PC/ABS can be mechanically recycled in some instances, more comprehensive solutions are desirable. Chemical / solvolytic methods may be of broad utility but are not always attractive for polymer blends due to additional compositional complexity. Pyrolytic processes may have utility to accept worn down plastics at end of life with a modest latitude to readily accommodate variation of compositional inputs. Pyrolysis generally aims to convert such inputs to naphtha which may be reformed to chemicals. Smart pyrolysis aims to target the most suitable chemical “building blocks” to polymers, and tailor the process to attain those as directly as possible. This minimizes the overall number of processing steps. In this talk we shall discuss our motivation and laboratory project, as well as provide some initial results and conclusions specific to PC/ABS. The extrapolation to a production scale recycling operation looks interesting at the first pass.

Linear economy of plastics from the twentieth century is being transformed into a circular economy by further developing new technologies such as smart pyrolysis.
Among the over 400 million tons of synthetic polymers produced worldwide annually, approximately half are vinyl polymers generated by radical polymerization. The widespread use of vinyl polymers has posed a significant challenge to the environment, as their hydrocarbon backbones are resistant to degradation. While degradable vinyl polymers via radical ring-opening polymerization have attracted increasing attention in both laboratory and industry, a major challenge in this field is the unfavorable reactivity ratios between the cyclic monomer carrying labile functional groups and the acyclic vinyl monomers, leading to inadequate material properties and partial degradation. In this presentation, we describe a photocatalytic approach to degradable vinyl polymers with tunable main-chain composition via radical ring-opening cascade polymerization (rROCP). Radical copolymerization of the macrocyclic monomers and a broad collection of acrylates or acrylamides mediated by visible light at mild temperatures afforded vinyl copolymers with tunable degradable units evenly distributed in the polymer backbone. This study provided a powerful approach to a new generation of degradable polymeric materials.
Systematic variation of polyolefin sequences to support measurements for materials circularity and end of life concerns

Sara V. Orski, sara.orski@nist.gov. Materials Science & Engineering, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Polyolefin compatibilizers, which often include statistical and block copolymers, aim to prevent phase separation in post-consumer resins (PCR) of mixed polymer type. As the US aims to increase recycling beyond the 10% average PCR material from consumer feedstocks, new strategies and measurements are required for increasingly complex mixtures of used plastics. Quantifying the molar mass, chemical composition, and architectural distributions of these materials is crucial for determining accurate structure-property-performance relationships and to optimize design of compatibilizers for mechanical recycling. This talk will highlight efforts to make systematically varied families of model polyolefins based on ring-opening metathesis polymerization (ROMP) of 1-alkyl-trans-cyclooctenes with successive hydrogenation to compare the dilute solution properties of varied branch length, branch frequency, and copolymer composition. Characterization of these model materials via high temperature size exclusion chromatography yield information about the distribution of molar masses, chain branching, and dilute solution properties. With this information, further characterization of these materials in bulk systems can be studied and results correlated to homogeneous, well characterized materials. Furthermore, for materials designed to degrade, where recovery and recycling is not practical, understanding environmental degradation kinetics on polymer topology and chemistry are crucial to material design. We will also highlight efforts in our laboratory to study environmental aging of polyolefins with systematic study of degradation with material depth in efforts to develop improved degradation models as benchmarks for next generation material comparison.
Dynamic crosslinked polymer nanocomposites with boronic ester from commodity thermoplastics enables exceptionally tough adhesion

Md Anisur Rahman, rahmana1@ornl.gov, Christopher Bowland, Sungjin Kim, Alexei P. Sokolov, Aditya Savara, Tomonori Saito. Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Structural adhesives are mostly made of thermoset polymeric materials with irreversible chemical bonding that exhibits strong but brittle behavior. Those thermoset adhesive materials are mostly single-used and ultimately end up in a landfill without an option for recycling. Therefore, it is highly desirable to develop recyclable/reusable tough adhesive materials that can provide high strength, high load-bearing capability, and longevity of bonded materials. Such tough adhesives can minimize adhesive failure, provide a path for recycling, and prevent unnecessary replacements of bonded materials, thus ultimately save significant energy and costs. Here, we report a design of tough reversible adhesive materials enabled by incorporating dynamic covalent bonds of boronic ester into commodity triblock thermoplastic elastomers, that reversibly bond with various fillers and substrates. A commodity thermoplastic elastomer, polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS) was modified with boronic ester and reinforced using unmodified silica nanoparticles (SiNPs). The dynamic covalent crosslinking between hydroxyl groups on SiNPs, boronic ester group on SEBS enables reprocessability, mechanical robustness, and rebondable tough adhesive property on various hydroxy-terminated surfaces such as aluminum, steel, and glass, which are also validated by density functional theory calculations. 20 wt % SiNPs loaded composite exhibit very strong adhesion at 9.38 ± 1.39 MPa and work of debonding of 733.96 ± 71.58 Nm^(-1) on aluminum substrate, which exceeds many existing commercial adhesives. This talk will demonstrate a simple and efficient way to make a tougher adhesive with significantly high strength, ductility, and reprocessability, that will open new opportunities in many applications.
Managing end-of-life plastics is a challenging problem for a variety of reasons, including the complexity of mixed waste streams. Most polymer pairs don’t mix, and any product made from such a mixture will exhibit poor properties. These polymer mixtures can be enhanced by their compatibilization with proper polymeric interfacial modifiers. Our group has developed a fundamental understanding of polymeric compatibilizers for amorphous polymer blends. However, most polymers that end up in the waste stream are crystalline. Extensive research has shown that the roles of polymeric compatibilizers in amorphous phase separated polymer blends include entangling with both polymers, inhibiting droplet coalescence, and lowering the interfacial tension between phases. In crystalline polymers, the compatibilizer may also co-crystallize with either homopolymer providing an additional mechanism to strengthen the biphase interface. However, the importance of this additional mechanism, and understanding the compatibilizer molecular characteristics required to improve blend properties via co-crystallization, is poorly understood.

Studies that investigate the ability of random or blocky chlorinated polyethylenes (c-PE) to compatibilize polyolefin elastomer-poly(vinyl chloride) blends provide insight into this problem. These studies show that the blocky c-PE strengthens the polymer-polymer interface much more than a random copolymer, while the blocky copolymer also co-crystallizes with the homopolymer, but the random copolymer does not. This presentation will provide the current state of our understanding of the role of co-crystallization in the compatibilization of crystalline polymer blends, and provide insight into the molecular characteristics of effective copolymeric compatibilizers for phase separated crystalline polymer blends, including those that are most relevant for mixed waste streams in polymer recycling.
POLY – Circular Economy of Polymers

Controlled depolymerization and upcycling of PVC

Jason E. Bara¹, jbara@eng.ua.edu, Ali A. Alshaikh¹, aalshaikh@crimson.ua.edu, David McEachern², James W. Bridges¹, Kathryn E. O’Harra¹, Paul Rupar². (1) Chemical & Biological Engineering, The University of Alabama, Tuscaloosa, Alabama, United States (2) Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, Alabama, United States

PVC is the 3rd most produced plastic worldwide. Rigid PVC is the common material of construction for most modern plumbing systems, and other forms of PVC find their way into a wide range of consumer products. The presence of chlorine atoms in PVC presents unique challenges for its disposal as the uncontrolled decomposition of PVC releases HCl and chlorinated organic compounds, presenting waste management and environmental problems. However, the design of chemical reactions and processes which control the decomposition of PVC affords unique opportunities for depolymerization and upcycling. This presentation will detail our efforts to date in the conversion of waste PVC into an array of value-added small molecules and polymer products.
4D printable naturally derived photopolymers from terpenes and terpenoids: Additive manufacturing and the circular economy

Andrew C. Weems, weemsac@ohio.edu, Eric Constant, David Merckle, Scott Brooks. Ohio University, Athens, Ohio, United States

Green materials for manufacturing have risen to the forefront of public attention, provoked by the ongoing plastics pollution crisis and climate change. With these problems in mind, alternatives to the petroleum-derived and non-degradable plastics have gained substantial attention in the research spheres. Terpenes and terpenoids, as well as other natural products, have been successfully incorporated in polyesters, polyamides, and polythioethers, although the utility of such bioderived materials has been fairly limited in additive manufacturing (AM) applications. A series of such natural products has been explored as AM photopolymers, using a variety of simple strategies to rapidly solidify the liquid resins and inks into solid prototypes using either digital light processing (DLP) or direct ink writing (DIW) 3D printing techniques. Initially, small molecule terpenes and terpenoids (i.e., limonene, β-myrcene, linalool) without modification are discussed, exploiting thiol-ene “click” reactions for production of prototypes. These are further compared with modified terpenes and terpenoids (i.e., urethane-linked linalool) as well as those produced from free radical polymerizations or derivatives processed by ring opening polymerizations (polyesters containing limonene oxide) to produce 4D shape memory polymer complex prototype scaffolds. Finally, recycling of these materials is presented, leveraging low-cost depolymerization strategies as well as more common hydrolytic degradation at elevated temperatures to recover small molecules and modified polymers that are suitable upcycling to 3D printing materials with minimal modifications. Characterizations including physical properties, synthetic procedures, and processing required to achieve AM-suitable materials are used to demonstrated significant enhancements to the upcycled material properties.
Building upon associative exchange chemistries, vitrimers have emerged as a one-of-a-kind class of materials possessing properties similar to both thermosets and thermoplastics. In the context of sustainability, these crosslinked materials are especially attractive for their ability to be reprocessed while retaining their original properties. We depict here our efforts to fabricate novel photopolymerized thiol-ene networks capable of undergoing dynamic covalent exchange through ketoenamine linkages derived from cyclic triketones. Uncatalyzed transamination also enabled rapidly depolymerization down to monomers thereby facilitating chemical recycling. A 5,5-dimethyl-2-(pent-4-enoyl)cyclohexane-1,3-dione was reacted with a 15% molar excess of 1,6-diaminohexane. The networks exhibited subambient glass transition temperature ($T_g \sim 3-7°C$) and the topology freezing temperature ($T_v$) was calculated to be $-31°C$ by extrapolating to a viscosity of $10^{12} \text{ Pa.s}$. Small oscillatory stress experiments helped us identify the factors controlling topological rearrangement and practical reprocessing conditions. Conveniently, the vitrimers were degraded back to repolymerizable monomers with either strong acids or excess primary amine demonstrating the circularity of the approach. This work paves the way for the development of sustainable, multifunctional materials and their implementation in a plethora of applications, viz. high-performance composites and coatings.
This perspective provides an overview of the micro-/nanofabrication methods developed for structural biopolymers, highlighting recent advances in the rapid and ease construction of complex and multifunctional silk fibroin-based devices by integrating top-down manufacturing with bottom-up molecular self-assembly. Of particular interest is the development of a new nanofabrication strategy that employs templated crystallization to direct silk fibroin folding and assembly from a suspension of disordered, random coil molecules to ordered, hierarchical mesostructured materials. Such advancements in structural biopolymers fabrication provide the basis for engineering a new generation of technical materials that can be interfaced with food and plants. In this presentation, we highlight newly developed techniques to direct the assembly of structural proteins into nanostructured materials that can serve as: edible coatings to prolong the shelf-life of perishable food and microenvironments to boost seed germination in saline soil. These examples will provide an opportunity to discuss how the establishment of a successful interface between biomaterials and plants tissues requires the development of a basic scientific knowledge on: mechanics of disorder to order transitions in proteinaceous materials during condensation phenomena and biopolymers-plants interface.

Templated crystallization of silk fibroin may be used to control the protein disorder to order transition and direct assembly in hierarchical materials.
Design of high performance vitrimers for circular economy

Over 300 million tons of solid plastics are globally produced annually and only ~9% of those are currently recycled in U.S.. It is estimated that, in the absence of a circular economy for polymers, >20% of all oil and gas consumption will be used for manufacturing and distribution of plastics. Recycling 1 ton of plastic is estimated to save ~130 million kJ of energy. One approach to enable circular economy is to develop new recyclable crosslinked polymers. Crosslinked polymers comprise 15-20% of all produced polymers, and do not exhibit recyclability due to their unpliable nature. Vitrimers represent recyclable or reprocessable crosslinked polymers by the presence of dynamic exchangeable groups, and this presentation will summarize our efforts on the design, synthesis, and processing of novel vitrimers for circular economy. These novel vitrimers exhibit solvent resistance and remarkable mechanical toughness, while they can be processed at elevated temperature. In one system, we have developed boronic-ester functionalized triblock copolymers that have dynamic exchange interactions with multiple surfaces. They exhibit exceptionally tough adhesion onto multiple surfaces, and their recyclability were also demonstrated. In another system, we have developed 3D printing of vitrimers that can form various shapes, provide recyclability and exhibit exceptional solvent resistance. Third system includes robust vitrimer resins for carbon fiber composite application. Our study reveals new design principles for upcycled vitrimers, specially tailored in viscoelasticity, mechanical toughness, recyclability and processability.
Stereoselective electrochemical ring opening polymerization to synthesize functionalized polyesters

Xiaoqian Wang, Rong Tong, rtong@vt.edu. Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Ring-opening polymerization is used to prepare polyesters with precisely controlled molecular weights, molecular weight distributions, and tacticities. Herein, we report a newly developed Co/Zn catalytic system that can be activated by an electrical current to mediate efficient ring-opening polymerization of enantiopure O-carboxyanhydrides, allowing for the synthesis of isotactic functionalized polyesters with high molecular weights (>140 kDa) and narrow molecular weight distributions (Mw/Mn < 1.1).

We began our studies of electrochemical ring-opening polymerization (eROP) of l-1 under galvanostatic (constant current) conditions in an undivided cell and thoroughly evaluated the electrode materials, electrolyte, current, and temperature, aiming to avoid a cumbersome electrochemical reaction setup from an industrial scale-up standpoint (Figure 1a). We found that Mg was optimal for the anode (working electrode) and that Pt was best for the cathode (counter electrode). THF proved to be the ideal solvent. The use of tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M in THF) as the electrolyte led to better control of the polymerization than other tetraalkylammonium salts. Better polymerization results (i.e. Mn value close to the calculated MW) were obtained at 0 °C than at room temperature. Under these conditions, the Mn of the poly(l-1) product increased linearly with initial [l-1]/[Co-1]/[Zn-1] ratio up to 1000/1/1 (Figure 1b).

We also demonstrate that the Co/Zn catalysts can be used for stereoselective ring-opening polymerization of racemic O-carboxyanhydrides to synthesize syndiotactic or stereoblock copolymers with different glass-transition temperatures (Figure 1c). The difference in microstructure between the two obtained polymers was confirmed by differential scanning calorimetry: poly(sb-1) had a glass transition temperature (Tg) of 46 °C, whereas poly(sd-1) exhibited a Tg of 58 °C. Note that the atactic poly(rac-1) had a Tg of 51 °C.

Figure 1 Controlled electrochemical ring-opening polymerization of O-carboxyanhydrides. (a) Reaction scheme and setup. (b) Plot of MW and MW distribution of polymer versus feeding ratios. (c) Stereoselective electrochemical polymerization.
In this presentation we discuss a commercially viable seaweed-based technology aimed to replace single use plastic in food-service industry. Seaweed-derived materials present an attractive alternative to well know plastic substitutes like paper and plastic from bio renewable sources due to the fact that seaweed (kelp) can grow several meters per day unattended in the ocean, requiring no agricultural resources or fresh water, presenting an ideal renewable and abundant natural resource for disposable plastic items. Moreover, seaweed is known to be an excellent CO2 sequesterer, contributing to the climate change mitigation during the growth cycle.

Here we demonstrate the first example of producing seaweed-based pellets and consequent processing into desired form-factors via conventional hot melt extrusion process (HME) using commercially available machinery.

Obtained samples underwent thermal and mechanical testing, correlation curves of formulation composition vs tensile strength, compression strength and elongation at break as were constructed.
APK Newcycling®: Heading for 'un-recyclable' plastic packaging

Klaus Wohnig, Hagen Hanel, hagen.hanel@apk-ag.de. APK AG, Merseburg, Germany

APK Newcycling® - heading for 'un-recyclable' plastic packaging With the EU Commissions’ 2020 Green Deal and an ambitious new Circular Economy Action Plant the plastics and packaging industries are challenged to deliver on clear definitions of recycled content, raising quality of recyclates and creating volumes (Circular Plastics Alliance: 10 mio t by 2025 in products on the market in the EU).

Meeting these demands means closing plastic cycles for products that could not be closed up to now – such as post-consumer multi-layer packaging waste.

APK’s technology is targeting these 'unclosed loops' by driving mechanical recycling a decisive step further and adding a solvent-based purification step. Initially APK is concentrating on pre-consumer (post-industrial) PE/PA film combinations. Further mixes such as PE/PP have been testes successfully-The soon to be realized goal is the recycling of post-consumer material streams. Regarding the process: first step is a site reduction of PE/PA rolls and bales to bring the material into a flake shape enlarging the specific surface. Second step is the conveying into a solvent-bath, where the PE is physically dissolved and the PA remains solid. Afterwards a special solid-liquid separation is applied to separate the polymer solution and the PA-flakes. Finally, the solvent is devolatized in both material streams and both materials are extruded to bring them to pellet-shape. Key is the recirculation of the solvent, that is cleaned inline.

The targeted use of solvents in combination with mechanical recycling holds concrete benefits with regard to chemical recycling approaches: the polymer is retained and so is the energy invested in its polymerization. Recyclate produced with APK’s Newcycing® technology holds decisive emissions reduction potential compared to conventional mechanical and also chemical recycling processes.
Decontamination of pyrolysis oil allow its use for new polymer production

Bettina Siggelkow, Nina Karpyne, nina.karpyne@clariant.com, Vinicius Celinski, Vinicius.Celinski@clariant.com. Clariant Produkte Deutschland GmbH, Frankfurt am Main, Hessen, Germany

The pyrolysis process offers a good complementary solution to mechanical recycling for treating the remaining plastic waste.

The output of the process is pyrolysis oils that are often intended to be used as cracker feedstock. Due to the nature of the plastic waste used as feedstock in the thermochemical process, pyrolysis oils often contain high amounts of contaminants. Significant amounts of metals, chlorides, sulphur or other contaminants in pyrolysis oils reduce their use as cracker feedstock.

Clariant has developed different products/solutions to remove these contaminants. By applying these solutions, the pyrolysis oil can be enhanced to make it fit for purpose.

Clariant’s experts establish the right solution based on the specific situation of the customer process. This solution is part of the company’s EcoCircle Initiative, enabling the industry to transition towards a circular plastic value chain.
Economical and practical routes for the chemical recycling of PET

Muhammad Rabnawaz, rabnawaz@msu.edu. Packaging, Michigan State University, East Lansing, Michigan, United States

Chemical recycling of PET is highly desirable but currently less economical due to challenges such as energy intensive depolymerization. In this lecture, I will describe the rapid chemical upcycling of PET via multiple creative approaches without using any organic solvent. We have been able to achieve 100% depolymerization in less than 1 hour at 160°C, which, compared to the traditional methods, will take place 4 hours. This 4 fold increase in the polymerization of PET will offer new energy to the chemical recycling of PET.
Radical ring opening polymerization as a powerful tool to prepare degradable materials

Noémie GIL, noemie.gil@univ-amu.fr, Didier Siri, Didier Gigmes, Catherine Lefay, Yohann Guillaneuf. Aix-Marseille Université, Marseille, Provence-Alpes-Côte d’Azur, France

Among the different classes of polymers, vinyl polymers are used in a wide range of applications. The development of degradable polymer is currently the focus of great attention given their extensive use in many different areas including (nano)medicine, microelectronics and packaging. Nevertheless, due to its radical mechanism such vinyl-based polymers contain a carbon backbone and cannot be degraded, which is a detrimental for the environment.

The degradability of a polymer can be provided by the insertion of labile functions in the polymer backbone by copolymerization. The development of the radical ring-opening polymerization (rROP) in the 1980s, allowed for example the incorporation of esters in the carbon chain via the copolymerization of Cyclic Ketene Acetals (CKA)\(^1\). The copolymerization of such cyclic monomer bearing an exo-methylene function with an acrylate, a styrene, a vinyl ether or a vinyl ester derivatives makes it possible to obtain a degradable copolymer by the hydrolysis of ester functions introduced by the addition/fragmentation of the CKA moiety. Recently thionolactones\(^2\) were introduced as RROP monomer allows the incorporation of weak bonds (thioester functions) in the backbone of vinyl-based polymers. The difference between these two cyclic monomers is their difference of reactivity ratios with common vinyl monomers. A random incorporation of the weak bonds is mandatory to obtain a homogeneous degradation to the materials and avoid long poorly degraded fragments.

Our project consists in understanding the impact of the structure of the cyclic monomer on the degradability of the copolymer obtained. To this end, a theoretical study has been carried out to understand the reactivity of CKA and thionolactone during the copolymerization of various vinyl monomers. Subsequently, an experimental study was carried out with the copolymerization of CKA and thionolactones with the same vinyl comonomer and the resulting copolymer was degraded. These studies have made it possible to highlight key parameters to obtain degradation products with low molar masses and thus to conclude on the impact of the structure of the cyclic monomer on the copolymerization.
Polyhydroxyurethane-graft-poly(ε-caprolactone) copolymers: Designing complex polymer architectures through sustainable routes

Charalampos Pronoitis, chpr@kth.se, Minna Hakkarainen, Karin Odelius. Fibre and Polymer Technology, Kungliga Tekniska Hogskolan, Stockholm, Sweden

Polyhydroxyurethanes (PHUs) have attracted increasing attention as a sustainable alternative to conventional polyurethanes (PUs). PHUs are synthesized by reacting cyclic carbonates and amines in an atom-economical, catalyst-free route under relatively mild conditions avoiding the use of harmful isocyanates. Many of the cyclic carbonates are obtained from platform chemicals such as diols in combination with dimethyl carbonate or through the incorporation of CO₂ in epoxides, an environmentally important reaction. Such a large feedstock availability gives access to a library of cyclic carbonates and the opportunity to tailor PHUs depending on the properties sought. The formed pendent hydroxyl groups along the PHU backbone are sites available for subsequent reactions, yet their presence enhances the intramolecular H-bonding and limits the solubility of PHUs, which in turn hinders further post-polymerization modification or copolymerization. To approach this challenge and advance the utilization of PHUs towards more complex copolymer architectures, we utilized polymer-in-monomer solubility as a tool to synthesize graft copolymers from a tailor-made PHU. The design of the PHU structure enabled its solubility in ε-caprolactone (CL) at elevated temperature, creating ideal conditions for the graft ring-opening polymerization of CL from the pendent hydroxyl groups of the PHU. Structural characterization (¹H, DOSY, ³¹P NMR) of the PHU-graft-PCL copolymers proved the efficiency of the strategy as solely copolymers were formed, and all of the hydroxyl groups reacted. The molar mass of the grafted PCL chains was modulated simply by controlling the CL:OH ratio, impacting the thermal properties of the copolymers. Our strategy demonstrates that a simple approach can overcome common hurdles and provide intriguing opportunities to design sustainable polymers.
Degradable and thermally stable spiro polycycloacetals from renewable resources

Minjie Shen, Srikanth Vijjamari, Hongda Cao, Fahimeh Khakzad, Yanchun Tang, Karla Solis, Megan L. Robertson, mlrobertson@uh.edu. Chemical and Biomolecular Engineering, University of Houston System, Houston, Texas, United States

A series of partially bio-based spiro polycycloacetals were synthesized using bio-renewable feedstocks, such as vanillin and its derivative syringaldehyde, along with pentaerythritol and commercially available co-monomers including 4,4′-difluorobenzophenone and bis(4-fluorophenyl) sulfone. These spiro polycycloacetals displayed high thermal stabilities (degradation temperatures in the range of 343 – 370 °C, as quantified by 5% mass loss) and glass transition temperatures (in the range of 179 – 243 °C). Importantly, these polymers were effectively degraded to small molecules under acid-catalyzed hydrolytic conditions in less than 7 h. The kinetics of hydrolytic degradation was quantified through in situ NMR analyses.

Degradation Pathway of Sustainable Polyacetal
POLY – Circular Economy of Polymers

Effects of alkyl and phenyl substituents in ethylene glycol or 1,3-propanediol in binary copolyesters with 2,5-furandicarboxylic acid

Massoud J. Miri¹, mjmsch@rit.edu, Derek Lohmann², Daniel S. Honeycutt¹, Daniel Verrico¹, Alex J. North¹, Sara L. Cobb¹, William Charbonneau¹, Red O. Smith-Sweetser³. (1) School of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, New York, United States (2) Vice President of Sales & Business Development, PSS-USA Inc., Amherst, Massachusetts, United States

Polyesters with furan groups have become of interest because of the renewability of the sugar derived furan. A series of 17 diols were evaluated in the binary copolymerizations with the dimethylester of 2,5-furandicarboxylate. These include 1,3-propanediol, 2-alkyl-1,3-propanediols and 2,2-dialkyl-1,3-propanediols, whereby the alkyl groups were methyl, ethyl, propyl, and butyl. Another series was based on ethylene glycol and 1,2-alkanediols, in particular, 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol and 1,2-hexanediol. Furthermore, three monomers containing phenyl groups were applied: 2-phenyl-1,3-propanediol, 2,2-diphenyl-1,3-propanediol, and 1-phenyl-1,2-ethanediol. Both the conversion and molecular weight properties decreased with the aromatic substituents. The majority of these copolyesters is amorphous, and they have different solubilities in applied polar solvents. As determined by DSC, the length of the alkyl chains has an effect on T₉, and in case of the dialkyl-substituted 1,3-propanediols it is not following a monotonous trend. The T₉ values were relatively high with the 1,2-alkanediols and relatively low with the 2-alkyl-1,3-propanediols. By selecting a specifically substituted diol it is possible to tune the glass transition temperatures of these polyesters over a wide range. Molecular weight properties of the copolyesters were determined by gel permeation chromatography using hexafluoroisopropanol as solvent.
DSM Science & Technology Award: Bright Science Award for PhD Students
Judith Johanna Van Gorp, Organizer, Presider, DSM; Rolf Vanbenthem, Organizer, DSM
Materials Science Center; Craig Hawker, Presider, Univ of California; Ajay Padsalgikar, Presider; Ruud Rulkens, Presider, DSM
Session Type: Oral - Virtual
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Tuesday, 10:30am - 12:30pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 39
Architectural control in high performance sustainable aliphatic polyester block polymers
10:50am - 11:30am USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 39
Marc Hillmyer, Presenter, University of Minnesota

Molecular design of high performance ionenes and ionic liquid composites
11:30am - 12:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 39
Kathryn O'Harra, Presenter; Prof. Jason E. Bara, University of Alabama

Macromolecular building blocks in vitrimers
12:00pm - 12:30pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 39
Jacob Lessard, Presenter; Georg Scheutz; Kevin Stewart; Charles Easterling; Michael Sims; Rhys Hughes; Luis Garcia; Seung Sung; Kayla Lantz; Kyle Bentz; Scarlett Arencibia; Daniel Savin, University of Florida; Thomas Epps; Prof. Brent S Sumerlin, University of Florida

Tuesday, 02:00pm - 04:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42
From UHMwPE powder to the world strongest fiber: Dyneema®, a story on morphology and creep control
02:00pm - 02:30pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42
Dr. Gert De Cremer, Presenter, DSM Protective Materials; John Severn; Romain Berthoud; Martin Vlasblom; Tom Engels; Luigi Balzano

Catalyzed chemical synthesis of designer PHAs: Tuning function, microstructure, topology, and property of biodegradable polymers
02:30pm - 03:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42
Andrea H Westlie, Presenter, Colorado State University; Eugene Chen

Percolated aggregates in precise sulfophenylated polyethylenes: Pathways to facilitate proton and ion transport
03:00pm - 03:30pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42
Benjamin Paren, Presenter; Bryce Thurston; Manuel Maréchal; Arjun Kanthawar; Justin Kennemur; Mark Stevens; Dr. Amalie Frischknecht, Sandia National Laboratories; Karen Winey, University of Pennsylvania

Panel Discussion
03:30pm - 03:55pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42

Concluding Remarks
In this presentation I will cover our recent work in controlling the architecture and properties in aliphatic polyester block polymers. The typical ABA triblock copolymer architecture for thermoplastic elastomers has proven to be quite effective for the generation of mechanically robust and competitive materials using poly(methyl caprolactone) as the midblock and poly(L-lactide) as the glassy and semi-crystalline end blocks; the macromolecules in both blocks are industrially compostable and can be derived from annually renewable resources. We have expanded our approach to generate both star and graft block copolymers using these principal sustainable components. Both of these architectures have proven to be very effective in enhancing the properties in poly(styrene)-based block polymers. In the case of star polymer architectures, the ring-opening transesterification polymerization mechanism is quite conducive to the ready preparation of multi-arm compounds from polyol initiators. For graft polymers, we devised a new synthetic approach that allows for the controlled introduction of poly(L-lactide) grafts along a poly(methyl caprolactone) backbone. I will discuss our synthetic strategies, the characterization of these block polymers with more complicated architectures, and the resultant material properties.
Molecular design of high performance ionenes and ionic liquid composites

Kathryn E. O’Harra, keoharra@crimson.ua.edu, Jason E. Bara. Chemical and Biological Engineering, The University of Alabama System, Tuscaloosa, Alabama, United States

We have designed and developed a library of high-performance (HP) ionenes, or polymers which contain ionic groups along the main chain rather than as pendants. These materials merge functionality utilized in high-performance engineering polymers, structural features associated with leading gas separation media, and precisely spaced ionic segments. These ionenes incorporate imidazolium cations paired with delocalized molecular anions (i.e. Tf$_2$N), which are produced from established synthetic methods that impart great control over repeat unit complexity, functional group sequence, charge density, and regiochemistry. Through methodical variation of substituents, connectivity along the backbone, and the sequence of functional and ionic segments, we have expanded the opportunities for incorporating, distributing, and alternating structural features. These ionenes possess excellent thermal and mechanical properties, while the structural tailorability provides access to an array of interesting behaviors and architectures. These polymeric materials exhibit self-assembly and local structuring when impregnated with “free” imidazolium-based ionic liquids (IL) or functional ionic fillers, which contributes additional tunability and alters intramolecular interactions in the ionene matrix. These HP-ionenes and IL composites are thoroughly characterized to develop structure-property relationships and to elucidate the coordination between the dispersed, discrete additives and the polymeric ionene matrix. The applicability of these ionenes-IL composite systems is demonstrated by analyzing their performance as gas separation membranes, fibers, and 3D printing materials.
Macromolecular building blocks in vitrimers

Jacob J. Lessard¹, lessard@illinois.edu, Georg M. Scheutz¹, Kevin A. Stewart¹, Charles P. Easterling¹, Michael B. Sims¹, Rhys W. Hughes¹, Luis F. Garcia¹, Seung H. Sung², Kayla A. Lantz², Kyle C. Bentz¹, Scarlett Arencibia¹, Daniel A. Savin¹, Thomas H. Epps², Brent S. Sumerlin¹. (1) Chemistry, University of Florida, Gainesville, Florida, United States (2) Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States

The exploitation of defined polymer backbones was used to elucidate the roles of chain structure, topology, and functionality on the dynamic behavior of associatively crosslinked polymers, commonly referred to as vitrimers. While the field of covalent adaptable networks has highlighted the potential of exploiting dynamic-covalent bonds to prepare materials with characteristics of both thermosets and thermoplastics, expanding the vitrimer concept to existing commercially relevant polymers has obvious benefits. Our approach allows the chemical composition and physical properties of the materials to be tuned in a modular manner. Critically, this strategy decouples the network curing and polymerization steps, allowing for variation of polymer structure, topology, and functionality. The modularity of our approach creates a viable platform for elucidating fundamental structure-property relationships of vitrimers while also providing design principles for engineering vitrimers with unprecedented chemical and mechanical properties.
From UHMwPE powder to the world strongest fiber: Dyneema®, a story on morphology and creep control

Gert Cremer¹, gert.cremer-de@dsm.com, John Severn¹, Romain Berthoud¹, Martin Vlasblom¹, Tom Engels², Luigi Balzano². (1) DSM Protective Materials, Koninklijke DSM NV, Geleen, Limburg, Netherlands (2) Applied Science Center, Koninklijke DSM NV, Geleen, Limburg, Netherlands

Utilizing the chain of knowledge has been core to the discovery and continual development of the world strongest fiber, Dyneema®, which has allowed the humble polyethylene molecule to be used in (off-shore) mooring applications (see figure), for stopping bullets, in surgical sutures, protective clothing (see figure), and in many more challenging applications. Made from bio-based feedstocks, these fibers are now an important enabler of increased sustainability e.g. by reducing weight and increasing durability.

Key to the performance of the Dyneema® fibers is the control over molecular organization and orientation in the gel-spinning process, in order to achieve extraordinary strengths. Moreover, for permanent mooring applications (e.g., securing off-shore windmills, tethering tidal energy devices) in which the light-weight, high strength fibers of Dyneema® are put under a static load for extended periods of time, controlling creep behavior is the key to success.

This contribution focuses on the different aspects of minimizing creep behavior: catalyst research, synthesis of ultra-high molecular weight (UHMwPE), microstructure control, analytical technique development, processing of the powder into low-creep fibers, and application. We will demonstrate how this chain of knowledge has been exploited to increase our scientific understanding and innovation capability in order to extend the performance of this marvelous molecule and the fabulous fiber it forms.
Catalyzed chemical synthesis of designer PHAs: Tuning function, microstructure, topology, and property of biodegradable polymers

Andrea H. Westlie, awestlie@colostate.edu, Eugene Y. Chen. Chemistry, Colorado State University, Fort Collins, Colorado, United States

Despite the remarkable ability of polyhydroxyalkanoates (PHAs) to biodegrade in ambient environments, such microbiologically produced PHAs currently suffer from slow reaction kinetics, low production volume, and thus high production cost of their biosynthetic pathways. In addition, microbial PHAs typically exhibit inferior thermal and mechanical properties compared to today's commodity plastics. Recognizing the advantages of the catalyzed ring-opening polymerization (ROP) for its fast chain-growth kinetics to produce condensation polymers with facile tunability and scalability, we have developed the catalyzed chemical synthesis of PHAs by the ROP of eight-membered diolides to address the above critical challenges. Replacing the aliphatic side-chain groups with aromatic ones, for example, renders the glass-transition and degradation temperatures to record high values. Synthetic random PHA copolymers resulted from methyl, ethyl, and n-butyl substituted diolides exhibit mechanical properties similar to those of polyethylene and polypropylene. The synthesis of well-defined stereoregular triblock PHA copolymers, accessible only by the catalyzed chemical route with high precision and control, has also been accomplished, creating novel target designer PHAs with new microstructures, topologies, and thus properties beyond what can be achieved by microbes today.
Percolated aggregates in precise sulfophenylated polyethylenes: Pathways to facilitate proton and ion transport

Benjamin Paren\(^1\), bparen@seas.upenn.edu, Bryce Thurston\(^2\), Manuel Maréchal\(^{4,5}\), Arjun Kanthawar\(^1\), Justin G. Kennemur\(^3\), Mark J. Stevens\(^2\), Amalie L. Frischknecht\(^2\), Karen I. Winey\(^1\). (1) University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Sandia National Laboratories, Albuquerque, New Mexico, United States (3) Florida State University, Tallahassee, Florida, United States (4) Centre National de la Recherche Scientifique, Grenoble, Île-de-France, France (5) University of Grenoble Alpes, Grenoble, France

We present a set of precise, ring-opening polymerized, single-ion conducting polymers that self-assemble into percolated aggregates which serve as pathways for rapid proton conductivity in the hydrated state (proton exchange membrane), or anhydrous decoupled ion transport of metal cations (solid polymer electrolyte). These polymers consist of a polyethylene backbone with a sulfonated phenyl group pendant on every 5\(^{th}\) carbon. We study this polymer in the pure acid form (p5PhSA) under hydrated conditions and fully neutralized by different counterions (p5PhSA-X, X\(^+=\)Li\(^+\), Na\(^+\), or Cs\(^+\)) in anhydrous conditions, using X-ray scattering, electrical impedance spectroscopy, and atomistic molecular dynamics (MD). In hydrated p5PhSA, the polymer backbone nanophase separates from the percolated acid/water domain, through which the protons travel. p5PhSA has proton conductivity of 0.28 S/cm at 40°C and 95% relative humidity, exceeding that of Nafion. The dry p5PhSA-X polymers form fully percolated ionic aggregates, and have metal cation transport decoupled from the glassy polymer backbone up to at least 180°C. This behavior, only possible due to the percolated nature of p5PhSA (-X), demonstrates the potential of precise polymers to effectively form pathways for facilitating transport.
Fourth CME NASA Symposium: Chemistry for Resilient Human Space Exploration

Dr. Michael A Meador, Organizer, Meador Aerospace Materials Group, LLC; Prof Robert Nolan, Organizer, The City University of New York; George Rodriguez, Organizer; Ksenia Takhistova, Organizer, Presider, CME; Jonathan Rall, Presider; Dr. Michael A Meador, Organizer, Presider, Meador Aerospace Materials Group, LLC; Mary Kirchhoff, Presider, American Chemical Society

Session Type: Oral - Hybrid
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Monday, 08:00am - 10:00am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314

Ladder of life detection
08:01am - 08:30am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Dr. Mary E Voytek, Presenter, NASA Headquarters; Michael New

Searching for life on ocean worlds
08:30am - 09:00am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Mark Nevau, Presenter

Nitrogen and habitability on Mars: Insights from missions, meteorites, and terrestrial analogs
09:00am - 09:30am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Dr. Jennifer C Stern, Presenter, NASA

NASA composites technology: A chronicle
09:30am - 10:00am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Mr. John Vickers, Presenter, NASA

Monday, 10:30am - 12:30pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314

Fundamental understanding and optimization of long-range orders in CNT assemblages for high-performance structural composite applications
10:30am - 11:00am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Richard Liang, Presenter, Florida State University

Light as a selection pressure in photochemical “directed evolution”
11:00am - 11:30am USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Prof. Julia Kalow, Presenter, Northwestern University

Withdrawn

HEMAfoam: A novel foaming resin expands applications for lithographic 3D printing
12:00pm - 12:30pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
David M Wirth, Presenter, UCSD; Anna Jaquez; Sofia Gandarilla; Justin Hochberg; Derek Church; Jonathan Pokorski

Monday, 02:00pm - 04:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314

Overview of additive manufacturing and in space manufacturing at NASA
02:00pm - 02:30pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Mr. John Vickers, Presenter, NASA

In space manufacturing of point-of-care diagnostic devices
02:30pm - 03:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Dr. Jessica Koehne, Ph.D., Presenter, NASA Ames Research Center

PMSE CME STUDENT & MENTOR AWARDS PRESENTATION
03:00pm - 03:01pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314
Two dimensional polymers and their applications  
03:01pm - 03:30pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314  
Dr. Austin M. Evans, Presenter, Columbia University

Synthesis supramolecular polymerization of nanotubes based on protonation induced assembly of macrocycles  
03:30pm - 04:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314  
Prof William Dichtel, Presenter, Northwestern University

Monday, 04:30pm - 06:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314

The road to intrinsically dynamic materials: Disulfide chemistry as a solution  
04:30pm - 05:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314  
Dr. Qi Zhang, Presenter, University of Groningen

Dynamic assembling for smart materials  
05:00pm - 05:30pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314  
He Tian, Presenter, East China University of Sci. & Technology

Molecular motors for responsive materials  
05:30pm - 06:00pm USA / Canada - Eastern - August 23, 2021 | Room: A313-A314  
Ben L Feringa, Presenter, University of Groningen

Tuesday, 08:00am - 10:00am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314

What can chemistry do to enable the next great leap in space science?  
08:01am - 08:15am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314  
Jonathan Arenberg, Presenter

ISS national lab and in space production applications  
08:15am - 08:30am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314  
Dr. Kenneth Allen Savin, Presenter, CASIS

Polymers for a resilient future  
08:30am - 08:45am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314  
Anne Shim, Presenter

Performance assessment and flight heritage of carbon nanotube based thermal interface  
08:45am - 09:00am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314  
Dr. Craig Green, Ph. D, Presenter, Carbice Corporation

Industry panel on applications for advanced materials, energy and systems  
09:00am - 10:00am USA / Canada - Eastern - August 24, 2021 | Room: A313-A314

Tuesday, 10:30am - 12:30pm USA / Canada - Eastern - August 24, 2021 | Room: A311-A312

Advances in conversion type electrodes for lightweight batteries  
10:30am - 10:45am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312  
Dr. Gleb Yushin, Presenter, Georgia Institute of Technology

Potential roles of graphene composites and metamaterials in human space exploration  
10:45am - 11:00am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312  
Dr. Thomas M Orlando, Ph.D., Presenter, Georgia Institute of Technology

Electrochemical capture and conversion of carbon dioxide into all carbon nanostructures  
11:00am - 11:15am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312  
Dr. Anna Douglas, PhD, Presenter, SkyNano Materials innovation for now and tomorrow at DuPont  
11:15am - 11:30am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312  
Dr. Marty W DeGroot, PhD, Presenter, DuPont; Cathie Markham

Panel Discussion
Shaping a new era of space exploration with perseverance, ingenuity, and resiliency  
02:00pm - 02:25pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
Dr. James L. Green, Presenter

Enabling sustainability through transformational change  
02:25pm - 02:45pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
Amy Chronis, Presenter

Formulating climate change solutions under deep uncertainty  
02:45pm - 03:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
Judith Curry, Presenter

Creating localized carbon reduction strategies  
03:00pm - 03:15pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
Dr. Marilyn Brown, Regents Professor, Presenter, Georgia Tech

Panel: Creating resilient approaches to climate change  
03:15pm - 03:50pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
George Rodriguez, Presenter, Argeni; Judith Curry, Presenter; Marilyn Brown, Presenter

CME lectures and awards introduction  
03:50pm - 04:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 50  
George Rodriguez, Presenter, Argeni

Tuesday, 04:30pm - 06:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42

Withdrawn

Exploring catalytic space  
05:00pm - 05:30pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42  
Ben L. Feringa, Presenter, University of Groningen

4th CME NASA Symposium: Summary, Reception, Instructions, Adjournment  
05:30pm - 06:00pm USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 42  
Dr. James L. Green, Presenter; Ksenia Takhistova, Presenter, CME; George Rodriguez, Presenter, Argeni
Introduction to the fourth CME NASA symposium

Jonathan Rall, jonathan.rall@nasa.gov, Michael A. Meador, michael-meador@sbcglobal.net. NASA, Washington, District of Columbia, United States

POLY in the proud sponsor of the Fourth CME NASA Symposium which Brings Together Industry, Academia, Government and the Public to Enlarge and Enhance the STEM Talent Pool. The goal is to propel cutting-edge developments in chemical sciences to advance human space travel and translate them into new knowledge to improve the lives of people and make their dreams a reality. Join us for these two days packed with inspirational research, industry advances and job trends.
Ladder of life detection

Mary Voytek, mary.voytek-1@nasa.gov, Michael New. NASA, Washington, District of Columbia, United States

The talk will describe the history and features of the Ladder of Life Detection, a tool intended to guide the design of investigations to detect microbial life within the practical constraints of robotic space missions. To build the Ladder, we have drawn from lessons learned from previous attempts at detecting life and derived criteria for a measurement (or suite of measurements) to constitute convincing evidence for indigenous life. We summarize features of life as we know it, how specific they are to life, and how they can be measured, and sort these features in a general sense based on their likelihood of indicating life. Because indigenous life is the hypothesis of last resort in interpreting life-detection measurements, we propose a small but expandable set of decision rules determining whether the abiotic hypothesis is disproved. In light of these rules, we evaluate past and upcoming attempts at life detection. The Ladder of Life Detection is not intended to endorse specific biosignatures or instruments for life-detection measurements, and is by no means a definitive, final product. It is intended as a starting point to stimulate discussion, debate, and further research on the characteristics of life, what constitutes a biosignature, and the means to measure them.

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<tr>
<th>CRITERIA</th>
<th>EXPLANATION</th>
<th>EXAMPLES / NOTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitive</td>
<td>Signal for feature of life selectively quantified above instrumental limit of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>quantification, within response time and dynamic range</td>
<td>Encompasses all quantitative measures of instrumental performance (Amsbeker &amp; Py</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2008)</td>
</tr>
<tr>
<td>Contamination-free</td>
<td>Signal for feature of life not selectively detected (below instrumental LoD)</td>
<td>“Below LoD” implies signal indistinguishable from noise given instrument sensitivity</td>
</tr>
<tr>
<td></td>
<td>in abiotic samples</td>
<td>and stability (Amsbeker &amp; Py 2008)</td>
</tr>
<tr>
<td></td>
<td>Distinguish indigenous signals from contamination signals arising from:</td>
<td>• Hardware</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Other samples (cross-contamination)</td>
</tr>
<tr>
<td>Repeatable</td>
<td>No. 3 measurements is the typical burden of proof in microbiology and chemistry, also depends on other factors (Table 2)</td>
<td>N measurements per sample, for as many samples as needed to capture the heterogeneity of the setting</td>
</tr>
<tr>
<td>Detectable</td>
<td>Physical, chemical, or geological conditions in the sample’s current environment do not prevent the measurement from being made</td>
<td>• Reaction of organisms with solvent upon heating</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Vatization suppression by salts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Some antibody methods in “sticky” briny liquid</td>
</tr>
<tr>
<td>Survivable</td>
<td>Physical, chemical, or geological conditions in the suite of environments encountered by the sample between its synthesis and its measurement have not destroyed targeted signs of life</td>
<td>• Photo-destruction of biosignature gasses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Radicals of organics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Renaturation</td>
</tr>
<tr>
<td>Reliable</td>
<td>Propensity to be produced by life and distinguished from abiotic backgrounds from any of the environments encountered by the sample between its synthesis and its measurement</td>
<td>Test from Hohler (2017); N = 1 to a few units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{[\text{bio}]}{[\text{bio}]-[\text{abio}]} &gt; $ Instrument precision</td>
</tr>
<tr>
<td>Compatible</td>
<td>The feature must not be excessively different from what is known of life on Earth (specificity vs. generality). Limits can be pushed within bounds.</td>
<td>• Organic molecules, carbon-based (this would include e.g. proposed “snoe-OH” (Wolfe-Simon et al., 2011)).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Temperature not too high. Prices survive combustion at 600°C (Brown et al. 2004).</td>
</tr>
<tr>
<td>Last-resort hypothesis</td>
<td>The measurement, either alone or taken together with sufficient complementary measurements, precludes an abiotic origin with sufficiently little ambiguity.</td>
<td>Not just an appeal to authority (Sagan et al., 1993); as this criterion has been informally adopted by the astrobiology community as a standard.</td>
</tr>
</tbody>
</table>
Searching for life on ocean worlds

Mark Nevau, Presenter

Several icy moons of the giant planets harbor subsurface oceans. At least one has a chemistry (pH, major elements, redox gradients, simple and macromolecular organic compounds) similar to inhabited places in our ocean. Progress in approaches to searching for life is being infused into ocean moon missions designed to discover either life beyond Earth or the first habitat where life is unseen.
Nitrogen and habitability on Mars: Insights from missions, meteorites, and terrestrial analogs

Dr. Jennifer C Stern, Presenter, NASA

Life on Earth evolved metabolic pathways to fix atmospheric nitrogen to more biochemically available molecules for use in proteins and informational polymers. For this reason, “Follow the nitrogen” has been proposed as a strategy in the search for life on Mars. We discuss detections of fixed nitrogen on Mars by the Mars Science Laboratory (MSL) Curiosity Rover, recent evidence of nitrogen bearing compounds in Martian meteorites, and nitrogen systematics in terrestrial analogs to illuminate the role of nitrogen in the habitability on Mars.
Advancements in composites materials and manufacturing supports the future of space exploration as well as national competitiveness needs. NASA research and development efforts in composites materials over the past 25 years has been well integrated across the TRL spectrum. NASA is seeking to take advantage of spacecraft applications that would benefit from substantial weight savings and important cost savings compared to traditional state of the art materials. This presentation examines past and present NASA R&D efforts, together with the technical and cultural barriers, and future directions of research and innovation.
This presentation examines our research towards engineering CNT networks to realize high mechanical and electrical performance. We discovered the unique geometrically constrained self-assembling and graphitic crystal packing of flattened and aligned CNTs during the stretching process of CNT networks. The new microstructures can improve the ultimate surface contact among the CNTs to substantially improve load transfer and mechanical properties. This feature provides the potential to realize microstructures capable of achieving desired long-range orders, fewer defects, and ordered crystalline packing, which are essential for fully transferring the CNT mechanical and electrical properties into macroscopic composite materials. Figure 1 shows an example of CNT self-assembling in a stretched CNT network.
Light as a selection pressure in photochemical “directed evolution”

Julia A. Kalow, jkalow@northwestern.edu. Northwestern University, Evanston, Illinois, United States

The evolving demands of the modern world call for new materials with advanced performance and minimal environmental footprint. As the structural complexity of these materials increases, the traditional iterative approach to synthesis, testing, and optimization becomes prohibitively time consuming and labor intensive. Here, I will present an abiotic approach to the discovery of new organic materials inspired by directed evolution. The key advance that makes this approach possible is the discovery of reaction mechanisms that link a stimulus (light) to the target (photophysical) properties.
HEMAfoam: A novel foaming resin expands applications for lithographic 3D printing

David M. Wirth, dwirth@ucsd.edu, Anna Jaquez, Sofia Gandarilla, Justin Hochberg, Derek Church, Jonathan K. Pokorski. NanoEngineering, University of California San Diego, La Jolla, California, United States

An ordinary commercial MSLA printer can be harnessed to create a large scale foam manufacturing platform using our novel highly expandable foaming resin. This unique formulation allows for isotropic expansion of printed parts up to 40x (by volume), digital control over density, porosity and cell morphology. Our process represents nearly 2 orders of magnitude improvement over the prior art, and can be accomplished using a low-cost system (under $300) with a simple, commercially available chemical formulation. Our process allows for the fabrication of structures significantly larger than the build volume of the 3D printer which produced them. Complex geometries such as Voronoi structures, functional airfoils, and floatation aids composed of porous foams are presented with videos of their fabrication and testing. The potential applications for our system include architecture, aerospace, energy, and biomedicine. Screening and characterization of resin formulations, print parameters, observed mechanical properties, and resultant foam structure of the printed and expanded foam objects is presented as well.
Overview of additive manufacturing and in space manufacturing at NASA

John Vickers, john.h.vickers@nasa.gov. NASA Huntsville, Huntsville, Alabama, United States

NASA is rapidly advancing additive manufacturing technology to support NASA missions in space exploration, science, aeronautics, and technology, as well as the aerospace industry, other Government Agencies, and to address related national needs. NASA performs this work at NASA Centers, through contracts/grants and in public private partnerships. NASA’s focus is generally on applied research and development activities where substantial enhancements in NASA mission capabilities are needed. NASA has extensive experience in additive manufacturing technologies with involvement in more than 30 different machine systems in the past 30 years. NASA is taking a lead role in areas specific to NASA missions such as propulsion and in-space manufacturing and not trying to lead in all AM technology areas. NASA’s in-space manufacturing objective is to identify and implement on-demand manufacturing solutions for fabrication, maintenance, and repair required for sustainable Exploration Missions. The Agency portfolio spans a range of mission applications and discipline areas such as computational modeling, design, materials, processes and certification across technology readiness levels/manufacturing readiness levels (TRLs/MRLs).
Miniaturized biosensing devices for point-of-care diagnostics are of upmost importance to ensuring astronaut crew health and safety. As human space missions extend to longer durations, sensor resupply will not be a viable option. By relying on additive manufacturing and simple printing technology, biosensors can be fabricated in space, thus enabling adaptive crew health monitoring on long-duration space missions and habitation. Here we report a generic electrochemical biosensor platform that can be fabricated using a single printer and will require minimal crew time to operate. Functional inks manufactured from carbon nanotubes, gold nanoparticles and silver nanoparticles were used to print a 3-electrode electrochemical device. Biosensor devices were fabricated on both paper and Kapton substrates by either a piezo drop-on-demand inkjet printer and an atmospheric pressure plasma jet printer. The working electrodes were functionalized with both aptamer and antibody probes specific to troponin-I and cortisol. Sensor performance was characterized by cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy. The results demonstrate that these biosensors can serve a miniaturized, low cost, point-of-care devices for detection of proteins, hormones and other small biomolecules. In the future, these biosensor devices will be fabricated and characterized on the International Space Station and the approach will be evaluated for future in-space manufacturing of point-of-care diagnostic devices.
Two-dimensional polymers (2DPs) are a unique macromolecular architecture that combine covalent connectivity, permanent porosity, and structural regularity. Recently, synthetic advances have led to the production of 2DPs as single-crystals and high-quality films, both of which are ideal for property and device measurements. Here, I will discuss recent findings regarding the thermal, mechanical, optical, and electronic properties of macromolecular sheets. I will also describe first-generation 2DP-based devices, which show promising combinations of behaviors not accessible with other material classes.
Synthesis supramolecular polymerization of nanotubes based on protonation induced assembly of macrocycles

William R. Dichtel, wdichtel@northwestern.edu. Northwestern University, Evanston, Illinois, United States

Macrocycles that assemble into nanotubes exhibit emergent properties stemming from their low dimensionality, structural regularity, and distinct interior environments. I will present a versatile strategy to synthesize diverse nanotube structures in a single, efficient reaction by using a conserved building block bearing a pyridine ring. Imine condensation of a 2,4,6-triphenylpyridine-based diamine with various aromatic dialdehydes yields chemically distinct pentagonal [5+5], hexagonal [3+3], and diamond-shaped [2+2] macrocycles depending on the substitution pattern of the aromatic dialdehyde monomer. Modifying these macrocycles to achieve emergent mechanical and transport properties will also be discussed.
The road to intrinsically dynamic materials: Disulfide chemistry as a solution

Qi Zhang, qi.zhang@rug.nl. Rijksuniversiteit Groningen, Groningen, Groningen, Netherlands

Understanding dynamic chemistry systems in Nature inspires chemists to design biomimetic synthetic materials. Disulfide bonds, the bonds that tie peptides, feature their dynamic covalent nature, that is reversible covalent bonds. Here we propose that making polymers with disulfide bonds can be a solution towards intrinsically dynamic materials. Unlike traditional plastics and noncovalent (supramolecular) polymers, poly(disulfides) can simultaneously exhibit chemical recycling ability and excellent mechanical performances. We will focus on the poly(disulfides) derived from thiocystic acid, a natural small molecule, to show the promising applications of these intrinsically dynamic materials in self-healing elastomers, adhesives, and actuators.
Dynamic assembling for smart materials

He Tian, tianhe@ecust.edu.cn. East China University of Science and Technology School of Chemistry and Molecular Engineering, Shanghai, China

Molecular machine and its related multi-level dynamic assemblies have been one of the trending topics for designing smart materials in chemical approaches. A more recent strategy to develop smart materials with excellent stimuli-responsiveness, dynamic reversibility, self-healing ability as well as self-adaptability is to build molecular elements into a multi-level assembly via dynamic covalent and non-covalent interactions. Recently, our group have successfully developed some dynamic smart materials based on dynamic covalent/non-covalent bonding, referring as some representative examples for this multi-level assembly approach. Moreover, one of the key principles for future green chemistry and designing sustainable materials is replacing conventional covalent interactions with non-covalent ones in the synthesis of functional materials. However, what are the dual effects of incorporating covalent interactions with non-covalent interactions in material design and synthesis? Is it feasible for recycling dynamic reversible polymers in a close-looped manner? Several important but challenging questions are yet to be addressed, e.g. how to achieve selective depolymerization, solvent-free synthesis and recycling reusable monomers.
Molecular motors for responsive materials

Ben L Feringa, B.L.Feringa@rug.nl. Rijksuniversiteit Groningen, Groningen, Groningen, Netherlands

The fascinating molecular motors and machines that sustain life offer a great source of inspiration to the molecular explorer at the nanoscale. The focus is on the dynamics of functional molecular systems as well as triggering and assembly processes. We design motors in which molecular motion is coupled to specific functions. Responsive behavior will be illustrated in self-assembly and responsive materials with a focus on cooperative action, amplification along multiple length scales and 2D and 3D organized systems. The design, synthesis and functioning of rotary molecular motors and machines will also be presented with a prospect toward future responsive materials.
What can chemistry do to enable the next great leap in space science?

Jonathan Arenberg, jon.arenberg@ngc.com. Chief Mission Architect, Science and Robotic Missions, Northrop Grumman Aerospace Systems, Redondo Beach, California, United States

The space sciences are technologically limited. Many of the technical limitations on system performance lie in the properties of the materials the instruments and systems consist of. These properties have their roots in the chemistry. We will review some recent advances in space science and show how chemistry played both an enabling and limiting role. Understanding the limitations enables us to formulate critical questions that can be addressed by chemistry and when answered will help power the next great leap in space science.
Access to the microgravity environment of low Earth orbit offers industry production opportunities not possible terrestrially. This presentation will focus on ISS National Lab efforts around in-space production, manufacturing processes, and intellectual-property generation that enable new business growth and represent markets that could generate revenue from access to space. This is a unique opportunity to keep up with the production and IP opportunities for advanced products and pharmaceuticals. Examples of organizations that have partnered to support advanced materials or physical science investigations on the ISS National Lab are:

National Science Foundation
Adidas
Goodyear Tires
Delta Faucet
Made In Space/Redwire Space
Eli Lilly & Company
Merck
Hewlett Packard Enterprise
Lamborghini
Cobra Puma Golf
Lockheed Martin
Nickelodeon
At BASF, one of the leading chemical companies, we are constantly developing novel materials and enhancing existing materials to meet the needs of our customers. This talk will give a brief overview of BASF and how we address the challenge of resiliency in polymers for everyday use.
Performance assessment and flight heritage of carbon nanotube based thermal interface

Craig Green, craig.green@carbice.com. Carbice, Atlanta, Georgia, United States

While greater functionality in the current generation of spacecraft has increased heat dissipation, thermal design in these systems is driven by design constraints that extend beyond the requirements of terrestrial applications. Effective spacecraft thermal design must account for the combined needs for simple and cost effective integration of large complex systems, along with the need to operate reliably and predictably in harsh environments for extended mission times without maintenance. We present a suite of space qualified thermal interfacing solutions based on a platform of polymer encapsulated vertically aligned carbon nanotube arrays all covalently anchored to an aluminum foil substrate.

The Carbice Carbon® Nanotube Array

The Carbice Carbon® nanotube matrix is a UNIQUE material!
It is not like ANY other Thermal Interface Material
The thermal and mechanical properties of the matrix allows it to flow like a liquid – while being a dry pad...
Industry panel on applications for advanced materials, energy and systems

Tara Ruttley2, tara.m.ruttley@nasa.gov, Ksenia Takhirsova1, ktakhist@gmail.com. (1) CME - Chemical Marketing & Economics, Branchburg, New Jersey, United States (2) NASA, Washington, District of Columbia, United States

Leaders from CME and NASA will co-moderate industry panel for Advanced Materials, Energy and Systems
Advances in conversion type electrodes for lightweight batteries

Gleb Yushin, yushin@gatech.edu. Sila Nanotechnologies, Alameda, California, United States

Specific energy density of Li-ion batteries based on intercalation compounds are closely approaching their limits. Conversion-type active materials offer an opportunity to triple specific energy, reduce their cost, and improve cell safety. These materials may be produced from safer, cheaper, and globally available resources and contribute to accelerated adoption of electric transportation. This talk will focus on the latest developments of both active and inactive (supporting) battery components.
Potential roles of graphene composites and metamaterials in human space exploration

Thomas M. Orlando, thomas.orlando@chemistry.gatech.edu. Georgia Institute of Technology, Atlanta, Georgia, United States

Human exploration of the Moon requires strong light-weight materials with exceptionally high thermal and electrical conductivities. Polymer composites utilizing reduced graphite/graphene-oxide rGO have been developed as potential space-suit laminates. These coatings have 10 ohm per square sheet resistances; sufficient to provide static discharge paths for dust mitigation. The graphene field-effect transistor platform has also been used to develop radiation-sensitive metamaterials. Using CVD graphene transfer, electron beam lithography, and various fabrication methods, two neutron-series prototypes detectors have been developed. Ultimately, these will be integrated into space-suit material and interfaced with helmet displays for real time active dosimetry during extravehicular activity.
Despite over 37,000,000,000 metric tons of CO$_2$ being released into the atmosphere each year, the cost and practicality of carbon capture and conversion hinges on the ability to produce products from CO$_2$ that have a market value greater than the cost of production (including the cost of both carbon capture and conversion). To date, there are very few, if any, economic cases that can be made for existing technologies without assumptions of generous free electricity or significant carbon tax credits. SkyNano has developed a technology that relies on the electrochemical capture and conversion of CO$_2$ into all-carbon nanomaterials mediated by molten carbonate salts.
DuPont materials have long been at the forefront of the world’s most significant technology challenges. New applications require materials that provide reliable and sustainable solutions for the most demanding applications. These range from materials robust enough for the rigors of space exploration, to those required to enable sub-5 nm circuits, 5G communications, and autonomous vehicles. This talk will summarize some of the key innovation challenges at the leading edge of these and other applications, with an emphasis on reliability and sustainability as key components of product design, enabled by chemistry, to ensure our planet and people continue to thrive.
People all over the world were elated by the success of humanity's most daring mission to the Red Planet to date: the landing of the Perseverance rover and the Ingenuity helicopter. Ingenuity is the first aerial vehicle to conduct remote and autonomous research and exploration starting at a distance of over 60 million km from Earth. Find out the extraordinary initial research results on the search for life on Mars and what is next at NASA for industry partnering and find out how you may help in supporting human exploration beyond low Earth orbit.
Sustainability is a global societal and business challenge facing all industries. As the global population nears nine billion people, Earth's resources will continue to be strained, and global waste will increase. Finding innovative solutions and policies to solve for the many dimensions of sustainability will take an ecosystem of partners, with the chemical industry uniquely positioned to lead the efforts. In this presentation, Duane will discuss how the chemical industry can address the challenges of waste, pollution, and toxicity. He will share how materials technology will provide solutions for energy generation, storage, and purification. Duane will focus on (1) how carbon footprint mitigation technologies can support a differentiated model for chemical capacity, production, and operations to contribute to a cleaner and more sustainable environment, and (2) how digital technologies can be the catalyst for driving a sustainable agenda, positioning the chemical industry for long-term success.
World leaders have made a forceful statement that climate change is the greatest challenge facing humanity in the 21st century. However, there is a wide gap between ambition and implementation of policies to address climate change. Oversimplification of the climate change problem and its solution have resulted in a political stalemate. Understanding the many dimensions of uncertainty surrounding the climate change problem helps us to better assess the risks. A framework is presented for a 'Plan B' to strategize on how we can formulate pragmatic solutions for responding to climate change while improving human well-being.

Climate sensitivity to doubling of CO₂
factor of 3-6 uncertainty
Localized carbon-reduction strategies are especially critical in states and regions that lack top-down climate leadership. This paper illustrates the use of coupled systems in assessing subnational climate solutions with a case study of the state of Georgia. The paper illustrates how robust place-specific plans for climate action can be derived from foundational global and national work and by embedding that research into the context of socio-ecological-technological systems. Our replicable methodology advances the traditional additive sectoral wedge analysis of carbon abatement potential by incorporating solution interdependencies and by spanning both carbon sources and sinks. The solutions are affiliated with an array of social co-costs and co-benefits that highlight societal concerns extending beyond climate impacts, including public health, environmental quality, employment, and equity.
Climate change has become one of the most prominent topics of this century. Two notable figures in the field of sustainable systems and climatology will share their insights on how the central theme of this ACS national meeting--resiliency of science--calls for a practical multidisciplinary and systemic approach to develop resilient frameworks for the most efficient use of resources to deal effectively with the colossal challenges of global climate. This is a unique opportunity to join the conversation about the latest information on the technologies, systems, social impact and the future of climate change by interacting directly with two renowned thought leaders.
POLY – Fourth CME NASA Symposia

CME lectures and awards introduction

George L. Rodriguez, cmewebcast@gmail.com. CME--Chemical Marketing & Economics, Branchburg, New Jersey, United States

This exciting session will feature Nobel Laureates Ben Feringa (U. Groningen) and Robert Grubbs (Caltech) and two eminent figures in climate change, Judith Curry, and system sustainability, Marilyn Brown. In 2019 this session included Nobel Laureates Frances Arnold and Eric Betzig.
Transition metal catalysts continue to be at the frontier in the search for novel reactivity and synthetic methodology. Controlling chemo- and stereo-selectivity and low E-factor methods offer major challenges while novel approaches toward dynamic functions controlled by catalysis. In this lecture various approaches to address these challenges will be discussed. Specific topics are Murahashi-Feringa cross coupling with organolithium reagents, sustainable low-E-factor transformations and adaptive chiral catalysts. In addition, a green route to novel industrial coatings using photocatalytic oxidation as a key transformation will be presented.
General Topics: New Synthesis & Characterization of Polymers
Dana Garcia, Organizer, Arkema inc; Ferenc Horkay, Organizer, National Institutes of Health; Yongfu Li, Organizer, Dow Chemical Company; Mary Kirchhoff, Presider, American Chemical Society; Kevin McCue, Presider, American Chemical Society
Session Type: Oral - In-person

Sunday, 04:30pm - 06:30pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314

Enhanced aminolysis of cyclic carbonates by \(\beta\)-hydroxyamines for the production of fully biobased polyhydroxyurethanes
04:30pm - 04:50pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Baptiste Quienne, Presenter, Institut Charles Gerhardt de Montpellier; Rinaldo Poli; Julien Pinaud; Sylvain Caillol

Poly(ethylene-co-propylene) grafted silica nanoparticles prepared via surface initiated RAFT polymerization
04:50pm - 05:10pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Richard Ly, Presenter; Brian Benicewicz

New class of imidazolium based polymeric ionic liquids for gas separation membranes
05:10pm - 05:30pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Sudhir Ravula, Presenter, The University of Alabama System; Kathryn O’Harra; Prof. Jason E. Bara, University of Alabama

Aqueous self-assembly of ABA triblock bottlebrush copolymers
05:30pm - 05:50pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Logan Dugas, Presenter; Cheyenne Liu; Robson Storey; Prof. Yoan C Simon, The University of Southern Mississippi

Withdrawn

Accelerating the development of new polymeric materials: The convergance of automated experimentation, cloud computing, and predictive modeling
06:10pm - 06:30pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Nathan Park, Presenter; Pedro Arrechea; Tim Erdmann; J Hedrick, IBM Research; Dmitry Zubarev

POSTER – IN PERSON
Sunday, 07:00pm - 09:00pm USA/Canada-Eastern-August 22, 2021 | Room: B2 EXHIBIT HALL

Investigating the effects of phase separation on morphology and properties of PEEK aerogels
Glenn Spiering, Presenter; Garrett Godshall; Alexander Hutchins; Emily Trotto; Kalista McCoy; Joong Lee; Robert Moore
Withdrawn

Sustainable polymers: A more efficient synthesis of the monomer dihydrocarvide
Mackenzie Claypool, Presenter; Chris Schaller

Chemical synthesis of silk inspired polymer
Kayla Mancini, Presenter; Amrita Sarkar
Withdrawn

Synthesis of biobased phenol-formaldehyde wood adhesives from biorefinery derived lignocellulosic biomass
Archana Bansode, Presenter; Maria Auad, Auburn University

Open air synthesis of oligo(ethylene glycol)-functionalized polypeptides from non-purified N-carboxyanhydrides
Zhengzhong Tan, Presenter; Jianjun Cheng

Polymerization of organometallic sandwich monomers using organic catalysts
Kjersti Oberle, Presenter; Christopher Turlington, Presenter, Hope College
Withdrawn
Withdrawn
Withdrawn
Synthesis and characterization of polyaryl ethers containing hexafluoroisopropylidene enchainment via direct Friedel-Crafts polymerization of diaryl ethers and hxafluoroacetone hydrate
Gustavo Munoz, Presenter; Sumudu Athukorale; Charles Pittman; Dennis Smith

Friedel-Crafts polycondensation of diphenyl ether and commercial diacyl chloride monomers toward Versatile polyetherketoneketones (PEKKs)
Alison Duckworth, Presenter; Gustavo Munoz; Charles Pittman; Dennis Smith
Division: [POLY] Division of Polymer Chemistry

Synthesis of new diketopyrrolopyrrole scaffolds for the formation of novel donor-acceptor and n-type semiconductors
Ranganath Wahalathantrige Don, Presenter; Colleen Scott

Tuesday, 04:30pm - 06:30pm USA / Canada - Eastern - August 24, 2021 | Room: A313-A314
Withdrawn

Recent advancements in gel state functionalization of PEEK
Christopher Kasprzak, Presenter; Lindsey Anderson; Robert Moore

Non-contact measurement of deflection of conductive polymer actuators in liquids using smartphone camera
Najathulla Bhagavathi Chalil, Presenter; Mudrika Khandelwal; Atul Deshpande

Withdrawn

Aluminum-based initiators for copolymerization of propylene sulfide and epoxide with controlled architecture
Ms. Niloofar Safaie, Presenter, Michigan state university; Danielle Dejonge; Jessica smak; Shiwang Cheng; Robert Ferrier Jr.

Depolymerizable polymeric micelles for the release of H2S via COS
Sarah Swilley-Sanchez, Presenter, Virginia Polytechnic Institute and State University; Chad Powell; John Matson, Virginia Tech

POSTER - VIRTUAL
Tuesday, 07:00pm - 09:00pm USA / Canada - Eastern - August 24, 2021 | Room: Row 17

Adding transient bonds into hyperelastic models
Camaryn Bennett, Presenter; Dominik Konkolewicz; Dhriti Nepal; Ali reza Sarvestani; Leilah Petit

Predicting the electrospinnability of polymer solutions using tubeless siphoning
Taslim Ur Rashid, Presenter; Wendy Krause; Russell Gorga
Synthesis and applications of structurally well-defined functionalized polyolefins
Mateusz Malus, Presenter; Jakub Kruszynski, Presenter; Miloud Bouyahyi; Nydia Badillo; Maciej Sienkiewicz; Lidia Jasinska-Walc; Rob Duchateau

Hyperbranched polymers increase the stimuli-responsiveness of hydrogels
Prathyusha Chimala, Presenter; Mario Perera; Aissatou Wade; Tucker Mckenzie; Neil Ayres

Synthesis of rotaxane cross linkers with a radical type mechanophore to visualize dynamic behavior of slide ring materials
Daisuke Aoki, Presenter; Hirogi Yokochi; Roman Boulatov; Hideyuki Otsuka

Preparation, stability and film properties of cationic polyelectrolyte latexes
Chen Hua; Kaimin Chen; Prof. Xuhong Guo, Presenter, ECUST

High throughput characterization of phase behavior in polymeric aqueous two-phase systems
Graham Abramo, Presenter; Lizbeth Rostro; Kaylie Young; Caroline Nimako-Boateng; Tyler Webber

Fluorescence active waterborne epoxy adhesive for art conservation via GQDs stabilized RAFT mediated emulsion polymerization
Sarthik Samanta, Presenter; Nikhil Singha

Linear and hyperbranched perylene based polyimides: Polymerization and hybridization with molybdenum disulfide nanosheets
Amal Abdulrahman, Presenter; Ishrat Khan

Sustainable controlled radical polymerization of para-substituted styrene by alkali metal lewis-base hydrogen atom transfer catalyst
Saerona Kim, Presenter; Hyun Yu; Udaya Dakarapu; Junha Jeon; Gyu Leem

Wednesday, 07:00pm - 09:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40

Microstructures and reaction mechanisms of cationic Pd(II) α-diimine catalyzed polyolefins
07:00pm - 07:20pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Dr. Anthony Gies, Presenter, Dow Chemical Co; Zhe Zhou; Sukrit Mukhopadhyay; Alex Kosanovich; Richard Keaton; Evelyn Auyeung; Huong Dau; Anthony Keyes; Dain Beezer; Eva Harth, Vanderbilt Univ

Styrenic star polymers via RAFT polymerization
07:20pm - 07:40pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Madalyn Radlauer, Presenter, San Jose State University; Dana Wong; Jessica Rodarte

CTA concentration effects on rate retardation in RAFT
07:40pm - 08:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Kate Georgia Elizabeth Bradford, Presenter, Miami University; Leilah Petit; Richard Whitfield; Athina Anastasaki; Christopher Barner-Kowollik; Dominik Konkolewicz, Miami University

Depolymerizable ROMP polymers based on fused ring cyclooctene monomers
08:00pm - 08:20pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Dr. Junpeng Wang, Presenter, University of Akron

Soft and bright multiscale, multicolored fluorescent polymer particles for labeling
08:20pm - 08:40pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Nikunjkumar Visaveliya, Presenter, The City College of New York

Tailor-made self-healable polymers using exchangeable ‘click chemistry’
08:40pm - 09:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 40
Dr. Prantik Mondal, Presenter; Nikhil Singha
Thursday, 08:00am - 10:00am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312

Characterization of equilibrium and non-equilibrium properties of bio-based polymers
08:00am - 08:20am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Alina Alb, Presenter, Kemira Chemicals

Structure property relationships of branched polyethylene in dilute solution
08:20am - 08:40am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Dr. Robert J. S. Ivancic, Presenter, National Institute of Standards and Technology (NIST); Dr. Chase Thompson, National Institute of Standards and Technology Material Measurement Laboratory; Sara Orski, NIST; Debra Audus

Lignin based polyesters: Synthesis and characterizations of lignin-graft-poly(ethylene brassylate)
08:40am - 09:00am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Sundol Kim, Presenter; Hoyong Chung

Renewable bio-based benzoxazine thermosets based on di-furan amines (dfda) with superior performance
09:00am - 09:20am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
MENGWEN YU, Presenter; Giuseppe Palmese

Accessing olefin containing polymers with high-cis content via stereoretentive olefin metathesis polymerization
09:20am - 09:40am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Ting-Wei Hsu, Presenter, Texas A&M University; Samuel Kempel; Quentin Michaudel, Texas A&M University

Characterizing the connection between polymer structure and rare-earth element chelation in water
09:40am - 10:00am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Michael Schulz, Presenter, Virginia Tech; William Archer

Thursday, 10:30am - 12:30pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39

Green analogs of polybutadienes from carbon dioxide and epoxy based feedstocks
10:30am - 10:50am USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39
Dr. Muhammad Rabnawaz, Ph.D., Presenter, Michigan State University

Water-soluble polyion complex (PIC) micelles covered with polyampholyte shells
10:50am - 11:10am USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39
Dr. Shin-ichi Yusa, Presenter, University of Hyogo

Swelling behavior and tunable mechanical properties of lactose containing polyurethane hydrogels
11:10am - 11:30am USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39
Emily Dalton, Presenter; Neil Ayres

Novel enzyme mediated ternary radical initiating system for producing hydrogels
11:30am - 11:50am USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39
Miss Neica I Joseph, Presenter, Duke University; Jennifer West; Teng Su

Withdrawn

Formation mechanism of hydrogel microspheres during precipitation polymerization
12:10pm - 12:30pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 39
Yuichiro Nishizawa, Presenter; Haruka Minato; Takumi Inui; Takayuki Uchihashi; Daisuke Suzuki

Withdrawn

Withdrawn
Thursday, 10:50am - 11:10am USA / Canada - Eastern - August 26, 2021 | Room: A313-A314

Polyaniline based on phenoxazine and carbazole derivatives with improved electrochemical stability and processability
11:10am - 11:30am USA / Canada - Eastern - August 26, 2021 | Room: A313-A314
Mohammed Almtiri, Presenter; Colleen Scott

Withdrawn

Design and synthesis of discrete polymer-protein conjugates
11:50am - 12:10pm USA / Canada - Eastern - August 26, 2021 | Room: A313-A314
Wencong Wang, Presenter, MIT; Yivan Jiang; Bin Liu; Hung V Nguyen, MIT; Zhihao Huang; Manuel Hartweg; Masamichi Shirakura; Jeremiah Johnson

Structure kinetic relationships for the NAl catalyst for epoxide polymerizations
12:10pm - 12:30pm USA / Canada - Eastern - August 26, 2021 | Room: A313-A314
Ms. Niloofar Safaie, Michigan state university; Jessica smak; Austin Rodriguez; Jose Mendoza-Cortes; Robert Ferrier, Presenter

Thursday, 10:30am - 12:10pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312

Controlled Ring-Opening Metathesis of 8-Membered Cyclic Olefins Through the Addition of Excess Ligand
10:30am - 10:50am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Dr. Chase Thompson, Presenter, National Institute of Standards and Technology Material Measurement Laboratory; Robert Ivancic; Debra Audus; Sara Orski, NIST

Optimization of bottlebrush polymer synthesis by ring-opening metathesis polymerization
10:50am - 11:10am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Sarah Blosch, Presenter, Virginia Tech; Mohammed Alabaolirat; Samantha Scannelli; Cabell Eades; John Matson, Virginia Tech

Self condensing ring opening metathesis polymerization: A novel approach to hyperbranched polymers
11:10am - 11:30am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Hanan Almuzaini, Presenter

ROMP-boranes: Polymer supported Lewis Acid catalysts
11:30am - 11:50am USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
James McQuade, Presenter; Dr. Frieder Jaekle, Rutgers University-Newark

Controlled ring opening polymerizations in milliseconds by using sterically hindered strong bases
11:50am - 12:10pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Binhong Lin; Caleb Jadrich; Vince Pane; Pedro Arrechea; Tim Erdmann, Presenter; Charles Dausse; J Hedrick, IBM Research; Nathan Park; Robert Waymouth

Thursday, 02:00pm - 04:00pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36

Side chain density driven morphology transition in brush linear diblock copolymers
02:00pm - 02:20pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Jaemin Park; Dr. Sheng Li, Presenter, Korea Advanced Institute of Science and Technology

Solvent resistant self-crosslinked poly(ether imide)
02:20pm - 02:40pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Zhen Xu, Presenter, Virginia Tech; Gehui Liu; Guoliang Liu; Alan Esker

Sigmatropic rearrangements of polymer backbones
02:40pm - 03:00pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Aleksandr Zhukhovitskiy, Presenter; Rachael Ditzler; Maxim Ratushnyy
Investigation of stereoelectronic effects on the synthesis of novel, well-defined, and sequence-specific conjugated polymers by ROMP
03:00pm - 03:20pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Stephen Koehler, Presenter, Pennsylvania State University; Margaret C Gerthoffer; Tanner Wolf; Prof. Elizabeth Elacqua, The Pennsylvania State University

A convergent platform for translating synergistic drug combinations to nanomedicines: Application to multiple myeloma therapy
03:20pm - 03:40pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Alex Detappe; Hung V Nguyen, Presenter, MIT; Yivan Jiang; Michael Agius; Wencong Wang, MIT; Clelia Mathieu; Nang Su; Samantha Kristufek; Irene Ghobrial; P. Peter Ghoroghchian; Jeremiah Johnson

Solution behavior of oligodimethylsiloxane with an ionic liquid chain end (ODMS-IL)
03:40pm - 04:00pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Tianyu Li, Presenter; Hui Li; Yingdong Luo; Kunlun Hong

Interpenetrating responsive polymer networks within hydrogels for "smart" drug delivery
03:00pm - 03:20pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Daniel Massana Roquero, Presenter, Clarkson University; Paolo Bollella; Artem Melman; Evgeny Katz

Ternary thiol-ene/thiourethane covalent adaptable networks: a rapid and versatile route to vitrimeric materials
03:20pm - 03:40pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Mr. Reese K Sloan, Presenter; Derek Patton

A new class of zwitterionic materials: Phosphonium sulfonate monomers and polymers
03:40pm - 04:00pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Marcel Brown, Presenter; Todd Emrick

Kinetic investigation on the ring-expansion polymerization of o-phthalaldehyde
02:00pm - 02:20pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Anthony Engler, Presenter; Paul Kohl

Hydrolytically degradable epoxy amine thermosets utilizing hydrolyzable ketal-based epoxide monomers
04:30pm - 04:50pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Ketki Shelar, Presenter; Karl Mukeba; Charles Pittman; Dennis Smith

Improving the synthesis of PEGylated conjugated polymers with a water scavenging Grignard
02:00pm - 02:20pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Susan Cheng, Presenter, University of Toronto; Shuyang Ye; Chirag Apte, Presenter; Andrei Yudin; Dwight Seferos

Carbodiimide ring opening metathesis polymerization
05:10pm - 05:30pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Drake Johnson, Presenter; Jozsef Toth; Aleksandr Zhukhovitskiy

Light activated adhesion and debonding of underwater pressure sensitive adhesives
02:40pm - 03:00pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Yen-Ming Tseng, Presenter; Amal Narayanan; Kaushik Mishra; Xinhao Liu; Abraham Joy

Semi-fluorinated polymers containing corannulene, adamantane, and isosorbide from diols and aromatic trifluorovinyl ethers
04:50pm - 05:10pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Benjamin M Alameda, Graduate Student, Presenter, University of Southern Mississippi; Joseph Murphy; Jonathan Sisemore; Derek Patton

Solution of stereoelectronic effects on the synthesis of novel, well-defined, and sequence-specific conjugated polymers by ROMP
Synthesis and properties of precision, isostatic ethylene-vinyl alcohol polymers outside of a two carbon spacing
05:30pm - 05:50pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Gina Guillory, Presenter; Stephanie Marxsen; Rufina Alamo; Justin Kennemur

Poly aryl ether sulfones from perfluorocyclohexene and sulfone bisphenol
05:50pm - 06:10pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Karl Mukeba, Presenter; Behzad Farajidizaji; Ketki Shelar; Charles Pittman; Dennis Smith

Determination of the number average molecular weight of polyelectrolytes using NMR diffusometry
06:10pm - 06:30pm USA / Canada - Eastern - August 26, 2021 | Room: A311-A312
Veera Venkata Shravan Uppala, Presenter; Aijie Han; Ralph Colby; Louis Madsen

Thursday, 04:30pm - 06:10pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36

Stress relaxation behavior of tunable dynamic networks
04:30pm - 04:50pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Ipek Sacligil, Presenter; Christopher Barney; Alfred J Crosby, University of Massachusetts Amherst; Gregory Tew

Self emulsifying drug delivery systems: Mucolytic action of N-acetylcysteine (NAC) polymer hydrophobic complexes for effective mucopermeation
04:50pm - 05:10pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Ahmad Malkawi, Presenter

Reversible crosslinking based on Diels-Alder ‘click chemistry’ in polyolefinic elastomers
05:10pm - 05:30pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Mr. Sagar Kumar Raut, Research Scholar, Presenter, Indian Institute of Technology, Kharagpur; Dr. Prantik Mondal; Nikhil Singha

Withdrawn

Fine-Tuning of Solvation Environments in Liquid Phase Reactions Using Polymer-Modified Metal-Supported Catalysts
05:50pm - 06:10pm USA / Canada - Eastern - August 26, 2021 | Room: Zoom Room 36
Pengcheng Huang, Presenter, Universiteit Twente Faculteit Technische Natuurwetenschappen; Rick Baldenhofer; Aayan Banerjee; Leon Lefferts; Jimmy Faria Albanese
POLY – General Topics: New Synthesis & Characterization of Polymers

Enhanced aminolysis of cyclic carbonates by β-hydroxyamines for the production of fully biobased polyhydroxyurethanes

Baptiste Quienne1, baptiste.quienne@enscm.fr, Rinaldo Poli2, Julien Pinaud1, Sylvain Caillol1. (1) Institut Charles Gerhardt de Montpellier, Montpellier, Languedoc-Roussillon, France (2) Laboratoire de Chimie de Coordination, Toulouse, Midi-Pyrénées, France

Polyurethanes (PUs), ranking 6th among all polymers based on annual worldwide production, are commonplace in everyday life as foams, coatings, adhesives, elastomers, insulation, composites, and so forth. They are present in a wide range of applications due to the numerous industrially available polyols, which allow to cover a large panel of properties.

However, their synthesis requires the use of isocyanates, known to be harmful for human health and for the environment. In order to limit the use of isocyanates, the development of isocyanate-free PUs has emerged over the last decade and has gained increasing attention in both the academic and industrial communities. Hence, the aminolysis of 5-membered cyclic carbonates, which yields polyhydroxyurethanes (PHUs), is nowadays the most promising and described route to non-isocyanate polyurethanes (NIPUs). This route has the advantage that these carbonates are easily obtained by the carbonation of commercial epoxides. Moreover, the valorization of CO2 as a cheap, renewable and non-toxic resource makes this pathway the least toxic and most eco-friendly route to PHUs. However, 5-membered cyclic carbonates suffer from lower reactivity compared to isocyanates or larger cyclic carbonates. Therefore, the aminolysis of cyclic carbonates has been thoroughly investigated in order to understand and optimize the ring opening reaction.

In this study, we highlighted the higher reactivity of β-hydroxyamines toward cyclic carbonate in comparison to classical alkylamines through the determination of their reaction rate constants. The key role of the β-OH substituent in the aminolysis was enlighten by a DFT investigation. In addition to their higher reactivity, biobased β-hydroxyamines were easily synthesized by a one-step process and used for the synthesis of fully biobased PHU thermosets. The higher reactivity of β-hydroxyamines was also confirmed in the thermoset synthesis, the thermal and thermo-mechanical properties of PHUs were then compared.
Poly(ethylene-co-propylene) grafted silica nanoparticles prepared via surface initiated RAFT polymerization

Richard Ly, rl10@email.sc.edu, Brian C. Benicewicz. Dept of Chem Biochem, University of South Carolina College of Arts and Sciences, Columbia, South Carolina, United States

Recent development in surface-initiated polymerizations has opened up a facile route towards various brush nanocomposites. However, synthesizing well-defined olefin copolymer grafted nanocomposites through surface-initiated reversible addition-fragmentation chain transfer (SI-RAFT) poses a challenge due to use of gaseous monomers, obtaining low dispersity (<1.2), and controllable molecular weight. This work will present a synthetic approach toward poly(ethylene-co-propylene) grafted silica nanoparticles with controllable graft density and molecular weight. Varying ratios of propylene/ethylene can be obtained. The synthesis, structural and thermal characterization, and challenges in preparation of these materials will be discussed.
New class of imidazolium based polymeric ionic liquids for gas separation membranes

Sudhir Ravula, sravula@ua.edu, Kathryn E. O’Harra, Jason E. Bara. Chemical and Biological Department, The University of Alabama, Tuscaloosa, Alabama, United States

Currently, membrane technology is enthusiastically investigated for gas separations due to its energy efficiency relative to alternative technologies utilized in industrial separation processes currently employed, including H₂/N₂ or H₂/CH₄ separations, natural gas (CO₂/H₂O removal), natural gas sweetening (CO₂/CH₄), etc. Toward this, charged polymers are one of the leading material classes being explored for gas separations. The development of poly(ILs), or polymers wherein the ionic moieties are pendant from the backbone which draw synthetic inspiration from advances in ionic liquid chemistries, has further accelerated the research because of the advantageous interactions with the polar gases (i.e. CO₂) within mixtures. Our work has been focused on designing the molecular structure of ionic membrane materials to improve transport properties, that is, permeability and selectivity, by modifying the number and connectivity of pendant cation-anion pairs. In the study outlined here, we have synthesized series of imidazolium-based poly(ILs) via ring-opening polymerization. Polymeric ionic liquids (poly(ILs)) obtained through this process have been characterized using Fourier transform infrared spectroscopy, nuclear magnetic spectroscopy, gel permeation chromatography, thermogravimetric analysis, and differential scanning calorimetry to evaluate the purity and other associated properties. The applicability of these poly(ILs) for membrane-based gas separations was quantified by analysis of pure gas permeabilities and selectivities. In this talk, we will emphasize studies of the process of synthesis and characterization of poly(ILs), as well as the gas separation performance.
Aqueous self-assembly of ABA triblock bottlebrush copolymers

Logan Dugas, l.dugas@usm.edu, Cheyenne Liu, Robson F. Storey, Yoan C. Simon. Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Nature has mastered the art of self-assembly in aqueous conditions, creating complex structures that facilitate intracellular communication and transport through complex barrier of the cell. Polymersomes are artificial vesicles that emulate cellular membrane towards the realization of synthetically derived stimuli-responsive functional self-assembled cell mimics. Here, we have devised a novel ABA triblock bottlebrush system that self-assembles into polymersomes in aqueous environments. The bottlebrush was obtained by ring-opening metathesis polymerization (ROMP) sequentially of A, B and A, whereby the hydrophilic A macromonomer is norbornene polyethylene glycol (NBPEG), and hydrophobic B macromonomer is either norbornene polyisobutylene (NBPIB) or norbornene polystyrene (NBPS). We carefully selected our side chain degree of polymerizations such that, within a single bottlebrush, our hydrophilic and hydrophobic chains would have constant length. P(NBPEG-b-NBPIB-b-NBPEG) were characterized by size-exclusion chromatography ($M_n = 420$ kg/mol, PDI = 1.151) and by dynamic light scattering (DLS, $R_h = 45$ nm). Self-assembly was then performed by slow addition of water to a THF solution (5 mg/mL) of P(NBPEG-b-NBPIB-b-NBPEG). DLS confirmed a substantial increase in $R_h$ from the initial triblock bottlebrush polymer (256 nm), which will be imaged by electron microscopy. The PS analogs are being characterized and will be discussed as well. Our results provide fundamental insight regarding the aqueous self-assembly behavior of non-entangling triblock bottlebrush copolymers; establishing a unique platform whereby multicompartmental cellular memetics might be achieved through rational architectural design.
Accelerating the development of high-performance materials requires advancements not only in the fundamental synthetic chemistry and catalysis, but also the surrounding laboratory infrastructure. Here, we demonstrate how our recent work on the integration of new methods for scalable carbonate monomer synthesis, rapid and automated continuous-flow ring-opening and step-growth polymerization, predictive modeling of historical polymerization data, the creation material-focused database infrastructure, and the use of the IBM hybrid cloud computing platforms enables precision synthesis of new materials with tailored properties and characteristics. This work emphasizes how convergence of automated experimentation, cloud computing, and predictive modeling is imperative in enhancing the rate of discovery within polymer chemistry and reducing experimental overhead required to access new, high-performance materials.
Investigating the effects of phase separation on morphology and properties of PEEK aerogels

Glenn A. Spiering\textsuperscript{1,2}, gaspiering@vt.edu, Garrett Godshall\textsuperscript{1,2}, Alexander Hutchins\textsuperscript{3}, Emily Trotto\textsuperscript{3}, Kalista McCoy\textsuperscript{2}, Joong Lee\textsuperscript{3}, Robert B. Moore\textsuperscript{1,2}. (1) Macromolecules Innovation Institute, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (3) Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Polymeric aerogels are highly porous, mechanically robust materials that have shown promising properties for applications such as structural insulation, heterogeneous catalyst support and chemical adsorbents. These polymeric aerogels are traditionally prepared by a sol-gel process, where the reaction conditions influence the aerogel properties. While synthetic expertise is necessary to prepare crosslinked polymeric aerogels, semicrystalline polymeric aerogels can be prepared by the facile process of thermally induced phase separation. In this study, poly(ether ether ketone) (PEEK) aerogels were prepared through thermally induced phase separation by cooling a PEEK solution from an elevated temperature to a desired phase separation temperature. Tuning the phase separation parameters allowed manipulation of the aerogel morphology. Use of a poor solvent allowed liquid-liquid phase separation to occur upon cooling of the PEEK solution. Differences in the observed aerogel morphology were attributed to competition between polymer crystallization and solution phase separation. The resulting phase-separated morphology was investigated with ultra-small angle x-ray scattering, nitrogen porosimetry, scanning electron microscopy, and helium pycnometry. The aerogel morphology was linked to the mechanical properties with compression testing.

SEM image highlighting the effect of gelation temperature on aerogel morphology
Sustainable polymers: A more efficient synthesis of the monomer dihydrocarvilde

Mackenzie Claypool, mclaypool001@csbsju.edu, Chris P. Schaller. Chemistry, College of Saint Benedict and Saint John's University, Saint Joseph, Minnesota, United States

Sustainable polymers are a topic of interest due to their environmental benefits. Dihydrocarvilde is a monomer for ring-opening polymerization, derived from citrus peels. This monomer can be obtained by the Bayer-Villiger oxidation of dihydrocarvone with oxone, a green oxidant, and sodium bicarbonate in methanol/water. Although this reaction has been investigated in prior studies, it has been complicated by epoxidation of the double bond. The approach for this study in organic methodology was to run multiple trials while varying conditions such as mode of reagent addition, stirring time, and the presence of co-oxidants. Progress was monitored via $^1$H NMR spectroscopy. A single addition of reagents followed by a 4-hour stir provided the most promising result. An observed ratio of 2:1 alkene:oxymethine integration in the $^1$H NMR indicated the Baeyer-Villiger oxidation without epoxidation. The result remained consistent through a scale-up of the reaction. The monomer will be used in ring-opening polymerizations leading to numerous possible application directions illustrating the advantages of green chemistry.

Baeyer-Villiger oxidation of dihydrocarvone with oxone to synthesize the monomer dihydrocarvilde with no epoxidation.
Chemical synthesis of silk inspired polymer

Kayla Mancini, mancinik1@montclair.edu, Amrita Sarkar. Chemistry, Montclair State University College of Science and Mathematics, Montclair, New Jersey, United States

Silk protein Spidroin is a highly desirable biomaterial used in a myriad of applications both in frontier research and biomedical field due to its remarkable mechanical properties and biocompatibility. This extraordinary mechanical property results from its unique molecular composition and architecture, consisting of hydrophobic blocks rich in alanine and hydrophilic blocks rich in glycine, linked via hydrogen bond and crystalline β-sheet nanostructure. Chemically synthesized polymers structurally similar to Silk protein are in demand for studying their structure-property relationship. Thus, we present here a facile synthesis strategy of developing Silk-inspired ABA and (AB)$_n$ polymers via ring opening polymerization (ROP), microwave-induced Diels-Alder (DA) cycloaddition, and step-growth polymerization. A detail characterization of the synthesized polymer including mass spectrometry, nuclear magnetic resonance and gel permeation chromatography will be elaborated.
Synthesis of biobased phenol-formaldehyde wood adhesives from biorefinery derived lignocellulosic biomass

Archana Bansode, asb0062@auburn.edu, Maria L. Auad. Auburn University, Auburn, Alabama, United States

Lignocellulosic biomass is a sustainable alternative to the petroleum-derived chemical for the development of biobased wood adhesive, which motivates the integrated biorefineries to effectively convert biomass feedstock into desirable chemicals. Herein, lignin recovered from kraft biorefinery (L-KB) and two bio-oils, BO-SL/L and BO-FP/PW, prepared from laboratory scale solvent liquefaction of lignin and fast pyrolysis of pinewood, respectively, have been used to substitute 50% (w/w) of phenol in phenol-formaldehyde (PF) resin system. To this end, we first studied the molecular structural characteristics of moieties derived from lignin and polysaccharides present in L-KB, BO-SL/L, and BO-FP/PW via FTIR, $^{13}$C-$^1$H HSQC 2D-NMR, and GCMS techniques. Further, the obtained resin adhesive structures were examined by FTIR and $^1$H-NMR spectroscopy, which confirms methylene bridges appearance during the resin preparation. Subsequently, to understand the curing behavior of each of the resin with hexamethylenetetramine (HMTA) curing agent, DSC analysis was performed, which helps to optimize the bonding process. The resulting bonding strength of each of the resin adhesive, measured by gluing two pieces of wood, reported significantly different adhesion ability due to structural differences, which was analyzed by two-way ANOVA followed by Tukey's post hoc test. Overall, this study represents a comparative strategy for substituting biorefineries derived phenolic part in the PF resin system to conventional petroleum-derived phenol without compensating adhesion ability when applied to the wood. This provides an effective solution to produce biorefinery-derived PF for adhesives applications.
Open air synthesis of oligo(ethylene glycol)-functionalized polypeptides from non-purified N-carboxyanhydrides

Zhengzhong Tan, zt7@illinois.edu, Jianjun Cheng. Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

With PEG-like properties, such as hydrophilicity and stealth effect against protein absorption, oligo(ethylene glycol) (OEG)-functionalized polypeptides have emerged as a new class of biomaterials alternative to PEG with polypeptide-like properties. Synthesis of this class of materials, however, has been demonstrated very challenging, as the synthesis and purification of OEG-functionalized N-carboxyanhydrides (OEG-NCAs) in high purity, which is critical for the success in polymerization, is tedious and often results in low yield. OEG-functionalized polypeptides are therefore only accessible to a few limited labs with expertise in this specialized NCA chemistry and materials. Here, we report the controlled synthesis of OEG-functionalized polypeptides in high yield directly from the OEG-functionalized amino acids via easy and reproducible polymerization of non-purified OEG-NCAs. The prepared amphiphilic block copolypeptides can self-assemble into narrowly dispersed nanoparticles in water, which show properties suitable for drug delivery applications.
Metallopolymerization holds great promise for applications such as light harvesting and catalysis, but they are challenging to synthesize. New, mild polymerization strategies are needed to reliably synthesize metallopolymer with high molecular weights and high functional group tolerance. Our group is interested in exploring ring-opening polymerization reactions of organometallic sandwich complexes tethered to cyclic carbonates. Preliminary results indicate that a living, controlled polymerization can be achieved using organic co-catalysts (a thiourea plus an amidine base) at room temperature in three hours, with molecular weights > 10,000 g/mol. This polymerization is both faster and yields higher molecular weight metallopolymer than other room-temperature polymerization strategies. The organic co-catalysts are also compatible with common organic monomer classes, such as lactide, enabling the controlled synthesis of diblock copolymers with organic and inorganic regions.
Synthesis and characterization of polyaryl ethers containing hexafluoroisopropylidene enchainment via direct Friedel-Crafts polymerization of diaryl ethers and hexafluoroacetone hydrate

Gustavo Munoz¹,², gam318@msstate.edu, Sumudu Athukorale¹,², Charles U. Pittman¹,², Dennis W. Smith¹,². (1) Chemistry, Mississippi State University, Mississippi State, Mississippi, United States (2) MSU Advanced Composites Institute, Mississippi State, Mississippi, United States

Polyaryl ethers (PAEs) are high-performance thermoplastics composed of an ether-linked aromatic backbone. This class of material exhibits high thermal stability, chemical resistance, fire resistance, high mechanical strength, and good processability. Historically, much attention has been given to 1,1,1,3,3,3-hexafluoroisopropylidene (HFIP) derivatives due to the increased solubility, thermal stability, and glass transition, imparted by the -CF₃ groups. A good example of the HFIP improvements is the imminent industrial application of bisphenol AF. Semi-fluorinated PAEs of this kind are typically synthesized from halogenated bis-aryl monomers via nucleophilic aromatic substitution with the corresponding bis-phenoxide, which implies several synthetic steps. A less explored alternative is the electrophilic aromatic substitution (EAS) of aryl ethers to produce novel semi-fluorinated analogs. Herein, a practical and direct synthesis of semi-fluorinated PAE is presented via Friedel-Crafts polymerization of hexafluoroacetone trihydrate and diphenyl ether, catalyzed by triflic anhydride. Although prepared by indirect methods in 1966 (Stamatoff et al., US Patent 3,291,777) further pursuits and modern characterizations surprisingly have not been reported. This Polymer represents one of the most simple and obvious semi-fluorinated PAEs, yet it has remained unexplored for years. The methodology presented herein was applied to other aromatics monomers such as dibenzofuran and biphenyl. The polymeric materials were characterized by NMR, FTIR, GPC, XRD, TGA, and DSC. Results showed a successful polymerization with a low branching process depending on the temperature, thermal stability until 500 degrees Celsius under nitrogen, a glass transition (T₉) around 170 degrees Celsius, and molecular weights ranging between 57-60 kDa. Finally, as its possible application, the optical and dielectric properties of these materials were studied.

Friedel-Crafts polycondensation of diphenyl ether and hexafluoroacetone hydrate
Friedel-Crafts polycondensation of diphenyl ether and commercial diacyl chloride monomers toward Versatile polyetherketoneketones (PEKKs)

Alison K. Duckworth\textsuperscript{1,2}, akd293@msstate.edu, Gustavo Munoz\textsuperscript{1,2}, Charles U. Pittman\textsuperscript{1,2}, Dennis W. Smith\textsuperscript{1,2}. (1) Chemistry, Mississippi State University, Mississippi State, Mississippi, United States (2) MSU Advanced Composites Institute, Mississippi State, Mississippi, United States

Polyaryletherketones (PAEKs) are a family of high-performance thermoplastics with a highly aromatic backbone connected by ketone groups and ether linkages. They exhibit high thermal stability, chemical resistance, and high mechanical strength. Due to their restricted chain motions, PAEKs display higher crystallinity, glass transition temperatures (T\textsubscript{g}), and melting points (T\textsubscript{m}) compared to other thermoplastics. However, they are insoluble in many organic solvents, such that their study and characterization are mostly carried out in strongly acidic solutions such as sulfuric and trifluoroacetic acid. It is hypothesized that introducing geminal methyl groups into the backbone of PAEKs, such as polyetherketoneketones (PEKKs), can result in improved processability with some organic solvents without compromising their thermal performance. In this work, Friedel-Crafts polymerization of PEKK copolymers was performed using comonomers of terephthaloyl chloride, diphenyl ether, and dimethyl malonyl chloride in varying proportions. The synthesized copolymers were characterized by NMR, FT-IR spectroscopy, GPC, TGA, XRD, and DSC. Results showed that varying the stoichiometric ratios of the comonomers can tune the thermal performance and solubility of the resultant copolymers. The thermal properties of the prepared PEKK copolymers were also compared with PEKKs having unmodified backbones.
Synthesis of new diketopyrrolopyrrole scaffolds for the formation of novel donor-acceptor and n-type semiconductors

Ranganath W. Wahalathantrige Don, rww188@msstate.edu, Colleen N. Scott. Chemistry, Mississippi State University College of Arts and Sciences, Mississippi State, Mississippi, United States

In recent years, conjugated polymers with diketopyrrolopyrrole (DPP) units in the backbone have caught the attention of the organic device community for their potential application in solar cells and ambipolar field-effect transistors (FETs). The high charge mobility, self-organizing properties, and electron-deficient nature of these polymers make them perfect candidates for the aforementioned applications. Co-polymerization of DPP units with electron-rich aromatic species such as thiophene makes it possible to control (lower) the optical bandgap of the polymer. In this study, four DPP-thiophene polymers containing alkenyl spacers were synthesized to investigate the effect of the alkenyl group on the optoelectrical properties of the polymer. The polymers were synthesized by Stille polycondensation polymerization and characterized for their structural, optical, electrical, and charge mobility properties. The polymers A and B (Figure 1) were synthesized from vinyl flaked DPP moiety with bis-stannyl thiophene and bis-stannyl ethene, while C and D (Figure 1) were synthesized from thiophene flanked DPP with bis-stannyl thiophene and bis-stannyl ethene. The effect of the alkenyl groups' position on optoelectrical and charge mobility was characterized by UV/visible spectroscopy, cyclic voltammetry, and FET characteristics. Thermal properties of the synthesized polymers were characterized by Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). The structural morphology of the polymers was evaluated with Grazing Incidence X-ray Diffraction (GIXD) and Atomic Force Microscopy (AFM). We will discuss the results of our study in this presentation.

Structures of the synthesized DPP polymers
Biopharmaceutics are widely used to treat serious diseases, but the architectural and chemical complexity that makes proteins good therapeutics renders them susceptible to degradation and aggregation during manufacturing, transportation, and storage. Loss of intact biopharmaceutic causes patient under-dosing as well as adverse reactions. With the growth of biopharmaceuticals coming to market, the need increases for benign excipients to stabilize proteins against environmental stresses without posing a safety concern. A class of glycopolymers bearing a pendant trehalose, a natural sugar, was developed by our group and they each demonstrate the ability to stabilize a range of biopharmaceuticals. However, this research area had not yet explored the trehalose polymer for safety, mechanism of stabilization, physical properties, or potential optimization. This research focuses on the ongoing efforts to expand our knowledge base in applying the methacrylate trehalose polymer as an excipient to formulate biopharmaceuticals. In particular, it will highlight the glycopolymer's benign immunogenic, excretion, and biodistribution behaviors as well as how proteins are unaffected in vivo by the polymer. Next, because the mechanism by which proteins are stabilized as well as the conformation in which they are stabilized affects their onset of activity, how the glycopolymer stabilizes insulin will be shown. Due to the importance of patient comfort and compliance, the final segment of research explores the fluid properties of the glycopolymer, optimization of insulin formulations, and optimized formulations properties. Altogether, this work shows specifically how insulin is stabilized by the methacrylate trehalose polymer and, more broadly, that the glycopolymer can be broadly applied as an excipient to stabilize therapeutic macromolecules safely and without significantly changing the in vivo response or physical properties.
Strong and tough self-healing polymer with the thermodynamically stable whilst kinetically labile coordination bond

Jiancheng Lai\textsuperscript{1,2}, jiancheng.lai@outlook.com, Cheng-Hui Li\textsuperscript{1}, Jing-Lin Zuo\textsuperscript{1}, Zhenan Bao\textsuperscript{2}. (1) School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu, China (2) Department of Chemical Engineering, Stanford University, Stanford, California, United States

There is often a trade-off between mechanical properties and the dynamic nature of self-healing. In this work, we report the design and synthesis of a polymer containing thermodynamically stable whilst kinetically labile coordination complex to address this conundrum. The Hbimcp (2,6-bis((imino)methyl)-4-chlorophenol) ligand we used is a kind of alterdentate ligand, which provides two equivalent imine-N donor centers. However, due to the steric hindrance, the two equivalent imine-N donor centers can not coordinate with the same metal ion (Zn(II) in our study) at the same time and therefore the two coordination atoms are alternative and interchangeable. The Zn-Hbimcp coordination bond has a relatively large association constant ($2.2 \times 10^{11}$) but also undergoes fast and reversible intra- and intermolecular ligand exchange processes. The as-prepared Zn(Hbimcp)$_2$-PDMS polymer is highly stretchable (up to 2400 % strain) with a high toughness of 29.3 MJ m$^{-3}$, and autonomously self-heal at room temperature. Control experiments by varying the metal ions and metal-to-ligand molar ratios showed that the optimal combination of its bond strength and bond dynamics is responsible for the material’s mechanical toughness and self-healing property. This molecular design concept points out a promising direction for the preparation of self-healing polymers with excellent mechanical properties. We further show this type of polymer can be potentially used as energy absorbing material for car crash protection, sportswear, helmet liners, shockproof pad, armored clothing. It can also be potentially used as self-healing and self-adaptable electronic materials for biological interfaces.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{a. The structure of polymer complex Zn(Hbimcp)$_2$-PDMS; b. Strain–stress curves of a film healed at room temperature (25 °C) for different lengths of time show an increase of the stretching ability when the film is allowed to heal for a longer time; c. Possible energy dissipation process of [Zn(Hbimcp)$_2$]$^2$; d. The calculation of energy-absorbing efficiency; e. Optical images of the composite sponge under compression, healing, and recovery processes.}
\end{figure}
Developing sialic acid containing polymers for influenza inhibition

Rachel Bianculli, Rbiancu@vt.edu, Michael D. Schulz. Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Antiviral polymers have shown to significantly enhance the inhibition of viral infection in comparison to monomeric analogues.\textsuperscript{1-3} This observation is thought to be a result of polyvalency, where multiple binding sites on the same polymer have a synergistic effect and dramatically increase inhibition. Influenza infection and replication is initiated through interactions between hemagglutinin on the virus surface and sialic acid on the epithelial surface of the lungs. By using the hemagglutinin-sialic acid binding interactions as a model, “decoy receptors” (polymers containing sialic acid) can be designed and synthesized to bind to the viral surface and inhibit interaction with cells, therefore lessening infection. To do this, we will synthesize a library of polymers with systematically varied parameters (molecular weight, sialic acid amount, sialic acid linkage, comonomer identity, and topology) and measure their inhibition with the hemagglutination inhibition (HAI) assay. From this data, we can study structure-property relationships and optimize materials for enhanced inhibition of influenza.
Recent advancements in gel state functionalization of PEEK

Christopher R. Kasprzak\textsuperscript{1,2}, chriskasprzak123@gmail.com, Lindsey Anderson\textsuperscript{2}, Robert B. Moore\textsuperscript{1,2}. (1) Macromolecular Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Controlled functionalization of high-performance polymers has been a challenging goal for both industry and academia. We recently reported the thermoreversible gelation of poly(ether ether ketone) (PEEK) in dichloroacetic acid (DCA). Recent advancements have been made using this semi-crystalline gel system to impart a variety of functional pendant groups to PEEK. By taking advantage of the electronic structure of PEEK and the protic nature of DCA, we have been able to perform electrophilic aromatic substitution reactions in both the homogeneous solution state as well as the heterogenous gel state. Functionalization in the gel state preserves the crystallizability of PEEK through steric exclusion of the reagents from the crystalline regions and provides a semi-crystalline copolymer with novel properties. Functionalization of this industrially important high-performance thermoplastic provides a versatile platform for subsequent chemistries to generate a suite of advanced materials.

A schematic showing the architectural control of pendant group placement on PEEK afforded through performing electrophilic aromatic substitution reactions in either homogenous or heterogenous conditions.
Non-contact measurement of deflection of conductive polymer actuators in liquids using smartphone camera

Najathulla Bhagavathi Chalil, ms16resch11006@iith.ac.in, Mudrika Khandelwal, Atul Deshpande. Materials Science and Metallurgical Engineering, Indian Institute of Technology Hyderabad, Hyderabad, Telangana, India

Deflection of single or multi layered actuators prepared from conductive polymers or ionic polymer metal composites are normally measured using a costly laser displacement sensor. Here we have developed a cheap alternative method utilising a smartphone camera and MATLAB to track and measure deflection of the actuator. We have demonstrated and measured the deflection of an actuator with a least count of few microns inside an electrolyte, which is difficult even with a conventional laser displacement sensor. This can be used to measure deflection of actuators inside an electrolyte as well as free standing in air.
We developed a controlled method to construct well-defined, sulfur-containing polymers from thiol-containing Al-based initiators (SAI). Our SAI initiator polymerizes propylene sulfide to high molecular weight (ca., 100 kg/mol) with relatively narrow polydispersity (D < 1.4). We investigated this strategy on the copolymerization of epoxides (e.g., epichlorohydrin (ECH), propylene oxide (PO)) with propylene sulfide. Statistical and block-copolymers of propylene sulfide and ECH or PO were characterized by size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), $^1$H and $^{13}$C NMR spectroscopy, diffusion ordered spectroscopy (DOSY), and small angle X-ray scattering (SAXS). Furthermore, the introduced innovative and reliable methodology for the synthesis of SAI initiators enabled us to tune the polymer architecture to readily access more complex structure of polyepisulifides. We synthesized double-headed (d-H) and tetra-headed (t-H) SAI initiators to produce ter- and star-(co)polymers consisting of propylene sulfide and PO or ECH. This method demonstrates a simple and robust strategy to prepare copolymers consisting of episulfides and epoxides.
Depolymerizable polymeric micelles for the release of H$_2$S via COS

Sarah Swilley-Sanchez, sarahswilley@vt.edu, Chad Powell, John B. Matson. Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Gasotransmitters, such as hydrogen sulfide (H$_2$S), are endogenously produced, short-lived gaseous mediators which exist in most tissues throughout the body and play a critical role in cellular signaling and homeostasis.\textsuperscript{1} Previously, we have developed a linear, depolymerizable (sometimes referred to as self-immolative) poly(thiourea) (DPTU) that releases carbonyl sulfide (COS)/H$_2$S in response to reducing agents and carbonic anhydrase (CA) respectively. However, this system is prone to hydrolysis which can limit the depolymerization cascade along the polymer backbone.\textsuperscript{2} Therefore extending from this, we report here polymeric micelles composed of hydrophilic poly(ethylene glycol) (PEG) and hydrophobic DPTU within the core of the micelle to prevent premature depolymerization. Micelles were chosen to increase solubility and prevent rapid degradation, in turn increasing circulation time as well as drug release. Herein, we report the synthesis of PEG-b-DPTU micelles, degradation kinetics, and H$_2$S release profiles along with relevant controls as compared to our previously reported DPTU system.
Dynamic materials have many benefits that cannot be seen in static materials. They have the ability to dissociate stress, and many can even self-heal. Dissociating stress is a useful property for these materials to have as it can allow more stress to be applied to a system before it fails. The relaxation time can depend on temporary bonds breaking, or the untangling of polymers within the system itself. We proposed a theory that included a time-dependent element in the analysis of stress-strain curves of dynamic materials, thus accounting for the temporary bonds breaking in materials as opposed to just the stretching of bonds. This gives the ability to understand the relaxation time of dynamic materials so that they can be better characterized before being used. The time-dependent term has a second-order time dependence, which was found to predict the relaxation time more accurately and precisely than a first-order dependence. The model was tested out against a wide range of materials, both experimental and taken from the literature, and found to be sensitive and applicable across these materials. This model assists with the characterization of dynamic materials that includes their temporary bonds in the predictions of their behaviors.
Predicting the electrospinnability of polymer solutions using tubeless siphoning

Taslim Ur Rashid, taslimndcacce@gmail.com, Wendy Krause, Russell E. Gorga. Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina, United States

Electrospinning is a unique nanofiber fabrication technique that deals with the elongation of polymeric fluid under a high extensional force applied by electrical voltage. Over the years, researchers have been striving to develop a facile method to predict the electrospinnability of polymer solutions. In this work, we investigate the potential correlation between tubeless siphoning and the electrospinnability of polyethylene oxide (PEO) solutions in water. Polymer solutions manifest tubeless siphoning for a range of concentrations due to molecular entanglements which is the essential prerequisite for jet formation in electrospinning as well. Tubeless siphon heights for a wide range of concentrations (0.05-10 w/w%) of PEO solutions were measured by a mechanical set up to determine the siphonable range for the solutions. Electrospinnability for all the solutions was evaluated in terms of jet stability and the ability to form continuous fibers (evidenced by scanning electron microscopy (SEM)). Siphoning characteristics of the solutions were assessed by evaluating the effect of molecular weight of the polymer, nozzle diameter, flow rate and concentration of the solution on the siphon height. The results showed that PEO solution exhibited tubeless siphoning within the range of 0.25 and 6% forming a ‘jelly fish’ structure along siphon column for solutions above 2%. The electrospinning investigation of the solutions displayed the formation of beaded fiber starting at concentration 2% while bead free fibers were obtained at or above 6%. The results demonstrate that tubeless siphoning made it possible to predict the electrospinnability of the polymer solution and could help eliminate the arduous and cost-effective effort of finding desired electrospinnable concentration for a given polymer solutions that includes electrospinning for a series of solutions and subsequent SEM microscopy of each of the products.

Schematic of the tubeless siphoning setup with backlight imaging technique used to investigate the maximum shiphon height for polyethylene oxide solutions.
Synthesis and applications of structurally well-defined functionalized polyolefins

Mateusz Malus\textsuperscript{1}, mateusz.malus@pg.edu.pl, Jakub Kruszynski\textsuperscript{1,2}, jakub.kruszynski@sabic.com, Miloud Bouyahyi\textsuperscript{2}, Nydia Badillo\textsuperscript{2}, Maciej Sienkiewicz\textsuperscript{1}, Lidia Jasinska-Walc\textsuperscript{1,2}, Rob Duchateau\textsuperscript{2}. (1) Faculty of Chemistry, Polymer Technology Department, Politechnika Gdanska, Gdansk, Województwo pomorskie, Poland (2) Sabic Geleen, Geleen, Limburg, Netherlands

Conventional polyolefins such as polyethylene (PE) and polypropylene (PP) are extensively used in many applications in our modern life that demands increasingly advanced materials. The main reasons being their outstanding mechanical properties, processability, chemical stability and resistance, combined together with a relatively low price. Polyolefins are particularly well suited for packaging, automotive industry, and building and construction. Apart from the clear advantages of polyolefins, they exhibit certain technical limitations such as their poor compatibility and miscibility with other polymers or fillers.

Recent progress in organometallic catalysis revealed several new routes for polyolefin synthesis and allowed scientists to produce randomly or chain-end functionalized analogs. Another method for preparing functionalized polyolefins (FPO) is the reactive extrusion process, however, due to the free radical process, the thus obtained products are ill-defined. Incorporation of polar functionalities into polyolefins provides an amphiphilic character and expands the scope of applicability of such polymers to areas usually reserved for specialty materials.

Although many studies have been performed on FPO’s, no systematic comparison between in-reactor functionalized (IRF) and obtained by reactive extrusion (REX) FPO’s have been made. In this contribution, we will give an overview of the pros and cons of the production process, material properties, and application areas of IRF versus REX FPO’s.

During the last years, our group has investigated the synthesis and physicochemical properties of functionalized polyolefins. Potential applications of such materials i.e. polymer blends compatibilizers, self-healing & shape-memory materials, reactive bitumen modifiers were also indicated over the conducted studies. Affairs concerning potential catalyst deactivation by functionalized comonomers and other technical issues during in-reactor functionalization were also addressed in our research program.

SEM micrographs of foams based on PC/PP blend.
Left: blend without FPO, Right: blend with FPO as the interphase compatibilizer.

The middle graph presents time-dependent extensional viscosities of compatibilized foam.
Hyperbranched polymers increase the stimuli-responsiveness of hydrogels

Prathyusha Chimala, chimalaprathyusha@gmail.com, Mario Perera, Aissatou Wade, Tucker J. Mckenzie, Neil Ayres. University of Cincinnati, Cincinnati, Ohio, United States

Hydrogels that can undergo dynamic changes in properties including stiffness and swelling are becoming increasingly important in multiple technologies. For example, hydrogels that can behave as a dynamic cell matrix are recognized as able to more accurately capture cellular processes such as fibrosis compared to static hydrogels. However, it has been suggested that in order to observe meaningful changes differences in hydrogel stiffness of several kPa are required. In this work gels are prepared using hyperbranched poly(2-hydroxypropyl methacrylate-stat-mercaptoethyl methacrylate) (poly(HPMA-stat-MEMA)) polymers containing pendent thiol groups. Softening experiments with these gels resulted in stiffness changes of around 9 kPa after a thiol-disulfide exchange reaction using as a small-molecule thiol, compared to only 4 kPa for similar gels prepared using linear polymers. The hydrogels also demonstrated healing behavior when treated with external stimuli such as hydrogen peroxide. These results demonstrate how polymer architecture can be used to increase the stimuli-responsiveness of synthetic hydrogels.
Synthesis of rotaxane cross linkers with a radical type mechanophore to visualize dynamic behavior of slide ring materials

Daisuke Aoki¹, daoki@polymer.titech.ac.jp, Hirogi Yokochi¹, Roman Boulatov², Hideyuki Otsuka¹. (1) Tokyo Kogyo Daigaku, Meguro-ku, Tokyo, Japan (2) University of Liverpool, Liverpool, Merseyside, United Kingdom

Rotaxane cross-linked polymers (RCPs) have been attracted attentions because of their excellent capacities to dissipate local stress accumulated at the cross-linked points. However, the correlation between microscopic and macroscopic failure mechanism derived from a ring-sliding process has not been revealed yet. In this study, to reveal the failure mechanism of RCPs, deformation and stress relaxation processes derived from rotaxane structures at the cross-linked points were visualized through the activation of mechanophore. Namely, mechanochromic rotaxane-linked polymers (MCRPs) was developed by the introduction of difluorenylsuccinonitrile (DFSN) mechanophore which is homolytically cleaved into pink-colored stable radicals upon mechanical stress, into the rotaxane cross-linked points. The generated carbon-centered radicals can be evaluated quantitatively by electron paramagnetic resonance (EPR) spectroscopy in the bulk, which enables the quantitative evaluation of the extent of DFSN activation. The mechanocromic properties of the resulting MCRPs were characterized by comparison with covalently cross-linked polymers which were cross-linked by DFSN without rotaxane structure.
Preparation, stability and film properties of cationic polyelectrolyte latexes

Chen Hua¹, Kaimin Chen², Xuhong Guo¹, guoxuhong@ecust.edu.cn. (1) School of Chemical Engineering, East China University of Science and Technology, Shanghai, Shanghai, China (2) College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, China

Cationic latexes have gained wide attention due to their unique properties and potential applications in such as wood coatings and fabric treatment. However, the poor stability of cationic latexes hampers the practical applications. Herein, synthesis of stable cationic polyacrylate latex with core-shell structure was described. Methacrylatoethyl trimethyl ammonium chloride (DMC), 2-(dimethylamino) ethyl methacrylate (DMAEMA) and 2-aminoethyl methacrylate hydrochloride (AEMH) were used as cationic comonomers in the aqueous semi-continuous seeded emulsion polymerization of methyl methacrylate (MMA) and butyl acrylate (BA) using a commercial cationic emulsifier cetyl trimethyl ammonium bromide (CTAB) in the presence of a cationic azo initiator 2,2'-azobis[2-(2-imidazolin2-yl)propane] dihydrochloride (AIBI) at 75°C. The main structure of the three cationic comonomers is identical, however, the substituents on nitrogen atom are different. The core-shell structure and morphology of the resulted latex particles were observed by TEM. With increasing the DMC dosage, the particle size and water absorption increased, while coagulation rate and water contact angle decreased. It was revealed that the addition of cationic comonomer DMC could efficiently improve the alkali resistance of latex, while the same molar concentration of DMAEMA and AEMH didn't show the same effect on alkali resistance of the latexes.

Fig. 1 TEM micrograph of cationic polyacrylate latex particle P(MMA-BA)/P(MMA-BA-DMC) with core-shell structure.
High throughput characterization of phase behavior in polymeric aqueous two-phase systems

Graham P. Abramo², gp_abramo@yahoo.com, Lizbeth Rostro², Kaylie Young², Caroline Nimako-Boateng¹, Tyler Webber¹. (1) Dow Chemical Co Collegeville, Collegeville, Pennsylvania, United States (2) Dow Chemical Co, Lake Jackson, Texas, United States

Aqueous systems containing two water soluble polymers can separate into a biphasic system where each phase is enriched in one of the soluble polymers. The boundary between the monophasic and biphasic regions of the phase diagram is dependent on the concentration of the two polymers in solution. This type of phase behavior in polymeric systems, such as mixtures of dextran and polyethylene glycol, is well known and has been applied to the separation of biomolecules. High throughput phase analysis workflows have been developed by Dow, and they are well suited to the characterization of such biphasic systems. Automated image capture and image analysis allow for the quick determination of the boundary between the monophasic and biphasic regions of the phase diagram. Acrylic acid homopolymers and copolymers containing acrylic acid were blended with polyethylene glycol containing polymers, and the phase behavior was investigated. The effect of polymer composition on phase behavior will be discussed.
Fluorescence active waterborne epoxy adhesive for art conservation via GQDs stabilized RAFT mediated emulsion polymerization

Sarthik Samanta¹, sarthikpsta@gmail.com, Nikhil K. Singha¹,². (1) Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India (2) School of Nanoscience and Technology, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India

Nowadays, epoxy-based adhesives are mostly used in art conservation because of their glossiness and excellent adhesion strength. However, due to the colorless nature of the epoxy adhesives, it is very difficult to detect an artifact’s repaired location. Thus, a fluorescent adhesive is needed which can emit the bright color under UV light but remains invisible in normal light so that we can easily detect the joint without affecting its physical appearance. Herein, we have developed waterborne epoxy-based fluorescent adhesive for art conservation. The adhesive is prepared by graphene quantum dots (GQDs) ornamented block copolymer, (poly(1-vinyl-2-pyrrolidone)-block-poly(glycidyl methacrylate) (PVP-b-PGMA)) synthesized via reversible addition-fragmentation chain transfer polymerization (RAFT) mediated emulsion using polymerization-induced self-assembly (PISA) technique. The adhesive shows the blue color under the UV light but remains colorless in normal light, indicating the fluorescence property which is confirmed by both the UV-visible and Photoluminescence (PL) spectra. The fluorescent emulsion was glued on both glass and ceramic substrates for measuring the adhesive property. Moreover, the whole process was carried out in aqueous media and the graphene quantum dots (GQDs) used for the fluorescent property was synthesized from citric acid, leading to the sustainability and environmental friendliness of this work. Finally, we believe that this kind of new waterborne epoxy-based fluorescent adhesive will provide a new contrivance among the art conservators to repair or reconstruct the artifacts.
Linear and hyperbranched perylene based polyimides: Polymerization and hybridization with molybdenum disulfide nanosheets

Amal Abdulrahman, Amal.mo.sa@hotmail.com, Ishrat M. Khan. Chemistry, Clark Atlanta University School of Arts and Sciences, Atlanta, Georgia, United States

In the past few decades, conjugated polymers have been discovered and later recognized by a Noble Prize in 2000. Polythiophene with low band gap of 1.9 eV is one of the most studied conjugated polymers. However, polythiophene is a p-type polymer, and there is a need to develop n-type low band gap polymers to achieve unique advantages over traditional metallic materials and fullerene such as light-weight and tunable photoconductivity. Here we show that the dimensional geometry in linear-, tri- and tetra-perylene-based polyimides significantly affects the conductivity and the possible hybridization with 2D-molybdenum disulfide in both solvothermal and hydrothermal synthesis. The hydrothermal synthesis of linear and hyperbranched polyimides in only water without a catalyst or organic solvents was examined resulting in unique properties such as the crystals with regular repeating array. The thermal stability of the polyimides was examined demonstrating high decomposition temperatures as observed for Tetra-PPI at (899 °C) with only 29.5 % weight loss. Furthermore, morphologies of the linear and hyperbranched polyimides reflected fibril- or flake-like structures. The presence of MoS2 promotes not only the conductivity but also the thermal properties and the 2D polymerizations and growth noting that the dispersions stability of various nanocomposite samples were stable > 8 months in water. The calculated band gap of linear PPI/MoS2 resulted in a low band gap of 1.25 eV, and almost forty-degree increase in the glass transition of Tri-PPI. Therefore, hyperbranched structures can be a far superior matrix for nanocomposites. We anticipate this study to be a starting point for more n-type polymers and nanocomposites due to the possible correlation between the design and the tunable properties based on the perylene core substitutions, the nature of the connected monomers and the filler.
Sustainable controlled radical polymerization of para-substituted styrene by alkali metal lewis-base hydrogen atom transfer catalyst

Saerona Kim¹, skim216@esf.edu, Hyun Yu¹, Udaya S. Dakarapu², Junha Jeon², Gyu Leem¹,³. (1) Chemistry, SUNY College of Environmental Science and Forestry, Syracuse, New York, United States (2) Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas, United States (3) The Michael M. Szwarc Polymer Research Institute, Syracuse, New York, United States

Hydrogen atom transfer (HAT) mediators are useful for radical chemistry in chemical synthesis. HAT is involved in the termination step of radical reactions between hydrogen atom and carbon-centered radical. This work focused on the kinetic aspects of the Lewis base-catalyzed, complexation-induced hydrogen atom transfer (LBCI-HAT) polymerization by evaluating the following key factors: (1) the extent of para-substituted styrene bearing electron-withdrawing and electron-donating groups, the coordinating agents effects, and (3) ligand effects in the presence of LB. The FT-NIR allows the time-resolved measurement of monomer conversion in radical polymerization to study polymerization reaction kinetics. The coordinating agent, 18-crown-6-ether, has a significant influence on the polymerization rate. The value of –dln[M]/dt obtained by linear fitting of the first-order kinetic plots of the monomer conversion was 11×10⁻² s⁻¹ for the presence of 18-crown-6-ether. In addition, the polymerization rate of styrene without a substituent showed four times faster than that of the EDG-substituted styrene (St-OMe). Moreover, we elucidated the LBCI-HAT-radical polymerization pathways and structure-reactivity correlation in LBCI-HAT. The LBCI-HAT-radical polymerization offers the scope of controlled polymer architectures in open air.

LB: Lewis base catalysis, R: substituents containing electron-withdrawing and electron-donating
Microstructures and reaction mechanisms of cationic Pd(II) α-diamine catalyzed polyolefins

Anthony P. Gies¹, apgies@dow.com, Zhe Zhou¹, Sukrit Mukhopadhyay², Alex Kosanovich¹, Richard Keaton¹, Evelyn Auyeung³, Huong Dau⁴, Anthony Keyes⁴, Dain Beezer⁵, Eva Harth⁴, (1) Core R&D, Dow Chemical Co Freeport, Lake Jackson, Texas, United States (2) Core R&D, Dow Chemical Co, Midland, Michigan, United States (3) Packaging and Specialty Plastics R&D, Dow Chemical Co Freeport, Lake Jackson, Texas, United States (4) Chemistry, University of Houston, Houston, Texas, United States (5) Chemistry, Fisk University, Nashville, Tennessee, United States

Recently, metal-organic insertion light initiated radical (MILRad) polymerization was reported as a new route for producing diblock copolymers of 1-hexene and methyl acrylate. This method combined coordination-insertion and radical polymerization using a single cationic Pd(II) α-diamine (CPD) catalyst, where the polymerization mechanism could be selectively switched by an external photo-stimulus. The novelty of using a single photo-responsive catalyst for block copolymer synthesis prompted the need to elucidate the mechanism of this unique polymerization. In this presentation, a combination of ultra-high resolution mass spectrometry (MS), MS/MS fragmentation, and nuclear magnetic resonance (NMR) spectroscopy will be used to probe the reaction mechanisms, endgroups, and architectural distributions within CPD-catalyzed polyolefins. Highlights of this study include a number of key findings: (1) MALDI-MS, NMR, and TEMPO radical trapping studies effectively demonstrated that metal-organic insertion light initiated radical (MILRad) polymerization proceeds through both coordination-insertion and radical processes, where reactivity can be selectively switched by an external blue light irradiation resulting in homolytic cleavage of the Pd-carbon bond; (2) detailed characterization information was used to update the CPD-catalyzed polyolefin end-capping hypothesis to include a range from one to three terminal methyl acrylate groups, with preference for one methyl acrylate group, before rearrangement into a stable six-membered ring resting state; and (3) lastly, it was discovered that the MS/MS fragmentation patterns displayed “fingerprint” product ions that could be used to explain the CPD “chain walking” induced hydrocarbon branch distributions, observed by NMR, via C-C bond cleavage and 1,3- and 1,4-hydrogen shift reactions. This diagnostic information was used to develop a general degradation model to assist in the characterization of CPD-catalyzed polyolefins. Examples will be given on the use of this general fragmentation model, and computational chemistry, to probe the reaction mechanisms of MILRad polyolefins.
Styrenic star polymers via RAFT polymerization

Madalyn R. Radlauer, madalyn.radlauer@sjsu.edu, Dana A. Wong, Jessica C. Rodarte. Chemistry, San Jose State University, San Jose, California, United States

Structured polymers can be used in a host of applications from adhesives to catalysis. This project focuses on the synthesis of polystyrene-based star polymers by reversible addition-fragmentation chain transfer (RAFT) polymerization to achieve reproducible size and arm density for each star. RAFT polymerization is ideal for our future research goals because of the functional group tolerance of the method. Our optimization studies of arm-first synthesis of star polymers included altering the solvent, temperature, chain transfer agent (CTA), and ratios of reagents in the cross-linking reactions to make the cores of the stars. RAFT polymerization to make the polystyrene arm, also called the macro-CTA, proceeded with low dispersity and high end group fidelity. In the cross-linking reactions to form the cores of the star polymers, varying the ratio of macro-CTA to cross-linker to monomer significantly impacted the number of arms incorporated into each star and the overall efficiency of the reaction. Both crude and purified star polymer products were characterized via spectroscopic and chromatographic methodologies. Ongoing studies include the incorporation of functional monomers into the star polymer cores using the optimized synthesis.
CTA concentration effects on rate retardation in RAFT

Kate G. Bradford¹, bradfokg@miamioh.edu, Leilah Petit¹, Richard Whitfield², Athina Anastasaki², Christopher Barner-Kowollik³, Dominik Konkolewicz¹. (1) Miami University, Oxford, Ohio, United States (2) Eidgenossische Technische Hochschule Zurich Departement fur Materialwissenschaft, Zurich, Zürich, Switzerland (3) Queensland University of Technology, Brisbane, Queensland, Australia

Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization is an extremely powerful tool for polymer chemists as it allows for low molecular weight distribution, controlled molecular weight, and is compatible with a wide variety of functional groups. An unusual phenomenon that is seen in RAFT polymerization is rate retardation which occurs when polymerization deviates from ideal linearity in the form of induction periods and a decrease in the steady state rate. Kinetic models, such as Slow Fragmentation and Intermediate Radical Termination, have been extensively studied and debated over the past twenty years in order to understand why these deviations occur. Most of these experiments used to explore rate retardation used more active monomers (MAMs) with dithiobenzoate chain transfer agents (CTAs). In this paper, we explore a wide variety of different polymeric systems to see how rate retardation occurs beyond the traditional scope of dithiobenzoate CTA with MAMs, while maintaining constant concentrations of radical initiator. We found that rate retardation not only occurs with dithiobenzoates systems, but also for systems that use trithiocarbonates and xanthates CTAs. The data was analyzed using both the Slow Fragmentation and Intermediate Radical Termination models and showed that retardation can be described using a single relationship for a variety of monomer reactivity and corresponding optimized CTA. This provides evidence that the rate retardation is a universal phenomenon amongst a variety of different polymeric systems with varying CTA composition.
Depolymerizable ROMP polymers based on fused ring cyclooctene monomers

Junpeng Wang. wangjp.duke@gmail.com. School of Polymer Science and Polymer Engineering, University of Akron, Akron, Ohio, United States

A promising solution to address the challenges in plastics sustainability is to replace current polymers with chemically recyclable ones that can depolymerize into their constituent monomers for the circular use of materials. Despite the progress, few depolymerizable polymers exhibit the excellent thermal stability and strong mechanical properties of traditional polymers. Here we report a series of chemically recyclable polymers that show excellent thermal stability (decomposition temperature > 370 degree celsius) and tunable mechanical properties. The polymers are formed via ring-opening metathesis polymerization of cyclooctene with a trans-cyclobutane installed at the 5,6-positions. The additional ring converts the non-depolymerizable polycyclooctene into a depolymerizable polymer by reducing the ring strain energy in the monomer (from 8.2 kcal/mol in unsubstituted cyclooctene to 4.9 kcal/mol in the fused ring). The fused-ring monomer enables a broad scope of functionalities to be incorporated, providing access to chemically recyclable elastomers and plastics that show promise as next-generation sustainable materials.
Soft and bright multiscale, multicolored fluorescent polymer particles for labeling

Nikunjkumar R. Visaveliya, nvisaveliya@ccny.cuny.edu. Chemistry and Biochemistry, The City College of New York, New York, New York, United States

Labeling through fluorescent materials are increasingly advantageous for in vivo and in vitro imaging applications for diagnostic and theranostic purposes. A wide range of various fluorescent organic dyes is routinely utilized for various labeling purposes due to their easy use, low cost, availability of full emission wavelength range. However, organic dyes are very sensitive to their surrounding in which they rapidly degrade either via chemical degradation or photodegradation. In order to avoid the concern of degradability, inorganic nanoparticles, in particular, quantum dots are highly versatile and photostable. However, quantum dots are relatively toxic to biological systems, and hence their widespread and safe uses are a concern. Alternatively, dye-doped polymer particles are promising for labeling and imaging due to their properties that overcome limitations of photodegradation as well as toxicity. Fluorescent polymer particles can be prepared simply by incorporating fluorescent dyes in the polymer nanoparticle matrix. In this work, various experimental strategies for the nanoscale fluorescent polymer particles have been developed to bind the fluorophores inside the matrix covalently or non-covalently, as well as at the surface through direct adsorption or based on bio-conjugation. Besides, hydrophilic and hydrophobic microscale fluorescent polymer particles were prepared via photopolymerization by droplet microfluidics. Highly controlled color compositions were inserted inside the fluorescent polymer microparticles, and a color combination library of the multi-colored fluorescent polymer microparticles was synthesized. Furthermore, soft and bright particulate assemblies were enabled through interfacial interactions at the intermediate scale between the nanometer and micrometer length scale.
Tailor-made self-healable polymers using exchangeable ‘click chemistry’

Prantik Mondal, mprantik3@gmail.com, Nikhil Singha. Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India

Traditional synthetic polymer materials often undergo macroscopic damages on countering several adventitious environmental stimuli that lead them to catastrophic failure. As a potential alternative to improve the longevity of synthetic polymer materials, self-healing is one of the on-demand strategies that has been effectively exploited to mitigate the concerns. In 2013, the World Economic Forum and Global Agenda Council announced the top 10 emerging technologies; “Self-healing materials” was one of them. Since its inception, the ‘click chemistry’ concept is widely exploited to design numerous advanced materials having interesting structural and functional properties (e.g., self-healing, shape-memory, etc.). The ‘click chemistry’ has become a ubiquitous tool, due to its high modularity and orthogonality, to prepare diverse polymer materials. Although the original definition of Sharpless is contradicted, the ‘click’ reactions that are reversibly exchangeable (under certain stimulus) have gained significant interest in developing recyclable/healable thermosets. With a motive to develop polymer materials that can find promising applications in specialty coatings, paints, adhesives, etc., herein, the investigations centralize on the execution of fast and exchangeable ‘click-unclick’ approaches to develop self-healing polymethacrylates associated with a few additional characteristics viz., recyclability, shape-memory, fluorescence, etc. via controlled polymerization procedures. The dynamic feature of different ‘click’ crosslinked polymers enabled the healing of microcracks generated in the polymer, exemplified in the present perspective.
Characterization of equilibrium and non-equilibrium properties of bio-based polymers

Alina M. Alb, linocika12@live.com. Kemira Chemicals, Atlanta, Georgia, United States

Natural polymers have become increasingly attractive to both research and industrial communities as need for exploring renewable sources of materials increased due to environmental and sustainability concerns. Their applicability covers multiple areas - food, energy, pharmaceutics, etc. - and continues to expand with the addition of synthetic polymers. Comprehensive characterization of materials is especially challenging in the case of natural products, due to variability in sources and extraction conditions. The aim of this study is to outline equilibrium and non-equilibrium properties of natural products, captured and quantified by light scattering-based separation and non-separation chromatographic techniques combined with thermal analysis methods. Relevant polymer characteristics such molecular weight, size, morphology, together with non-equilibrium processes, such aggregation, degradation, and thermal behavior are highlighted for selected case studies. It is hoped that the knowledge gained will lead to increased understanding and expertise.
While branched polyethylene is ubiquitous in technological applications, structural characterization of these polymers remains a challenge. Commercial separations of polyethylene often contain a mixture of linear, short-chain branched, and long-chain branched polymers that have overlapping hydrodynamic sizes and solubility making it difficult to determine the underlying mixture components. Here, we perform molecular dynamics simulations using an experimentally inspired potential to study the structure-property relationships of branched polyethylene in the dilute regime. In particular, we calculate experimentally accessible properties such as the hydrodynamic radius, radius of gyration, and intrinsic viscosity. When possible, we compare our results directly to experiments of linear low-density polyethylene in which branch spacings and lengths are precisely controlled and systematically varied. After validating our model, we expand the structure-property library of precisely generated low-density polyethylene beyond current experiments to include branch spacings that are commercially relevant.

This Mark-Houwink plot compares our molecular dynamics results to experiments of linear low-density polyethylene with precisely eight carbons between branches that are X carbons long where X is varied between two and ten.
Non-degradable plastics waste issue is a global challenge that requires urgent attention due to its harmful impact on humans and the environment. Lignin is an important biomass that can be a raw material to produce functional polymers. Lignin is abundant, cheap, sustainable raw material that contains high concentration of aromaticity. However, not well-defined chemical modifications and characterizations limit the practical applications of lignin as a new sustainable raw material. This presentation will discuss how the biomass lignin can be covalently integrated with aliphatic polyesters to produce biomass-based biodegradable polymers. Poly(ethylene brassylate) (PEB) is an aliphatic polyester that is graft copolymerized to a lignin. The synthesized new lignin-based polymer is lignin-graft-PEB. PEB is relatively unexplored polymer that is derived from sustainable resource, castor oil. Prior to the graft copolymerization, lignin was chemically modified by sebacic acid to introduce a carboxylic acids onto lignin. Lignin’s abundant hydroxyl groups were used for the modification forming ester links. Another precursor of the graft copolymer, PEB was prepared by ring-opening polymerization of ethylene brassylate in the presence of a catalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The graft copolymerization between modified lignin and PEB was occurred by thermally catalyzed esterification. The chemical structure of the synthesized lignin-graft-PEB was determined by 2D NMR, HSQC. The progress of the chemical reactions during polymerization was demonstrated by consumption of 1,5,7-triazabicyclo[4.4.0]dec-5-ene terminus of PEB and carboxylic acid of modified lignin.
Renewable bio-based benzoxazine thermosets based on di-furan amines (dfda) with superior performance

MENGWEN YU, mengwenyususie@gmail.com, Giuseppe R. Palmese. chemical and biological engineering, Drexel University, Philadelphia, Pennsylvania, United States

A new class of benzoxazine monomers made from difuran diamine (DFDA), obtained by the coupling of furfuryl amine using formaldehyde, will be discussed. The benzoxazine monomers were synthesized by reacting DFDA with several bio-based phenolic compounds and formaldehyde. These systems were purified by precipitation. Depending on composition, the resulting solid powders melt at temperatures ranging between 50 °C and 150 °C to form low viscosity liquids that can be readily used to impregnate fiber reinforcements. Onset cure temperature also varies depending on composition in the range of 150–240 °C. The resulting polybenzoxazines have Tgs ranging from 240 to 300 °C. By observing curing processes with the use of TGA and FTIR, it was found that the phenolic structure selected would affect curing mechanisms of DFDA-based benzoxazines; benzoxazines that have available ortho or para positions on the phenolic structures could finish curing reactions without any mass loss. It was also found that adding furan rings into the backbone of the polybenzoxazine network provided the added benefit of 800 °C char yield as high as 60%, as measured by TGA temperature ramps in an inert environment. Compared with benzene-ring-based benzoxazines, furan-based benzoxazines showed better thermal stability due to higher crosslink systems. In addition to promising processing and thermal characteristics useful for applications requiring high temperature ablation resistance, these materials contain high renewable content.
Olefin metathesis polymerizations have enabled the synthesis of a large variety of polymers such as polyalkenamers or poly(arylene vinylene)s. While numerous studies have shown that the stereochemistry of the alkenes in the polymer backbone has a notable impact on the physical properties of the polymer, the synthesis of stereodefined polymers via olefin metathesis remains a great challenge. Most metathesis catalysts operate under thermodynamic control, which generally favors E (trans) linkages. Therefore, the properties of polymers with high-cis content are generally underexplored due to a scarcity of synthetic methods to access these structures. Within these polymers, poly(p-phenylene vinylene)s (PPVs), consisting of alternating alkenes and phenyl groups in conjugation, is of special interest. Indeed, the cis/trans configuration of the olefins on the PPV backbone significantly affects its physical properties including optical behavior and solubility. In addition, one-way photoisomerization can readily transform olefins in the PPV backbone from the cis to the trans configuration, rendering PPVs a stimuli-responsive material. In this presentation, we will discuss a unique strategy to access all-cis PPVs with living characteristics capitalizing on the polymerization of paracyclophane diene monomers via stereoretentive ring-opening metathesis polymerization (ROMP). Investigation of the kinetics of the polymerization and its living character will be highlighted. Finally, applications to the synthesis of photoresponsive diblock copolymers will be presented with an eye towards the construction of intricate and well-defined polymeric architectures containing all-cis PPVs as stimuli-responsive materials.
Characterizing the connection between polymer structure and rare-earth element chelation in water

Michael D. Schulz, mdschulz@vt.edu, William Archer. Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Rare-earth elements (REEs: La–Lu, Y, and Sc) are integral to modern technology. As technological development continues, world demand for these metals will increasingly outpace supply. Consequently, new and sustainable sources are needed, as well as more efficient methods of extraction and purification. Many waste streams—mining effluents, desalination brines, e-waste, and wastewater from semiconductor fabrication plants—contain high concentrations of REEs, which could be extracted. Metal-chelating polymers have great potential in REE extraction and separation applications due to their relatively low cost and high affinity for target elements. To investigate the interplay between polymer structure and metal chelation, we used isothermal titration calorimetry to directly measure the binding affinity, enthalpy changes, and stoichiometry of the interactions between a series of REEs in solution and metal-chelating polymers. These measurements enabled us to characterize the complete thermodynamic profile of these polymer-metal interactions. Further measurements of changes in heat capacity and solvent isotope effects, along with computational data, reveal the key role of water during metal binding.
Green analogs of polybutadienes from carbon dioxide and epoxy based feedstocks

Muhammad Rabnawaz, rabnawaz@msu.edu. Packaging, Michigan State University, East Lansing, Michigan, United States

Polybutadiene has widespread use as a commodity as well as a specialty polymer, but currently, it is prepared from nonrenewable feedstocks. In this presentation, I will discuss our latest approach where rubbery unsaturated polycarbonates were designed as green alternatives for polybutadiene via the copolymerization of carbon dioxide and a mixture of saturated and unsaturated longchain epoxides using a Co catalyst. The RUPCs were reacted with a styrene monomer via free radical polymerization with styrene to prepare their graft copolymers. All of the prepared polymers were characterized by 1H nuclear magnetic resonance spectroscopy and gel permeation chromatography, and differential scanning calorimetry analysis. After polystyrene chains had been grafted onto the RUPC backbone, the Tg increased to 81°C. These green RUPCs have the potential to replace nonrenewable polybutadiene in some applications such as high impact materials.
Water-soluble polyion complex (PIC) micelles covered with polyampholyte shells

Shin-ichi Yusa, yusa@eng.u-hyogo.ac.jp. Department of Applied Chemistry, Hyogo Kenritsu Daigaku - Himeji Kogaku Campus, Himeji, Hyogo, Japan

We have prepared a polyampholyte \( \text{P(SA)}_{91} \) composed of anionic sodium 2-acrylamido-2-methylpropanesulfonate (AMPS, S) and cationic 3-acrylamidopropyl trimethylammonium chloride (APTAC, A) via reversible addition-fragmentation chain transfer (RAFT) radical polymerization. The subscript in \( \text{P(SA)}_{91} \) indicates degree of polymerization (DP). \( \text{P(SA)}_{91} \) can dissolve in pure water to form small inter-polymer aggregates. In aqueous solutions of NaCl, \( \text{P(SA)}_{91} \) can dissolve in the unimer state. When protein and polyelectrolytes were mixed in phosphate buffered saline (PBS), the hydrodynamic radius (\( R_h \)) and light-scattering intensity (LSI) increased. There was no interaction between \( \text{P(SA)}_{91} \) and protein, because corresponding increases could not be observed. Furthermore, AMPS was polymerized using \( \text{P(SA)}_{91} \) macro-chain transfer agent (CTA) to prepare an anionic diblock copolymer \( \text{P(SA)}_{91}S_{67} \). APTAC was also polymerized using \( \text{P(SA)}_{91} \) macro-CTA to prepare a cationic diblock copolymer \( \text{P(SA)}_{91}A_{88} \). The DP values were estimated with a quantitative \( ^{13} \text{C} \) NMR technique. Charge neutralized mixture of aqueous solutions of \( \text{P(SA)}_{91}S_{67} \) and \( \text{P(SA)}_{91}A_{88} \) formed water-soluble polyion complex (PIC) micelles comprising a PIC core and \( \text{P(SA)}_{91} \) shells (Figure 1). Interactions between the PIC micelles and protein in PBS were evaluated by changing \( R_h \) and LSI. Increases in \( R_h \) and LSI cannot be observed for the mixture of PIC micelle and protein in PBS. This observation suggests that there is no interaction between the PIC micelles and proteins, because the surface of the PIC micelles was covered with polyampholyte shells.

![Chemical structures](image)

**Fig. 1** Chemical structures of \( \text{P(SA)}_{89}S_{67} \) and \( \text{P(SA)}_{89}A_{88} \) and schematic representation of polyion complex (PIC) micelle formed from \( \text{P(SA)}_{89}S_{67} \) and \( \text{P(SA)}_{89}A_{88} \).
Swelling behavior and tunable mechanical properties of lactose containing polyurethane hydrogels

Emily Dalton, daltonemy@mail.uc.edu, Neil Ayres. Chemistry, University of Cincinnati, Cincinnati, Ohio, United States

Polyurethanes (PUs) are a broad class of versatile and widely used polymers due to their toughness, durability, flexibility, and biocompatibility. The controllable properties of polyurethanes such as elastic moduli and Tg, have allowed their use in the development of biomedical devices ranging from catheters to artificial hearts. Hydrogels, another broad class of biomaterials, find applications as scaffolds/implants in tissue engineering, synthetic extracellular matrices, and drug delivery. However, hydrogels prepared using conventional methods, such as free-radical polymerization, exhibit poor mechanical performance, thereby limiting their potential applications as biomaterials. This work presents the design and synthesis of functional sulfated lactose-containing PEG-PU hydrogels. The effects of PEG molecular weight, degree of crosslinking, degree of ionization, and resulting swelling behaviors were studied. The sulfated swollen hydrogels showed excellent swelling ratios (300-700%) and the corresponding dry materials exhibit high mechanical strength similar to traditional thermoplastic polyurethanes (G'~ 1 GPa). These PU-hydrogels combine the biocompatibility and durability of polyurethanes with the hydrophilic and high swelling nature of hydrogels to prepare materials with wide potential applications in tissue engineering and wound healing.
Enzymatic catalysis has been attracting increasing interest in the design and synthesis of functional polymers and hydrogels in a mild, efficient, and environmentally friendly fashion compared to conventional techniques including photo-irradiation and redox initiation. A well-established method of generating hydrogels involves the use of hydrogen peroxidase (H2O2) and β-diketone (e.g., acetylacetone (ACAC), 1,3-cyclopentadione) in the presence of horseradish peroxidase enzyme (HRP) to generate carbon-centered radicals that can initiate chain polymerization to create three-dimensional, cross-linked hydrogels. However, ACAC has relatively high toxicity and may cause an irreproducible induction period, calling for the need for a safer and more efficient system of hydrogel generation. It remains challenging to demonstrate an HRP-mediated initiating system without β-diketones.

Here, we report a novel ternary radical initiating system containing HRP, H2O2, and N-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (HONB). This initiating system readily generates a nitroxide radical to trigger polymerization and hydrogelation at room temperature (approx. 22 °C) in aqueous media with oxygen tolerance and works with a variety of monomers and crosslinkers of various concentrations, and nanoparticles of various sizes. Furthermore, the gelation time can be controlled by easily adjusting the pH value of reaction media ranging from 2.3 to 7.5 or varying the molar ratio of the individual components of the ternary initiating system. This technology can be used in various biological and industrial applications and bring forth the advancement of polymer chemistry.

![Diagram showing the ternary radical initiating system containing HRP, H2O2, and HONB, resulting in the formation of a hydrogel.]
Formation mechanism of hydrogel microspheres during precipitation polymerization

Yuichiro Nishizawa\textsuperscript{1}, 19hs113k@shinshu-u.ac.jp, Haruka Minato\textsuperscript{1}, Takumi Inui\textsuperscript{1}, Takayuki Uchihashi\textsuperscript{2}, Daisuke Suzuki\textsuperscript{1}. (1) Shinshu University, Ueda, Japan (2) Nagoya University, Nagoya, Japan

Although techniques to produce uniform-sized hydrogel microspheres (microgels) by aqueous free-radical precipitation polymerization are well established, the details of the polymerization mechanism remain mysterious because of the limitation associated with the spatio-temporal resolution of imaging techniques. In the present study, the structural evolution and thermoresponsiveness of the developing microgels during the precipitation polymerization were evaluated using temperature-controllable high-speed atomic force microscopy (TC-HS-AFM). This analysis revealed that the swelling properties of the precursor microgels formed in the early stages of the precipitation polymerization are quite low and that non-thermoresponsive decanano-sized spherical domains are present in the precursor microgels because of the high incorporation of cross-linkers which is consumed faster than the main monomer (Figure). Furthermore, we succeeded in tracking the formation of formation processes, which has never been fully understood, in aqueous solution using real-time observations. These findings will help us to design functional microgels with the desired nanostructures via precipitation polymerization.

![Temperature dependence of the height images and cross-sectional profiles](image)

Figure. Temperature dependence of the height images (top panel) and cross-sectional profiles corresponding to the red dotted line in height images (bottom) of the microgels polymerized for 1.5 min. Reprinted from [Y. Nishizawa, H. Minato, T. Inui, T. Uchihashi, D. Suzuki, Langmuir \textbf{2021}, 37, 151] with permission from American Chemical Society.
Polyaniline based on phenoxazine and carbazole derivatives with improved electrochemical stability and processability

Mohammed N. Almtiri, mna149@msstate.edu, Colleen N. Scott. Chemistry, Mississippi State University, Starkville, Mississippi, United States

Conductive polymers are characterized by a backbone of alternating single and double bonds, which have shown tremendous electrical, optical, and magnetic properties of metals while maintaining good processability. Among the conductive polymers, polyaniline (PANI) has been widely used due to its ease of preparation and excellent electrical conductivity. However, the emeraldine and pernigraniline salt forms of PANI share some common drawbacks with other organic electronic materials, such as (1) poor solubility in common organic solvents (2) low electrochemical stability of molecular constitutions, which lead to limited processability and insufficiently characterization of the polymer. Herein we present the synthesis and characterization of PANI-derivatives based on phenoxazine and carbazole cores. The polymers were stable and processable. Spectroelectrochemical cyclic voltammetry characterizations of the polymers show high redox stability between the emeraldine and pernigraniline salt forms with remarkable cyclability. The morphologies of the polymer films were studied using (AFM), SEM and TEM. The films were investigated for their conductivity in different dopants and solvent as well as the performance as supercapacitors. Finally, we have studied the polymers' magnetism using Electron Paramagnetic Resonance (EPR) with various dopants.
Iterative exponential growth (IEG) is an efficient, scalable, and convergent strategy for the synthesis of polymers that feature diverse functionality as well as defined stereochemistry, length, and distance between stereogenic centers. With discrete IEG-derived polymers in hand, we have synthesized a new category of polymer-protein conjugates with a controlled conjugation site and size, along with defined stereochemistry and rigidity of polymeric backbones. These discrete conjugates allow us to study the effect of synthetic polymer structure on protein stability, degradation rate under protease, and biological performances of conjugated proteins, which could potentially provide a new approach of controlling biomaterial properties.
A simple Lewis pair catalyst consisting of triethyl amine and trimethyl aluminum (NAl catalyst) was found by Lynd and co-workers to polymerize epoxides of various chemistries at a high rate when in the presence of an aluminum initiator. Here, we investigated the catalyst structure – polymerization kinetics relationships for epoxide polymerizations. Specifically, we synthesized 15 different NAl catalysts with different combinations of substituent groups on the amine and aluminum species. The substituent groups used consisted of alkyls, aromatic rings, and aliphatic rings. We monitored polymerizations of epichlorohydrin (ECH) in the presence of each of these catalysts with $^1$H NMR spectroscopy. We found that the observed polymerization rate constant ($k_{obs}$) varied over nearly four orders of magnitude depending on the catalyst chemistry. Additionally, synthesized polymers were characterized by size exclusion chromatography (SEC) and we found that while molecular weight was largely on target, polydispersity (D) varied wildly. No correlation between $k_{obs}$ and D was observed. Finally, density functional theory (DFT) was employed to better understand the difference in kinetics among the catalysts.
Controlled Ring-Opening Metathesis of 8-Membered Cyclic Olefins Through the Addition of Excess Ligand

Chase B. Thompson, chase.thompson@nist.gov, Robert Ivancic, Debra Audus, Sara V. Orski. Materials Science & Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Ring-opening metathesis polymerization (ROMP) has emerged as a convenient route for creating unsaturated polyolefin precursors with controllable molecular weight and stereoselectivity. ROMP is governed in part by the ring-strain of the monomer: highly strained cyclic species such as norbornene or cyclobutene have a favorable forward ROMP reaction, yielding polymers with controllable molecular weight and narrow dispersity. Cyclooctenes and cyclooctadienes, which exhibit a much lower ring strain than norbornene and cyclobutene monomers, pose a greater challenge when narrow dispersity (D < 1.3), high conversion, and well-defined polymer architectures are desired. These 8-membered rings are prone to side reactions such as back-biting and cross metathesis of growing polymer chains. Here, we present a strategy for reducing the propensity for side reactions by performing ROMP of cis,cis-1,5-cyclooctadiene, trans-cyclooctene, and 1-butyl-trans-cyclooctene 8-membered rings in the presence of excess organic ligand; the presence of these excess ligands serve to compete with monomer for occupation of the active catalyst site of Grubbs 3rd Generation Ruthenium catalyst and favor the propagation of polymer chains as opposed to side reactions such as cross-metathesis. Stereoselectivity and molecular weight control are explored by varying the strength and concentration of organic ligands and how they interact with 8-membered rings exhibiting different ring strains. Controlled polymerization of these 8-membered cycloalkenes is investigated as a pathway to synthesizing architecturally diverse model poly(ethylene) compounds with tunable branch length, branch content, and branch distribution.

A kinetic plot showing conversion of a ring opening metathesis polymerizion (ROMP) of cis,cis-1,5-cyclooctadiene (COD) with excess 3-bromopyridine (BrP) or pyridine (P).
Optimization of bottlebrush polymer synthesis by ring-opening metathesis polymerization

Sarah E. Blosch¹, sblosch@vt.edu, Mohammed Alaboalirat¹, Samantha J. Scannelli², Cabell B. Eades², John B. Matson²,¹. (1) Macromolecules Innovation Institute, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Ring-opening metathesis polymerization (ROMP) is a powerful tool to create bottlebrush polymers that have high grafting density and pendant chains with low dispersity. Specifically, the grafting-through method allows for “perfectly grafted” bottlebrush polymers due to each monomer unit containing a pendant side chain. However, grafting-through is limited to bottlebrush polymers with relatively low molecular weight pendant chains as well as backbones with lower degrees of polymerization when compared to other bottlebrush polymer synthetic methods. The objective of this research is to optimize grafting-through ROMP by determining the ideal polymerization conditions, specifically how solvent choice and purity affect the propagation kinetics. To achieve this, a polystyrene macromonomer was synthesized, and ROMP was performed using Grubb’s third generation ruthenium catalyst (Figure 1), and six different solvents with varying levels of purity. This solvent study allowed us to identify solvents that enable the greatest “livingness” in ROMP as well as determining which solvents are usable as received and which need further purification. By optimizing grafting-through in ROMP, bottlebrush polymers with longer backbones and/or pendant chain lengths as well as materials with unique shapes could be synthesized.
Self-condensing ring opening metathesis polymerization: A novel approach to hyperbranched polymers

Hanan Almuzaini, hanana@vt.edu, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Self-condensing vinyl polymerization and self-condensing ring-opening polymerization have long been used to prepare hyperbranched polymers using an inimer, a single molecule that can act as both initiator and a monomer. This concept of self-condensing polymerization has also been expanded to include radical chain transfer agent (CTA)-monomer molecules, which produce hyperbranched polymers via radical addition-fragmentation chain transfer (RAFT) polymerization. However, a self-condensing polymerization approach has not yet been applied to ring-opening metathesis polymerization (ROMP). In this study, we synthesized a ROMP-inimer with both an initiating and propagating site (Figure 1). The ROMP-inimer is a latent azo-based chelating ruthenium olefin metathesis catalyst with a polymerizable unsaturated ring. The inimer is stable at room temperature and readily activates upon heating. During polymerization, the norbornene anhydride on the benzylidene ligand opens and becomes a branch point on the growing polymer chains.

![Diagram of the ROMP-inimer synthesis](image-url)
Metal-free catalytic processes based on main-group elements have been demonstrated for a wide range of organic reactions, potentially enabling more sustainable and less toxic industrial processes. Frustrated Lewis Pairs (FLPs) are a particularly promising approach based on bulky Lewis acids and bases, whose steric crowding prevents the formation of a Lewis pair adduct. The unquenched Lewis basic and acidic centers are therefore able to interact cooperatively to activate substrates and thus catalyze reactions, including hydrogenations, hydrosilylations, and C-H activations among many others. However, the moisture-sensitivity and poor separability of typical small-molecule FLP catalysts hinder their applicability in comparison to established transition-metal catalysts.

One avenue to recyclable metal-free catalysts is the incorporation of catalytically active species into polymers, which allows for the immobilization of the catalyst using resins or separation using solvent-solvent techniques. Recently, we developed a new approach based on Ring-Opening Metathesis Polymerization (ROMP) to generate bench-stable polymer-supported Lewis acids for FLP catalysis. In this presentation we will discuss our further explorations of this ROMP-borane system. This work provides a novel adaptation of FLP chemistry to polymers as catalysts that combine the advantages of homogeneous and heterogeneous catalysis.
Controlled ring opening polymerizations in milliseconds by using sterically hindered strong bases

Binhong Lin², Caleb Jadrich², Vince Pane², Pedro Arrechea¹, Tim Erdmann¹, tim.erdmann@ibm.com, Charles Dausse¹, J Hedrick¹, Nathan Park¹, Robert M. Waymouth². (1) IBM Almaden Research Center, San Jose, California, United States (2) Department of Chemistry, Stanford University, Stanford, California, United States

Anionic ring-opening polymerization (ROP) of epoxides, cyclic esters, and cyclic carbonates with strong bases such as potassium tert-butoxide (KOTBu) or potassium bis(trimethylsilyl)amide (KHMDS) is typically performed as batch reaction, leading to broad dispersity and poor control over the molecular weight ($M_n$) mainly because of insufficient initiator efficiency and transesterification reactions.

We now present that combining a sterically hindered strong base such as KOTBu or KHMDS with a primary alcohol and using a continuous-flow apparatus can afford control and reliability over the ROP and, remarkably, enable the controlled polymerization of traditionally low-activity monomers such as δ-valerolactone and ε-caprolactone in milliseconds. These reactions exhibit characteristics capable of producing narrow dispersity with predictable molecular weights and can rapidly generate well-defined block copolymers at residence times below 0.1 s. With reaction rates that are orders of magnitude higher than the fastest rates reported for urea anions, these reaction conditions offer great potential to expand the breadth of materials accessible.

Comparison of GPC traces from batch and flow polymerizations, employed flow reactor configuration for preparing homopolymers, and used materials.
Side chain density driven morphology transition in brush linear diblock copolymers

Jaemin Park, Sheng Li, shengli@kaist.ac.kr. Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Daejeon, Korea (the Republic of)

Brush-linear type block copolymers represent an interesting class of material as they combine the unique morphological features of the brush polymer with the chain flexibility afforded by the linear polymer. They are expected to exhibit complex phase morphology with characteristics of both coil-coil and rod-coil block copolymers. Previous studies on brush-linear block copolymers have primarily focused on their phase behavior with respect to polymer composition, while the topic of brush density effect on microdomain morphology has not been well explored. In this study, we report the synthesis and self-assembly of brush-linear block copolymers where both the brush side-chain density and chain length are systematically varied. A poly(pentafluorophenyl acrylate-b-styrene) (PPFPA-b-PS) linear diblock copolymer is first prepared as the precursor polymer. The PPFPA block is then reacted with amine-functionalized poly(ethylene glycol) (PEG) to create brush-linear type block copolymers of the chain structure (PPFPA-g-PEG)-b-PS. Different degrees of PEG substitution are conducted, and the resulting brush-linear block copolymers are examined to determine their bulk morphologies by small-angle X-ray scattering (SAXS). As the degree of PEG side-chain substitution increases, block copolymer morphology is found to transition from lamellae to a newly formed frustrated lamellae then to hexagonally-packed cylinder. Furthermore, when PEG chains of longer chain length are used, the same morphology transition is again observed while these transitions occur at even lower degrees of side-chain substitution. Our results illustrate the importance of controlling side-chain density and chain length in determining the phase morphology of brush-linear block copolymers.

Schematic for block copolymer domain morphology transition induced by increasing side-chain density
Poly(ether imide) (PEI) is a high-performance polymer with outstanding thermal stability, mechanical strength, and processability, but a critical drawback of poor solvent resistance. Exposure to solvents including chloroform, dimethylformamide, dichloromethane, and N-methyl pyrrolidone severely compromises the mechanical and thermal performances. Herein, I report a method for preparing thermally crosslinked PEI (X-PEI) from azide terminated PEI (N₃-PEI-N₃) synthesized via a one-pot diazotization-azidation reaction. X-PEI affords unprecedented solvent resistance unpossessed by conventional PEIs, as well as solution processability unrivaled by counterpart high-performance polymers such as polyimide. The glass transition temperature, storage modulus, and swelling ratio correlate positively with crosslinking density, which is determined by the molar mass and azide concentration of N₃-PEI-N₃. This work advances the chemistry of high-performance polymers. The method is generic and applicable to other engineering polymers.
POLY – General Topics: New Synthesis & Characterization of Polymers

Sigmatropic rearrangements of polymer backbones

Aleksandr V. Zhukhovitskiy, alexzhuk@email.unc.edu, Rachael Ditzler, Maxim Ratushnyy. Chemistry, University of North Carolina System, Chapel Hill, North Carolina, United States

Polymer modification is one of the fundamental pillars of polymer chemistry because it grants the practitioner access to a broad scope of materials properties from a small number of polymer scaffolds. Thus far, the central paradigm of polymer modification has been to alter the composition of the polymer periphery—e.g., installation of side-chains—which limits the magnitude and variety of possible changes in polymer properties. In contrast, transforming the composition of the polymer backbone itself has, by and large, gone neglected; yet, the ability to carry out such modification would impart global changes to materials properties on demand. In this talk, I will describe our work on sigmatropic rearrangements of polymer backbones. More than a century since the first report of a sigmatropic rearrangement in 1912, and a plethora of applications in the context of "small" molecules, only ten studies have explored sigmatropic rearrangements in the context of polymers: five of these studies were theoretical, and the rest—peripheral modifications. Our work demonstrates that these powerful concerted rearrangements can, under mild conditions, induce a polymer chain to undergo a metamorphosis from one class of polymers to another, which leads to dramatic changes in polymer properties. Beyond stimulus response, such polymer backbone modification can grant entry to previously inaccessible scaffolds. More broadly, our work advances the sophistication of retrosynthetic analysis applied to polymers.
Investigation of stereoelectronic effects on the synthesis of novel, well-defined, and sequence-specific conjugated polymers by ROMP

Stephen Koehler, sjk73@psu.edu, Margaret Gerthoffer, Tanner Wolf, Elizabeth Elacqua. Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States

Iterative and step-growth methods have long been common means to achieve sequence specificity in conjugated materials. Our method uses tunable, highly strained paracyclophane-1,9-diene (pCpd) frameworks with a pre-defined Donor-Acceptor sequence. ROMP has historically been used to synthesize sequence-specific polymers from monomers based on norbornenes, cyclooctenes, and other cycloalkenes. The pCpd monomer architectures can be comprised of differing aromatic moieties that exhibit differences in electron density and steric encumberment, which has shown promise toward achieving well-defined conjugated polymers. Herein, we detail recent efforts to synthesize sequence-controlled conjugated polymers by interrogating the properties of our monomers, highlighting new routes and strategies to synthesize additional pCpd monomers, further exploring the utility of ROMP to achieve well-defined polymers.
A convergent platform for translating synergistic drug combinations to nanomedicines: Application to multiple myeloma therapy

Alex Detappe\textsuperscript{2,3,4}, Hung V. Nguyen\textsuperscript{1,2,3}, hvtn191@mit.edu, Yivan Jiang\textsuperscript{1}, Michael P. Agius\textsuperscript{2,3}, Wencong Wang\textsuperscript{1}, Celia Mathieu\textsuperscript{2,3}, Nang K. Su\textsuperscript{2,3}, Samantha L. Kristufek\textsuperscript{1}, Irene M. Ghobrial\textsuperscript{2,3}, P. Peter Ghoroghchian\textsuperscript{2,3}, Jeremiah A. Johnson\textsuperscript{1}. (1) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Dana-Farber Cancer Institute, Boston, Massachusetts, United States (3) Harvard Medical School, Boston, Massachusetts, United States (4) Institut de Cancérologie Strasbourg, Strasbourg, France

Current anticancer agents continue to face substantial challenges, including inherently narrow therapeutic indexes (TIs) as well as suboptimal therapeutic combinations, stemming from mixtures of active pharmaceutical ingredients (APIs) with dissimilar properties. While nanomedicine-based platforms for drug delivery can potentially address these challenges, key questions remain, including "do synergistic free drug ratios translate to nanocarriers?" and "are nanocarriers with multiple drugs better than mixtures of single-drug nanocarriers at the same dose?". Here, we report a prodrug platform that allows us to answer these questions in the context of advanced clinical therapies for relapsed multiple myeloma (MM), including bortezomib-based (Btz) monotherapy and combination therapies with Btz, pomalidomide (Pom), and dexamethasone (Dex). For Btz monotherapy, a Btz-“bottlebrush prodrug” (BPD) is designed that enables a 25-fold increase in API dosing when compared to Btz alone and without observable toxicities in mice. Moreover, Btz-BPD significantly slows tumor progression in vivo, providing marked enhancements in survival in subcutaneous and orthotopic models of MM. In the context of combination therapy, BPDs carrying Btz, Pom, and Dex exhibit in vitro synergistic, additive, or antagonistic patterns that are distinct from the free drug counterparts, which is a perhaps expected, yet undemonstrated, phenomenon. Moreover, a BPD carrying all 3 drugs in a synergistic ratio outperforms the free drug combination, mixtures of single-drug BPDs in the same ratio, as well as an antagonistic 3-drug BPD. Together, our results address unanswered questions in the field of combination nanomedicine, establishing a proof-of-concept for macromolecular prodrug-based approaches that are enabled by the unique BPD architecture in order to potentially improve current front-line mono- and combination therapies.
Solution behavior of oligodimethylsiloxane with an ionic liquid chain end (ODMS-IL)

Tianyu Li¹, tli30@vols.utk.edu, Hui Li², Yingdong Luo², Kunlun Hong². (1) Materials Science and Engineering, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States (2) Oak Ridge National Laboratory Center for Nanophase Materials Sciences, Oak Ridge, Tennessee, United States

Polymers modified with a functional group, such as chain end functionalization, have shown to alter their properties and polymer morphologies drastically. Chain end transformation is actually a well-established technique, and polymers with end group of various functionalities such as amine, carboxylic, and zwitterionic groups have been reported. Recently, chain end modifications have been applied to a broader range of polymers including conjugated polymers, polymer electrolytes, and a recent review provides an excellent overview in this area. We recently exploited the use of oligodimethylsiloxane (ODMS) functioned with an ionic liquid group to mimic lipid membranes. In this contribution, we report the synthesis and solution properties of several ODMS-ILs with the same cationic group but different anionic counter ions in various solvents. Dynamic light scattering and small-angle neutron scattering revealed the important roles of the counter ionic groups. These results help us design better polymeric materials for mimicking lipid membranes.
Kinetic investigation on the ring-expansion polymerization of o-phthalaldehyde

Anthony C. Engler, aengler3@gatech.edu, Paul Kohl. Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

Poly(phthalaldehyde) is a metastable polymer that has been shown to rapidly depolymerize from the solid state back into its constituent monomer, a consequence of its low ceiling temperature. This depolymerization upon triggering makes it well suited as a chemically recyclable polymer, and sacrificial materials in semiconductor or other manufacturing. Although interest in phthalaldehyde-based polymers has increased in the past several years, there has not been a thorough investigation of the polymerization kinetics since its discovery in 1967. In this work, a continuous flow reactor was utilized to probe the kinetics of this rapid, cationic polymerization in dichloromethane using boron trifluoride diethyl etherate as the Lewis acid catalyst. Under proper catalyst loadings, polymer nominal molecular weights exceed 250 kDa in 10 seconds of reaction time at -78 °C. Molecular weight and time–conversion data supports two polymerization regimes, which has not been observed before in batch polymerizations of this polymer. The initial chain growth regime involves the creation of many polymer chains of moderate molecular weight. At conversions greater than 70%, a kinetic transition is observed as the polymer chains fuse together at higher rates, causing the observed molecular weight to roughly double in the last 20% conversion. These findings provide fundamental kinetic and molecular weight understanding that enable greater synthetic control over depolymerizable poly(aldehydes).
Improving the synthesis of PEGylated conjugated polymers with a water scavenging Grignard

Susan X. Cheng, susanx.cheng@mail.utoronto.ca, Shuyang Ye, Chirag Apte, chirag.apt@mail.utoronto.ca, Andrei Yudin, Dwight Seferos. Chemistry, University of Toronto, Toronto, Ontario, Canada

Conjugated polymers bearing oligo- and poly(ethylene glycol) (PEG) side chains are increasingly being adopted as materials in optoelectronic devices, sensors, biological imaging agents, and drug delivery vectors. The contrast in physical and chemical properties – rigid, hydrophobic, charge-transporting polymer backbone versus flexible, hydrophilic, ion-transporting side chain – positions PEGylated conjugated polymers as the perfect candidate for next-generation functional materials. One of the major barriers towards further exploration of such materials is that the most controlled method of conjugated polymer synthesis – the Kumada catalyst transfer polycondensation (KCTP) – requires stringent drying of monomers, catalysts, and other reagents. Such synthetic conditions are inherently at odds with the hygroscopic and hydrophilic nature of PEG side chains. Here, we describe an approach to use a water scavenging Grignard reagent to alleviate many of the shortcomings that currently hinder the synthesis of PEGylated conjugated polymers. This method shows improved polymerization performance without the energy-intensive drying and purification methods traditionally employed when working with hygroscopic functional groups, thereby lowering the synthetic barrier to developing PEGylated conjugated polymers with polar or water-compatible functionalities.
Light activated adhesion and debonding of underwater pressure sensitive adhesives

Yen-Ming Tseng, yt26@uakron.edu, Amal Narayanan, Kaushik Mishra, Xinhao Liu, Abraham Joy. Polymer Science, University of Akron, Akron, Ohio, United States

Pressure-sensitive adhesives (PSAs) such as sticky notes and labels are a ubiquitous part of modern society. PSAs with a wide range of peel adhesion strength are designed by tailoring the bulk and surface properties of the adhesive. However, designing an adhesive with strong initial adhesion but shows an on-demand decrease in adhesion has been an enduring challenge in the design of PSAs. To address this challenge, we designed alkoxyphenacyl-based polyurethane (APPU) PSAs that show a photoactivated decrease in peel strength. With increasing time of light-exposure, the failure mode of our PSAs shifted from cohesive to adhesive failure, providing residue-free removal with up to 83% decrease in peel strength. The APPU-PSAs also adhere to substrates submerged underwater and shows a similar photoinduced decrease in adhesion strength.
Interpenetrating responsive polymer networks within hydrogels for "smart" drug delivery

Daniel Massana Roquero\(^1\), massand@clarkson.edu, Paolo Bollella\(^{1,2}\), Artem Melman\(^1\), Evgeny Katz\(^1\). (1) Chemistry and Biomolecular Science, Clarkson University, Potsdam, New York, United States (2) Chemistry, Universita degli Studi di Bari Aldo Moro, Bari, Puglia, Italy

Hydrogels are well-established materials for biomedical applications such as drug delivery. Their biocompatibility and biodegradability is commonly exploited to encapsulate a payload and deliver it at specific targets. However, the excessive porosity of some of these materials causes the fast leakage of entrapped (bio)molecules. This could lead to i) uncontrolled release profiles; ii) cargo degradation and iii) undesired immunological reactions. Interpenetrating polymer networks (IPN) are frequently used to customize hydrogels properties in an attempt to overcome their intrinsic limitations. The semi-interpenetration of a responsive polyvinylalcohol (PVA)/boronate polymer network (IPN) within alginate hydrogels allowed us to hit two targets with one stone. First, the IPN efficiently sealed larger pores of the hydrogel decreasing leakage of proteins 20-fold compared to plain hydrogels. Second, the degradation of boronate esters by biologically relevant concentrations of hydrogen peroxide (H\(_2\)O\(_2\)) made possible the design of a multi-biomarker responsive drug delivery system. Hydrogen peroxide, in bulk or catalytically produced in situ by oxidases in the presence of their biomarker substrates, degraded irreversibly the IPN. As a result, the pores of the hydrogel are reopened releasing the entrapped proteins. The developed strategy is independent of the hydrogel source and can be extended to other porous materials. In addition, the lack of cytotoxicity of aryboronates as well as the biocompatibility of both PVA and alginate, makes this material suitable for “smart” delivery of encapsulated protein drugs.

Top: Schematic representation of semi-interpenetration of PVA/boronate polymer network and its degradation in the presence of hydrogel peroxide.

Down: photograph of a semi-IPN hydrogel and its cross-section. SEM pictures at different locations of the cross-section.
Vitrimers represent an interesting class of materials that exhibit many of the desirable properties of conventionally crosslinked materials, while also being able to be reprocessed through the utilization of dynamic exchangeable crosslinks. Recently, the thiourethane moiety has been explored as a potential dynamic crosslink in vitrimeric materials, as it exhibits both associative and dissociative exchange pathways in response to an external stimulus – i.e. heat. Herein, we aim to utilize the selectivity of various thiol-X reactions to achieve rapidly forming vitrimeric systems. In the present study, a sequential “one pot – two step” process was utilized to develop a series of ternary thiol-ene/thiourethane networks from commercially available building blocks. Each network studied exhibited rapid curing under UV irradiation, consistent with photocured thiol-ene network fabrication, and excellent network reprocessibility imparted by the dynamic exchange of the thiourethane linkages. Through dynamic mechanical analysis, the rate of stress relaxation was shown to be directly dependent on the macromolecular architecture imparted by the diisocyanate monomer selection. Furthermore, we found that these materials exhibited excellent retention of mechanical properties upon reprocessing.
A new class of zwitterionic materials: Phosphonium sulfonate monomers and polymers

Marcel U. Brown, mubrown@umass.edu, Todd Emrick. Polymer Science & Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Zwitterionic polymers are mainly known for their strong hydrophilicity and application in antifouling coatings. A relative lack of diversity in current applications may be attributed to limited structural variety, especially within their cationic moieties, which are typically ammonium-based. This work establishes a new class of polymer zwitterions, with phosphonium groups as cations. Ring-opening of a novel substituted sultone precursor with a variety of alkyl and aryl phosphines yields zwitterionic phosphonium sulfonate monomers that are amenable to controlled free radical polymerization. The resulting polymers display solubility in various organic solvents, uncharacteristic for conventional polymer zwitterions, and tunable properties depending on the choice of the phosphonium R-groups. Incorporation of these phosphonium sulfonate zwitterions into block copolymer architectures highlights their potency to modify material properties and amenability to self-assembly in solution.
Semi-fluorinated polymers containing corannulene, adamantane, and isosorbide from diols and aromatic trifluorovinyl ethers

Ketki E. Shelar1,2, ketkishelar.niper@gmail.com, Karl Mukeba1,2, Charles U. Pittman1,2, Dennis W. Smith1,2, (1) Mississippi State University Department of Chemistry, Mississippi State, Mississippi, United States (2) MSU Advanced Composites Institute, Mississippi State, Mississippi, United States

Semi-fluorinated polymers exhibit excellent solubility and melt processability when compared to traditional perfluoropolymers. A leading class of semi-fluorinated aryl ether polymers include: perfluorocyclobutyl (PFCB), perfluorocycloalkenyl (PFCA), and fluoroarylene vinylene ethers (FAVE) aromatic ether polymers. Monomers containing aromatic trifluorovinyl ethers (TFVE) are used to synthesize PFCB via radical-mediated [2+2] cyclodimerization, or FAVE polymers via nucleophilic addition/elimination with bisphenols. Recently, our group has focused on polycyclic aromatic hydrocarbon (PAH) (e.g. acenaphthenequinone, phenanthrenequinone, corannulene, etc.) enchained semi-fluorinated polymers for potential use in optoelectronic, gas-separation, and advanced composite applications. To further expand our synthetic scope, polymers with contortions (adamantine diol), and from renewable sources (isosorbide) are now sought. These aliphatic diols readily polymerize with TFVE derivatives of bisphenol A and 6F (see Scheme) affording high molecular weight thermoplastics exhibiting excellent solubility and tough, transparent film-forming capability. The use of different monomer cores (aromatic, aliphatic, contorted, renewable) should help to develop general structure/property relationships for this versatile and expanding approach to semi-fluorinated aryl ether polymers. Synthesis and characterization including optical, thermal, and electronic properties of the new materials will be presented.
Hydrolytically degradable epoxy amine thermosets utilizing hydrolyzable ketal-based epoxide monomers

Benjamin M. Alameda, benjamin.alameda@usm.edu, Joseph S. Murphy, Jonathan D. Sisemore, Derek L. Patton. Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

The demand for degradable polymers has risen greatly in recent years due to the concerns of plastic waste in the environment and has inspired our investigation into degradable epoxy-amine thermoset materials. Fully degradable epoxy-amine thermosets were synthesized using hydrolyzable epoxide monomers in combination with a commercially available diamine. Ketal-based epoxide monomers were synthesized in high yield using scalable synthetic techniques and commercially available starting materials. All thermoset samples were cured at high temperatures (180°C) and resulted in glassy, well-defined networks that were capable of degrading in low pH aqueous solutions. Hydrolytic degradation of each thermoset composition was determined gravimetrically via mass loss vs. time experiments where degradation was found to be tunable based on monomer structure. Additionally, carbon-fiber composites were constructed using our ketal-based epoxide monomers in order to demonstrate the ability to recycle carbon fibers after complete degradation of the composite matrix.
Main-chain polycarbodiimides are widely utilized in industry as anti-hydrolysis stabilizers for polyester-based materials, e.g. under the trade name Stabaxol P. Additionally, they are precursors to a range of other polymer types. Yet, to date they have been prepared exclusively through step-growth methods, which typically afford low molecular weights and broad dispersity. Additionally, complex polymer architectures remain inaccessible. A controlled and living methodology like a carbodiimide analogue of olefin ring-opening metathesis polymerization (ROMP) could address these issues. Using cyclic carbodiimides and initiators with transition metal- and main-group-nitrogen double bonds, we demonstrate the first examples of chain-growth polymerization of carbodiimide monomers to make main-chain carbodiimides. Mechanistic analysis and materials properties will be discussed.
Synthesis and insight into the material properties of polyolefins with isotactic branches outside the two-carbon periodicity has been a long-standing challenge. Ring-opening metathesis polymerization (ROMP) has brought new opportunities to explore the properties of such materials. Recent reports have shown that bulky, stereospecific, allylic cycloolefins have the potential to produce precise, isotactic polymer microstructures. This presentation will discuss our success in using bulky trialkylsiloxy cyclopentenes to afford regioregular isotactic polymers with a hydroxyl functionality on every fifth carbon. These materials can be likened to an isotactic ethylene-vinyl alcohol copolymer with precision and stereopure alcohol branches. The thermal and semi-crystalline properties are examined to understand the effects of diverse tacticity on these precision polymers.

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Polymers containing fluorine are desired as high-performance materials due to their valuable combination of properties including, for example, high thermal stability, good chemical resistance, low surface energy, and low dielectric constant. Our research laboratories have established a general program to develop fluoroalkene step-growth polymerization methodologies to access fluorinated arylene vinylene ether (FAVE), perfluorocycloalkenyl (PFCA), and perfluorocyclobutyl (PFCB). Recently, our group has focused on semi fluorinated polymers containing property enhancing polycyclic aromatic hydrocarbon (PAH) bisphenols for specialty applications such as photonic or high-performance gas separation technologies. The step-growth copolymerization of perfluorocyclohexene (PFCH) with PAH bisphenols and bis(4-hydroxyphenyl) sulfone affording a variety of random copolymer compositions will be presented. The physico-chemical and thermal properties of these transparent and film forming polymers were evaluated by FTIR, NMR, GPC, DSC and TGA. DSC analyses of polymers revealed single glass transition temperatures ($T_g$) ranging from 180-220 °C.
Conventional methods used to determine the number-average molecular weight \( (M_n) \) of neutral polymers are considered widely inaccurate when applied to polyelectrolyte systems. Hence, we have developed models using polymer chain dynamics in the semidilute unentangled regime to determine \( M_n \) of polyelectrolytes. Our team has conducted rheology, diffusion, and scattering studies to determine the molecular weight of four cesium polystyrene sulfonate (CsPSS) standard samples (manufacture stated \( M_n \) varied from 43 to 2800 Kg/mol). Our preliminary results show that methods based on rheology measurements of the relaxation time \( (\tau) \) are limited to higher molecular weight samples 2800 Kg/mol). Thus, we are using specific viscosity \( (\eta_{sp}) \) and diffusion \( (D) \) measurements to determine \( M_n \) for our four samples over a wide \( M_n \) range. Using our theoretical framework, we observe deviation of the determined \( M_n \) from the expected \( M_n \) and this deviation increases for the shorter chains. This observation may result from non-uniform stretching along the chain of polyelectrolytes, which disappears in the long chain limit. These methods promise to enable straightforward determination of molecular weight and allow for wider application of more predictably synthesized polyelectrolytes. In cases where deviations from the expected theory are emerging, these studies also point towards new understanding of polyelectrolytes.
Stress relaxation behavior of tunable dynamic networks

Ipek Sacligil¹, isacligil@umass.edu, Christopher Barney², Alfred Crosby¹, Gregory N. Tew¹. (1) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Department of Mechanical Engineering, University of California Santa Barbara, Santa Barbara, California, United States

Dynamic networks have been extensively studied due to their stimuli responsiveness, self-healing ability, and stress-relaxation behavior. Metal-ligand mediated dynamic networks have been widely synthesized by addition of a metal salt into a ligand-decorated polymer solution. However, this method can often lead to inhomogeneities in the network structure which might hinder tunability of material properties. In order to overcome this challenge, we developed a crosslinking platform that ensures complete incorporation of stoichiometric amount of crosslinker into the network. We synthesized novel in-situ crosslinked networks utilizing bis(terpyridine)-metal complexes via ring-opening metathesis polymerization. The crosslinker bond strength can be tuned by varying the metal centers such as ruthenium-, iron-, nickel-, and zinc-complex cations. We introduced flat-punch indentation method to study stress-relaxation on these systems that had no crossover frequency observable by rheology. This methodology had the ability to capture differences in stress-relaxation behavior between metal centers and crosslink densities. Networks that contain “covalent-like” terpyridine-ruthenium interactions were shown to relax much faster than a covalently-bonded network. The crosslink density did not affect the stress-relaxation behavior when the bond strength was strong whereas crosslink density dictated the behavior when the interaction was weaker. In weakly interacting networks, additional dynamic crosslinkers decreased the stress relaxation time by providing more ligands as exchange partners. This work provides experimental evidence for decrease in stress-relaxation time with increasing crosslink density for in-situ crosslinked dynamic networks. Further studying in-situ crosslinked dynamic systems will elucidate tunable dynamic network design.
Self emulsifying drug delivery systems: Mucolytic action of N-acetylcysteine (NAC) polymer hydrophobic complexes for effective mucopermeation

Ahmad Malkawi, malkawi_ahmad@live.com. pharmaceutical sciences, Isra University Faculty of Pharmacy, Amman, Amman, Jordan

The mucolytic function of N-acetylcysteine (NAC) is necessary for the diffusion of mucoactive selfnanoemulsifying drug delivery systems (SEDDS) through the intestinal mucus gel layer. NAC instantly released from SEDDS leads to nonsignificant mucolytic activity and poor mucopermeation. It was the aim of this study to develop a novel mucoactive SEDDS based on the mucolytic function of NAC with improved mucopermeation. Therefore, NAC hydrophobic complexes with the cationic polymers polyethyleneimine (PEI), Eudragit E and RS were loaded in SEDDS and evaluated for size, polydispersity index (PDI), zeta potential and cytotoxicity. NAC release from the mucoactive SEDDS followed Ellman's method at pH 6.8. Interaction of mucoactive SEDDS with mucus was assayed using in vitro rheology, a Transwell diffusion model and intestinal residence time. SEDDS showed size stability in the range of 76 ± 12 nm over 4 h, as indicated by < 0.3 PDI and caused zeta potential increase from 17.3 mV to 7.7 mV. SEDDS showed no cytotoxicity on Caco-2 cells. The immediate release of NAC in a few seconds from SEDDS of PEI was significantly more sustained in 40e80 min with Eudragit E (p 0.05) and RS (p 0.001). Similarly, the SEDDS complexes showed a concentration- and time-dependent decrease of 52.55 ± 19.88% in mucus dynamic viscosity. Finally, Transwell diffusion showed approximately 2- and 1.8-fold higher amounts of diffused SEDDS anchoring NAC complexes with Eudragit E/RS (p 0.05), respectively. Mucoactive SEDDS slowly releasing low NAC levels while permeating exhibit better mucolytic targeting, which improves overall in vitro mucopermeation.
The extensive usage of polyolefinic elastomers (like EPDM, EVA, etc.) in various fields, starting from the commodity materials to automobile sector and in biomedical applications, leads to the stockpiling of their wastages. This causes health hazards and different environmental issues. Therefore, several sustainable techs have been introduced to reduce the wastage and to recycle the polymer materials. Introduction of reversible crosslinking not only leads to the easy recycle and reuse of the elastomers, but also inducts self-healing characteristics, which improve the service-life of these elastomer products.¹⁻³ Herein, we have used epoxy functionalized ethylene-vinyl acetate copolymer (EVA), which was further functionalized with fluorescence active anthracenyl as well as furfuryl moieties, which could act as the ‘click’ partner with bismaleimide (BM) derivative via dynamic Diels-Alder (DA) reaction (Scheme 1). It enabled to design the EVA based elastomers with reversible networks with promising healing and recycling efficiencies (> 90 %). Noticeably, the fluorescence characteristics of the functional elastomers can be tuned by varying the molar content of anthracenyl as well as maleimide functionalities.
Fine-Tuning of Solvation Environments in Liquid Phase Reactions Using Polymer-Modified Metal-Supported Catalysts

Pengcheng Huang, p.huang@utwente.nl, Rick Baldenhofer, Aayan Banerjee, Leon Lefferts, Jimmy Faria Albanese. Universiteit Twente Faculteit Technische Natuurwetenschappen, Enschede, Overijssel, Netherlands

Nowadays, there has been an increasing interest in tailoring catalysts with stimuli-responsive polymers to improve their selectivity, stability, and recyclability in liquid environments[1,2]. To create this materials the external surface of the catalyst is functionalized with polymer brushes that can undergo reversible conformational transitions from solvated state or “collapse” state depending on the conditions of the reaction environment (e.g. pH, temperature, solvent polarity). In the solvated state the catalytic active sites are easily accessible to molecules in the liquid and as a result the reaction can take place. Upon conformational transition to the “collapse” state the polymers form a dense layer at the surface of the catalyst that limits molecular diffusion of reactants to the active site[3]. The vast majority of the existing reports are focused on the utilization of this strategy to control either the dispersability of nano-catalysts in liquid environments or the molecular transport towards the active sites assuming that the polymer cannot modify the surface reaction energetics.

To challenge this idea, we have developed a family of catalysts that are free of mass transport limitations to investigate the interplay between the stimuli-responsive polymer brushes attached to the catalyst and solvation environment near the active sites using nitrobenzene hydrogenation as probe reaction. For this purpose, we employed poly(n-isopropylacrylamine), a typical thermo-responsive polymer that exhibits a sharp change in solubility at temperatures above 32 °C, to create a coating on Pd/SiO2 catalyst. The polymer coated catalyst shows a higher selectivity to P-aminophenol and a lower activation energy compared with the normal Pd/SiO2 catalyst. These results will be instrumental in the development of new mechanisms that could understand the solvation effect of polymer on a catalytic hydrogenation reaction.
Henkel Award for Outstanding Graduate Research in Polymer Science & Engineering Honoring Austin Evans

Prof William Dichtel, Organizer, Northwestern University; Dr. Mahesh Mahanthappa, Organizer, University of Minnesota; Prof William Dichtel, Presider, Northwestern University

Session Type: Oral - Hybrid
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Wednesday, 08:00am - 10:00am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314

Transformation of carbohydrate based small molecules and polymers into environmental and biomedical materials
08:00am - 08:30am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Karen L. Wooley, Presenter, Texas AM University

Stereoselective cationic polymerization
08:30am - 09:00am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Frank Leibfarth, Presenter, Massachusetts Institute of Technology

Using molecular contortion to create optoelectronic materials
09:00am - 09:30am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Colin Nuckolls, Presenter

Porous conductive polymers
09:30am - 10:00am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Zhenan Bao, Presenter

Wednesday, 10:30am - 12:30pm USA / Canada - Eastern - August 25, 2021 | Room: A313-A314

Collective logistics in artificial molecular farms
10:30am - 11:00am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Liang Feng; Yunyan Qiu; James Stoddart, Presenter

Unraveling the mystery of two dimensional imine linked covalent organic frameworks are formed
11:00am - 11:30am USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Prof William Dichtel, Presenter, Northwestern University

Understanding and controlling two dimensional polymerization
11:35am - 12:05pm USA / Canada - Eastern - August 25, 2021 | Room: A313-A314
Dr. Austin M. Evans, Presenter, Columbia University
Transformation of carbohydrate based small molecules and polymers into environmental and biomedical materials

Karen L. Wooley, wooley@chem.tamu.edu. Chemistry, Texas A&M University, College Station, Texas, United States

Carbohydrates possess high degrees of chemical functionality with rich diversity, making them abundant as small molecules and polymers throughout the plant and animal kingdoms of Nature, but also challenging substrates for synthetic polymerization chemistries. A primary interest in the Wooley laboratory is the production of functional polymers from renewable sources that are capable of reverting to those natural products once their purpose has been served. Target materials are designed for potential applications in diverse areas, from medicine, e.g., as nanotherapeutics or bioresorbable hemostatic agents, to the environment, e.g., as pollutant capture agents, climate resilient hydrogel materials or naturally-degradable plastics. This presentation will highlight the preparation of magnetically-responsive hybrid inorganic-organic nanoparticles derived from amphiphilic and hydrolytically-degradable poly(glucose carbonate) block polymers for capture and recovery of hydrocarbons of crude oil spills. It will also discuss the incorporation of cyclic glucose small molecules into membranes designed for passive and active water purification, which were modified to serve as templates for the construction of composite synthetic polymer-chitosan polysaccharide bioresorbable hemostatic agents.
Stereoselective cationic polymerization

Frank A. Leibfarth, FrankL@email.unc.edu. Chemistry, University of North Carolina System, Chapel Hill, North Carolina, United States

The stereochemistry of vinyl polymers, known as polymer tacticity, is intimately linked to their resultant material properties. Despite the well-developed stereoselective methods for the polymerization of propylene and other nonpolar a-olefins, general approaches to the stereoselective polymerization of polar vinyl monomers are not well developed. In this lecture, we will discuss the design of chiral counterions that systematically tune the reactivity and chain-end stereochemical environment during cationic polymerization. Our work has uncovered a number of approaches to engender stereoselectivity during cationic polymerization, including Lewis acid catalysis, Bronsted acid catalysis, and anion-binding catalysis. In this lecture, I will discuss the strengths and weaknesses of these approaches, along with the mechanistic underpinnings that inform stereoselectivity and substrate specificity. Overall, the methods provide access to a range of isotactic vinyl polymers with previously unprecedented degrees of isotacticity. Stereoselective polymerization of vinyl ether monomers yield isotactic poly(vinyl ether)s, which are a class of semicrystalline thermoplastics that display the tensile properties of commercial polyolefins but have an order of magnitude stronger adhesion to polar substrates. In a complementary example of stereoselective cationic polymerization, the asymmetric helix-chirogenic polymerization of N-vinyl carbazole yields optically active polymers with static helices. These materials demonstrate electronic and transport properties that are differentiated from their atatic counterparts.

![Coordination Polymerization > Anionic Polymerization > Cationic Polymerization ≈ Radical Polymerization](image)
Using molecular contortion to create optoelectronic materials

Colin P. Nuckolls, cn37@columbia.edu. Chemistry, Columbia University, New York, New York, United States

This presentation will describe our research in designing molecules for optoelectronic applications. In one series, we create conjugated nanoribbons. These nanoribbons are effective at accepting and transporting electrons. As such, they are efficient electron acceptors in organic photovoltaics, where they boast ~10% PCE for simple spin-cast solar cells. The ease with which these materials can be functionalized and derivatized points to numerous high performance optoelectronic applications. In a second series, we present new helicene based PDIs. We can make helical oligomers and polymers from these new building blocks, and these materials have the largest circular dichroisms of any material. In a third series, we can make high performance pseudocapacitors by creating contorted aromatics that have paths for electrons and ions.
Porous conductive polymers

Zhenan Bao, zbao@stanford.edu. Chemical Engineering, Stanford University, Stanford, California, United States

In this talk, we will present our recent work on synthesis of porous conductive polymers and their applications in energy storage.
Collective logistics in artificial molecular farms

Liang Feng, Yunyan Qiu, James F. Stoddart, stoddart@northwestern.edu. Northwestern University, Evanston, Illinois, United States

Constructing a molecular integrated system that can handle external cargoes courtesy of its internally organized molecular machines is a long-standing goal for synthetic chemists. Current dynamic systems, however, containing molecular machines, either operate in a disordered manner in solution or are incapable of processing external goods collectively in a condensed state. In this talk, we will describe our recent efforts aimed at the precise construction of chemically driven molecular logistics farms, where metal-organic framework nanosheets and nanoparticles function as extended stoppers, as well as coordinative organizers for arrays of artificial molecular pumps. These pumps in the solid-state farms are capable of undergoing the repeated and precise collection of cargoes with a pumping efficiency similar to that observed in solution, achieving synchronization and amplification effects in two and three dimensions. Remarkably, the molecular farms transport cargoes actively away-from-equilibrium, from a solution with 5.75 mmol/L cargoes to a condensed solid with 111 mmol/L cargoes. Moreover, the collected cargoes can be easily unloaded at a targeted location following an acid-base reaction, while the solid-state farms are recyclable for the subsequent uses. These molecular logistics farms serve as a basis for the future development of more complex molecular integrated systems with diverse functions.

Figure 1. (A) A graphical representation of a logistics mechanism summarizing how redox and acid-base chemistry can be used to load and unload precisely a set of cargoes between a solution phase and a solid-state molecular farm. (B) The cascaded chemical processes happening on each molecular threshing machine.
Unraveling the mystery of two dimensional imine linked covalent organic frameworks are formed

William R. Dichtel, wdichtel@northwestern.edu. Chemistry, Northwestern University, Evanston, Illinois, United States

Imine-linked covalent organic frameworks (COFs) represent the dominant class of these emerging crystalline polymers, both as targets for various intended applications and as intermediates towards networks with even more robust linkages. Mechanistic understanding into the formation and growth of imine-linked two-dimensional (2D) covalent organic frameworks (COFs) is needed to improve their materials quality and access larger crystallite sizes, both of which limit the promise of 2D COFs and 2D polymerization techniques. I will discuss the evolution of our understanding of imine-linked COF formation, including recent advances in obtaining high quality two-dimensional imine-linked COF products.
Two-dimensional polymer sheets are a desirable macromolecular architecture. However, challenges related to their synthesis have restricted their investigation. Recently, we developed a colloidal seeded growth approach to polymerize macromolecular sheets, which avoids the irreversible aggregation and precipitation processes that have complicated previous methods. This solution stabilization allows two-dimensional polymer nucleation and growth to be temporally resolved. Here, I will discuss these colloidal methods and the wealth of mechanistic insight gained from their study. I will also describe how these approaches can be leveraged to yield large-area single-crystalline macromolecular sheets. These controlled syntheses are now being generalized to other polymerization chemistries, monomer species, and morphologies. I will conclude by describing how developments in two-dimensional polymerization chemistry are enabling investigations into the properties and application relevance of macromolecular sheets.
Herman F. Mark Award in honor of Kristi Anseth
Jeffrey Hubbell, Organizer; Nicholas Peppas, Organizer, University of Texas Dept Chem Eng; Nicholas Peppas, Presider, University of Texas Dept Chem Eng; Jeffrey Hubbell, Presider
Session Type: Oral - Virtual
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Wednesday, 10:30am - 12:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 48

Materials and protein engineering for modulating immunity and tolerance
10:35am - 11:05am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 48
Jeffrey Hubbell, Presenter

Hydrogels in regenerative medicine
11:05am - 11:30am USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 48
Jennifer Eliseeoff, Presenter, Johns Hopkins University

Peptide conjugates for cardiovascular therapies
11:30am - 12:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 48
Matthew Tirrell, Presenter, University of Chicago

Bioconjugates by atom transfer radical polymerization
12:00pm - 12:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 48
Krzysztof Matyjaszewski, Presenter

Wednesday, 02:00pm - 04:00pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 47

Covalent adaptable networks in the design of functional materials
02:00pm - 02:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Christopher Bowman, Presenter, Univ of Colorado, Chemical Biological Eng

Designing biomaterials for healthcare applications
02:30pm - 02:55pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Molly M Stevens, FREng FRS, Presenter, Imperial College London

Engineered bacterial films
02:55pm - 03:25pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
David Tirrell, Presenter

Materials design for 4D biology
03:25pm - 04:00pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 47
Kristi Anseth, Presenter
POLY – Herman F. Mark Award in honor of Kristi Anseth

Materials and protein engineering for modulating immunity and tolerance

Jeffrey Hubbell, jhubbell@uchicago.edu. Pritzker School of Molecular Engineering, University of Chicago, Chicago, Texas, United States

Adaptive immune responses are triggered particularly powerfully in the lymph nodes and in the lymphoid tissues associated with mucosae. We are developing nanomaterials to exploit interstitial flow from the site of administration to the lymph nodes, using the nanomaterials to carry both antigen and adjuvant biomolecules. We are particularly interested in therapeutic vaccination in cancer, and we have determined that the tumor-draining lymph node is a particularly opportune lymphoid target for cancer vaccination. We are exploiting nanoparticles formed by emulsion polymerization and formed by self-assembly from block polymer amphiphiles and water soluble polymers as these delivery vehicles for both antigen and adjuvant molecules, creating multifunctional platforms that can be adapted to a wide variety of antigens.

In addition to inducing adaptive immune responses, so-called inverse vaccination to induce antigen-specific tolerance is of high interest. We are exploring biological and polymer approaches to deliver protein antigens in a tolerogenic manner, including targeting antigen to the surfaces of erythrocytes after injection, based on the premise that apoptosis cell debris is cleared tolerogenically, along with exogenous antigen cargo it may carry. We have shown the ability to induce antigen-specific anergy as well as T regulatory responses, working in models of autoimmunity and of immune response to protein drugs. The liver is a target of particular interest, and we are thus developing polymers that can target antigen, tolerogenically, to particular cell populations in the liver.
Hydrogels in regenerative medicine

Jennifer Elisseff, jhe@jhu.edu. Johns Hopkins University, Baltimore, Maryland, United States

Biomaterial implants have a long history in the clinic but hydrogels in regenerative medicine therapies present new opportunities to deliver cells and mimic tissue properties. Clinical translation provides a unique and critical opportunity to investigate the key therapeutic drivers of technology efficacy in people. Our clinical translation experiences with hydrogels in orthopedics and plastic surgery yielded the unexpected discovery of adaptive immune cells in the biomaterial response. We are now working to understand the role of the immune system and cellular senescence in the biomaterial response and repair across different tissues. This research now serves as the basis for the design of regenerative immunotherapies and a new therapeutic target in regenerative medicine.
Molecular engineering in our parlance means building functional systems from the molecular level up. Ten years ago, the University of Chicago launched what has now become the first school embracing and advancing this approach to applied science and engineering. This talk will describe the institutional aspects of how this is being done and some examples of the breadth of this approach. In-depth attention will be given to the molecular engineering of self-assembled nanoparticles that can target pathological cardiovascular endothelium and deliver anti-inflammatory therapeutics that retard progression of atherosclerosis and stenosis.
Krzysztof Matyjaszewski, matyjaszewski@cmu.edu. Center for Macromolecular Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Atom transfer radical polymerization has been successfully used to covalently attach polymer chains to various biomolecules such as proteins, exosomes and nucleic acids.
Covalent adaptable networks in the design of functional materials

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

The application of dynamic covalent chemistries in network polymers has resulted in the development of a broad variety of stimuli-responsive materials that rearrange their molecular bonds to accommodate physical stress. These covalent adaptable networks (CANs) take advantage of two general bond rearrangement mechanisms. Dissociative chemistries (e.g. reversible Diels Alder reactions) rely on the equilibrium between coupled, complementary reactive moieties and their unreacted counterparts. That equilibrium can be shifted by application of appropriate stimulus to modify the physical properties of the material. The dynamic nature of associative chemistries (e.g. thiol-thioester exchange, addition fragmentation chain transfer reactions) results from existing bonds undergoing exchange with complementary unreacted functional groups, without which the network is functionally static. A variety of dynamic chemistries have been employed in the design of CANs. In our group, we have focused on those that can be triggered exogenously via exposure to light and, to a lesser extent, to heat. The former is achieved via radical photoinitiation of those exchange reactions relying on a radical mechanism (e.g. addition fragmentation chain transfer and disulfide exchange reactions) and via employment of photolatent base catalysts for those exchange reactions employing an anionic-mediated mechanism (e.g. thiol-thioester exchange). The differences in mechanism, both general and specific, as well as the diversity of potential stimuli, make the concept of covalent adaptable networks broadly applicable in the development of functional materials across a wide array of research and potential commercial materials interests.
Designing biomaterials for healthcare applications

Molly Stevens, m.stevens@imperial.ac.uk. Department of Materials, Imperial College London, London, United Kingdom

This talk will provide an overview of our work in the design of functionalised polymer nanoparticles and hybrid biomaterials for healthcare applications. We engineer simple conceptually novel approaches to detect disease biomarkers, such as abnormally regulated enzymes, to extend the detection window for early disease Dx. We aim to design biosensing strategies that are simple, cost-effective and easy deploy to the point-of-care to democratise access to advanced diagnostic technology. We will discuss impactful biosensing applications for infectious and non-communicable diseases for example innovative smartphone enabled tests for epidemic surveillance in the field [2] and injectable nanoparticle-based sensing probes for in vivo detection of cancer that produce a colorimetric response in urine in under 1 hour [3]. We will provide an overview of our recent advances in Raman spectroscopy characterisation techniques for high-throughput tracking of surface functionalisation in single nanoparticles [4] and visualising 3-dimensional polymer structures for tissue engineering applications.
Engineered bacterial films

David A. Tirrell, tirrell@caltech.edu. California Institute of Technology, Pasadena, California, United States

This lecture will describe our ongoing effort to engineer the physical and biological properties of thin bacterial films by display of adhesive proteins on the cell surface, by release of matrix proteins into the extracellular space, and by mineralization subsequent to film formation. Studies of film fabrication, cell viability, film growth, film structure, indentation behavior, and regeneration following injury will be discussed.
Materials design for 4D biology

Kristi S. Anseth, kristi.anseth@colorado.edu. Department of Chemical and Biological Engineering and the BioFrontiers Institute, University of Colorado, Boulder, Colorado, United States

Our group is interested in the development of polymeric biomaterials that can interface with cells and promote tissue regeneration and repair. From a fundamental perspective, we seek to decipher the critical extracellular matrix (ECM) signals that are relevant for tissue development, regeneration, and disease and then design materials that integrate these signals. From an applied perspective, we use this knowledge to design materials that can promote tissue regeneration and wound healing in vivo. This talk will illustrate recent efforts towards the synthesis of new hydrogel chemistries for 4D cell culture, and how one can dynamically control biochemical and biophysical properties through orthogonal, photochemical click reaction mechanisms. Some specific examples will include the design of hydrogels that promote musculoskeletal tissue regeneration, super-swelling matrices to visualize cell-matrix interactions with unprecedented resolution, and materials-directed growth of an intestinal organoid from a single stem cell.
Controlling polyamide micro and nanostructure to improve performance in reverse osmosis membranes
10:35am - 11:05am USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 25
Dr. Caleb Funk, Presenter, DuPont Water Solutions; Jeffrey Wilbur

DuPont™ B-Free™: The biofouling prevention technology
11:05am - 11:35am USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 25
Dr. Guillem Gilabert Oriol, Presenter, DuPont Water Solutions; Gerard Massons; Marc Slagt; Eduard Gasia-Bruch

Drivers for meaningfully sustainable impact on building construction materials
11:35am - 12:05pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 25
Paul Doll, Presenter; Ramesh Iyer

Preparation of degradable microcapsules for cosmetic applications
02:00pm - 02:20pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 42
Kaouthar Oudoua, Presenter, Gem'Innov; Didier Gigmes; Hien Ho; Catherine Lefay; Yves Ortais; Yohann Guillaumeuf

Eastman molecular recycle technology to enable sustainable future
02:20pm - 02:50pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 42
Henry Li, Presenter, Eastman Chemical
Controlling polyamide micro and nanostructure to improve performance in reverse osmosis membranes

Caleb Funk, caleb.funk@dupont.com, Jeffrey Wilbur. DuPont de Nemours Inc, Edina, Minnesota, United States

Over the past 10-15 years, the reverse osmosis industry has seen major changes in the performance of available membranes. While these changes have been spreading through the portfolios of major manufacturers, work has been progressing in the background to better understand the structure-property relationship of polyamides with the goal of further challenging the flux/selectivity trade-off. Reverse osmosis polyamides have a unique and poorly understood microstructure that can be correlated to performance in some ways while defying convention in others. It is widely thought that with a firm understanding of the microstructure and how to control it, new insights could be gained on how to manipulate it for improved performance.

A flurry of recent work has revealed important information on polyamide microstructure. Related work with new imaging techniques have shown that nanostructure uniformity could also affect performance. Unfortunately, amid many proposals of what the ideal polyamide structure is, practical suggestions on how to manipulate the polyamide structure are rare. Potential methods will be discussed, along with new methods for visualizing the results.
Biological fouling, also known as biofouling, still remains as the top unsolved problem in the water treatment industry with reverse osmosis (RO) and nanofiltration (NF) membranes. It is reported that 70% of the plants in Middle East and 83% of surface water plants in USA suffer from some degree of biofouling. Biofouling happens when bacteria secrete exopolymeric substances, which adhere on the membrane and feed spacer, blocking the water flow. This leads to an increase in feed pressure, which is addressed through chemical cleanings (CIP). Ultimately, the membrane suffers and eventually effect membrane lifetime, thus affecting the plant availability and leading to a total cost of water increase up to 6%. The DuPont™ B-Free™ pre-treatment is a novel vessel-based media technology that efficiently mitigates the effects of biofouling in Reverse Osmosis systems. B-Free technology works under three main mechanisms which are smartly combined to provide a biostatic environment for downstream RO operations. The first one relies on providing phosphate reduction, then it uses a chemical barrier as safeguard protecting the system from the start-up, and finally it retains particles and bacteria to ensure no particle migration. Field validation in a biofouling environment equipped with a B-Free column demonstrated that biofouling is prevented in RO during a 35 days test and 8 chemical cleanings are avoided.
Drivers for meaningfully sustainable impact on building construction materials

Paul Doll, pdoll@dow.com, Ramesh Iyer. Dow Chemical Co, COLLEGEVILLE, Pennsylvania, United States

In 1987, the Brundtland Commission defined sustainability as meeting the needs of the present generation without compromising the ability of future generations to meet their own needs. Many different metrics and models have since been proposed to measure “improved sustainability.” However, for any metric to have a meaningful and lasting impact, it must align with feasible technology and, equally important, have value to the customer. One industry that has been successfully specifying, utilizing, and promoting use of more sustainable products and designs via green building certifications is Building and Construction. A review across leading certifications will be presented followed by a focus on LEED certification (Leadership and in Energy and Environmental design) with an emphasis on the metrics by which coatings are helping to raise the bar.
Preparation of degradable microcapsules for cosmetic applications

Kaouthar Oudoua\textsuperscript{1,2}, kaouthar.oudoua@etu.univ-amu.fr, Didier Gigmes\textsuperscript{2}, Hien T. Ho\textsuperscript{1}, Catherine Lefay\textsuperscript{2}, Yves Ortais\textsuperscript{1}, Yohann Guillaneuf\textsuperscript{2}. (1) Gém’Innov, Gemenos, France (2) Aix-Marseille Universite, Marseille, Provence-Alpes-Côte d’Azu, France

Microencapsulation technology has been employed in a wide range of industrial sectors including the pharmaceutical, engineering, energetic, and biotechnological fields. A large variety of active molecules like drugs, flavors, fragrances, dyes, pesticides, and vitamins have been encapsulated inside polymeric shell capsules ranging in size from one micron to a few millimeters. The main technology to create the shell is based on the reaction of melamine and formaldehyde that produce a crosslinked thermoset at the oil/water interface.

Recently, environmental concerns regarding non-degradable microplastic wastes have become a global issue. During the last few years, enormous attention has been given to poly(β-aminoester). This polymer has been successfully utilized in several biomedical applications due to its biocompatibility, biodegradability, and responsiveness.

Our research has explored and introduced new applications for poly(β-aminoester) as a non-toxic and biodegradable microcapsule-shell that is compatible with cosmetic applications. A range of molecules have been successfully encapsulated without side reactions.
Eastman molecular recycle technology to enable sustainable future

Henry Li, henryli@eastman.com. Eastman Chemical Co, Kingsport, Tennessee, United States

Eastman’s stated purpose is to enhance the quality of life in a material way. We are striving to become the world’s leading material innovation company. Our unique platform of solutions can significantly reduce plastic waste and support the evolution of the circular economy, delivering value to our stakeholders and the global community. Eastman has engaged in molecular recycling and recently started commercial-scale renewal technology to recover the valuable and versatile raw materials.
Recyclable tube development and industry partnership

Jun Wang, jun_wang@colpal.com. Colgate Palmolive Co, Piscataway, New Jersey, United States

Tubes are one of the most widely used forms of plastic packaging that previously could not be recycled. With the goal of recycling in the mind, Colgate’s packaging engineers re-designed the tube material compositions by 1) replacing all (L)LDPEs in tube laminate with a combination of HDPE and medium density PE, using EVOH as a barrier layer and 2) replacing the high melt flow HDPE resin with a lower melt flow HDPE for tube shoulders. After overcoming multiple engineering challenges, we achieved a recyclable tube that meets all performance requirements and is produced from the same manufacturing processes with the same productivity. The tube received an APR (Association of Plastic Recyclers) recognition for its compatibility with the HDPE recycling stream in April 2019, first of its kind in the world, as well as a Technical Approval from PRE (Plastic Recyclers Europe) in 2020. Following this openly shared technology from Colgate, all major tube manufacturers around the world have developed their versions of recyclable tubes. As a group, we are working with the recycling industry, trade associations/NGOs, municipalities and consumers to make tubes recycled.
Hiding and its importance in waterborne architectural coatings

Philip Harsh, harsh@dow.com, James Bohling. Dow Coating Materials, Collegeville, Pennsylvania, United States

The opacity of coatings, in both the wet and dry state, are highly important properties in determining the coverage and quality of the material. Often professional painters use the appearance of a coating in the wet state to determine the amount of the coating to apply to achieve the desired opaque coverage in the dried film. While dry opacity measurements are highly understood, the hiding of a wet coating is mainly done via an empirical visual rating. The development of laboratory wet hiding testing protocols have allowed for a more reproducible and direct comparison to real world application of coatings. The comparative results of contrast ratio, scattering and tint strength using these development methods will be discussed.
Preparation and performance of thermoset hydrogel sealant

Elizabeth Contreras, eqcontreras@gmail.com. Aramco Services Company, Houston, Texas, United States

The preparation and mechanical performance of thermoset hydrogels as a sealant for high-temperature high pressure (HTHP) application, must be soluble in water, a treatment fluid with low viscosity for deeper penetration of vacant spaces, must have controllable cure times and applicable over a higher temperature range. In this study, a water-based gel consisting of 30% (v/v) poly(maleic anhydride-co-isobutylene) composite is applied as a water-thin, low-viscosity fluid. At an engineered time at 100-200 °C and 7 MPa, the fluid rapidly sets at a right-angle as it cures in place into a strong set gel, as measured using oscillatory measurements. Designed to exhibit rapid and reversible strain in response to stress, elasticity is increased by 65% with the addition of PEG. This highly stable hydrogel is completely water-based and provides elasticity, flexibility, and thermal resilience over a wide range of temperature for HTHP applications.
Use of high throughput, automated synthesis to accelerate the innovation of industrially important polymers

Michael Petr1, mp3d@alum.mit.edu, Richard P. Woodworth2, Nick Irick2, Caroline Nimako-Boateng2, Melinda Einsla2, Graham P. Abramo2. (1) Wire and Cable R&D, Dow, Collegeville, Pennsylvania, United States (2) Formulation, Automation and Materials Science, Dow, Collegeville, Pennsylvania, United States

Developing new commercial products often requires significant laboratory research because of the large number of properties that must be attained in order to translate fundamental polymer innovations into commercially useful products. In an industrial world where there is less and less interest in spending the time and money required for such laboratory research, high throughput, automated reactors can compensate for this lack of resources and even accelerate the development process in order to introduce new products faster. To do so, Dow, in conjunction with Unchained Labs, has extended the use of the Large Volume-semi continuous Parallel Polymerization Reactor (LV-scPPR) to simultaneously produce four different solution polymers at the 60mL scale, plus Dow has used commercially available tools to add the capability to simultaneously produce four different solution or emulsion polymers at the 300mL scale. Many polymeric products are good candidates for this type of research because the small volumes produced are still representative of the materials made on larger scales and are enough for basic application screening. Furthermore, the smaller volumes can help preserve expensive raw materials, generate less material waste, and are safer because temperature, pressure, and reactivity can be more easily controlled. A variety of industrially relevant examples will be presented, including aqueous solution products, solvent solution products, and aqueous emulsion products for the oil production, home care, personal care, construction, and coatings markets.
Synthesis of tailored segmented polyurethanes utilizing continuous flow reactors and real time process monitoring

Xabier Lopez de Pariza\textsuperscript{2}, Tim Erdmann\textsuperscript{1}, tim.erdmann@ibm.com, Pedro Arrechea\textsuperscript{1}, Leron Perez\textsuperscript{3}, Charles Dausse\textsuperscript{1}, Nathan Park\textsuperscript{1}, J Hedrick\textsuperscript{1}, Haritz Sardon\textsuperscript{2}. (1) IBM Almaden Research Center, San Jose, California, United States (2) POLYMAT, Universidad del Pais Vasco, Donostia-San Sebastian, Gipuzkoa, Spain (3) University of Chicago, Chicago, Illinois, United States

Conducting polymerizations under continuous flow conditions affords distinct advantages over batch experimentation and has increasingly been employed by the research community for chain-growth polymerizations to accelerate materials discovery and to finely tune material properties. Our work now expands on the reported advances by demonstrating the utility of continuous flow for polyaddition reactions of polyurethanes (PUs). Various reactor configurations enable the on-demand organocatalytic synthesis of linear polyurethanes with tailored soft to hard segment ratios and under residence times of 3-5 min at room temperature. Implementing in-line analytics for real-time process monitoring increases the control over monomer conversion and minimizes batch-to-batch variations. Theoretical and experimentally determined molecular weights and material compositions were in good agreement and demonstrate reliability and reproducibility of the processes. Thus, these systems enable the straightforward preparation of libraries of commercially relevant PU materials and we demonstrate how the glass transition temperature can be modulated by composition. Finally, we discuss developed process control mechanisms aiming at increasing process automation and the underlying challenges due to employing reactive solutions.

Flow reactor for the on-demand synthesis of PUs containing variable amounts of hard segment (HS) and for in-line monitoring of monomer conversion in real-time by ATR-FTIR (a), section of the \textsuperscript{1}H NMR spectra holding information about the molar ratio of diols incorporated in the final product (b) and linear dependence of $T_g$ on HS weight fraction and molar fraction of HDO (c).
Grafting polymers by ATRP from solid and liquid surface
10:30am-11:00am USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 39
Krzysztof Matyjaszewski, Presenter, CMU

Imine based degradable semiconducting polymers
11:00am-11:30am USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 39
Helen Tran, Presenter

Bioelectronic materials: Nanostructured glassy carbon for dopamine detection
11:30am-12:00pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 39
Dr. Qinghuang Lin, Presenter, Lam Research Corporation

Molecular structure and ion solvation effects in oligomeric fluoroether electrolytes for lithium metal batteries
12:00pm-12:30pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 39
Chibueze Amanchukwu, Presenter

Responsive supramolecular materials
02:00pm-02:30pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 46
Egbert Meijer, Presenter, Eindhoven University of Technology

High efficiency organic solar cells: Impact of non-fullerene acceptors
02:30pm-03:00pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 46
Jean-Luc Bredas, Presenter

Thin film assemblies for short and long term wound healing
03:00pm-03:30pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 46
Dr. Paula T. Hammond, Presenter, Dept. of Chemical Engineering, MIT and Koch Institute of Integrative Cancer Research

Skin inspired polymer electronics
03:30pm-04:00pm USA/Canada - Eastern - August 25, 2021 | Room: Zoom Room 46
Zhenan Bao, Presenter
Grafting polymers by ATRP from solid and liquid surface

Krzysztof Matyjaszewski, km3b@andrew.cmu.edu. Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Various aspects of grafting polymers by ATRP from solid and liquid surfaces will be presented.
Next-generation electronics will autonomously respond to local stimuli and be seamlessly integrated with the human body, opening the doors for opportunities in environmental monitoring, advanced consumer products, and health diagnostics for personalized therapy. For example, biodegradable electronics promise to accelerate the integration of electronics with health care by obviating the need for costly device-recovery surgeries that increase infection risk. Moreover, the environmentally critical problem of discarded electronic waste would be relieved. The underpinnings of such next-generation electronics is the development of new materials with a wide suite of functional properties beyond our current toolkit. Organic polymers are a natural bridge between electronics and soft matter, where the vast chemical design space allows tunability of electronic, mechanical, and transient properties. Our research group leverages the rich palette of polymer chemistry to design new materials encoded with information for self-assembly, degradability, and electronic transport. In this talk, we will share our progress on the molecular design of acid-labile semiconducting polymers featuring imine bonds to maintain conjugation.
Bioelectronic materials: Nanostructured glassy carbon for dopamine detection

Qinghuang Lin¹,², qinghuang.lin@gmail.com. (1) Lam Research Corp, Fremont, California, United States (2) IBM Research, Yorktown Heights, New York, United States

Bioelectronic medicine employs electrical, magnetic, optical, ultrasound, chemical, etc. pulses to affect and modify neurological behavior which in turn modulates bodily functions as an alternative to drug-based interventions. It is envisaged to transform how we practice medicine and dramatically improve the outcome and reduce the cost of healthcare. In this talk, I will give an overview of Bioelectronic Medicine Roadmap formulated and published by the Semiconductor Synthetic Biology (SemiSynBio) Committee of Semiconductor Research Corporation (SRC). I will then discuss structured glassy carbon nanorods for electrochemical detection of dopamine—a neurotransmitter that is associated with brain reward system and some of the debilitating neurodegenerative conditions. These glassy carbon nanorods were fabricated by pyrolysis of a lithographically defined polymeric nanostructure. Compared with carbon fibers, the nanostructured glassy carbon nanorods provide about 2× higher sensitivity per unit area for dopamine sensing and more than 5× higher signal per unit area at low concentrations of dopamine. This scalable fabrication strategy glassy carbon nanorods offers the potential to integrate these nanoscale carbon rods with an integrated circuit control system and to transmit the data from the integrated dopamine sensor to datacenters for analysis and a closed-loop intervention.
Molecular structure and ion solvation effects in oligomeric fluoroether electrolytes for lithium metal batteries

Chibueze Amanchukwu, chibueze@uchicago.edu. Pritzker School of Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Lithium metal batteries have shown promise for the electrification of transport because they can double the energy density of current lithium-ion batteries. In contrast to lithium-ion batteries that use graphite as the anode, lithium metal batteries use lithium metal. However, lithium metal is highly reactive and continuously degrades the electrolyte. Hence, developing electrolytes that are compatible with lithium metal are vital. Fluoroether electrolytes have recently been synthesized that covalently bind two building blocks: ether building blocks with high reductive stability against lithium metal and fluorinated building blocks with high oxidative stability and propensity to passivate lithium metal. However, little is understood about the effect of building block connectivity and ion solvation in modifying the electrolyte properties. In this work, we synthesize a series of oligomers where we vary the length of the main chain and the identity of the end group to obtain structure-property relationships. We show that building block connectivity between ethers and fluorinated moieties play a significant role in modifying ionic conductivity and oxidative stability. Furthermore, we show that ion solvation within these oligomers is dependent on the molecular structure, and the solvation structure modifies electrochemical stability and long-term battery cycling performance. Our work illustrates the importance of molecular structure in designing improved oligomer/polymer-based electrolytes for lithium battery chemistries.
Responsive supramolecular materials

Egbert W. Meijer, e.w.meijer@tue.nl. Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands

Controlling the supramolecular interactions between molecular fragments made it easier to design materials with unconventional responsive behavior. A large variety of external stimuli is at our disposal leading to the fabrication of novel materials. Different supramolecular approaches and selected external stimuli will be discussed in the lecture, with special emphasis on highly ordered morphologies that will change their properties on the action of light, pressure, temperature, and the addition of chemicals. The results are used to discuss the trade-off between stability and dynamicity.
High efficiency organic solar cells: Impact of non-fullerene acceptors

Jean-Luc E. Bredas, jlbredas@arizona.edu. Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona, United States

With the emergence of efficient non-fullerene acceptors some five years ago, the power conversion efficiency of organic solar cells (OSCs) has increased remarkably, from some 12% to over 18%. In OSCs, the active layers consist of bulk-heterojunctions, that is blends of an electron donor component, usually a π-conjugated polymer, and an electron acceptor component. The inter-molecular charge-transfer (CT) electronic states that appear at the donor-acceptor interfaces play a crucial role in the exciton-dissociation, charge-separation, and charge-recombination processes.

In this presentation, we discuss how the combination of state-of-the-art electronic-structure calculations, fully quantum-mechanical 3-state vibronic approaches, and molecular dynamics simulations together with the results of temperature-dependent electroluminescence experiments: (i) allows a reliable description of the nature and energetic distribution of the CT electronic states; (ii) offers a unified description of the non-radiative voltage losses in both fullerene-based and nonfullerene-based devices; and (iii) provides clear guidance for the rational design of next-generation high-efficiency OSC blends.
Wound healing can go wrong when specific biological signaling is altered, often leading to the lowered or increased expression of specific proteins that play a role in tissue generation and remodeling. Ideally, one would be able to tune that wound healing, or enable it, when wounds have difficulty closing or healing is in some way impaired. The electrostatic layer-by-layer (LbL) process is a simple and elegant method of constructing highly tailored ultrathin polymer and organic-inorganic composite thin films. We have used this method to develop thin films that can encapsulate and release proteins and biologic drugs such as growth factors with highly preserved activity from the surfaces of biomedical implants or wound dressings with sustained release over periods of several days. We have engineered coatings that yield release of different drugs, DNA or protein, resulting in highly tunable multi-agent delivery nanolayered release systems. Depending on the nature of the LbL assembly, we can generate thin films that rapidly release proteins or peptides within minutes that induce rapid hemostasis to stop bleeding in soldiers on the battlefield while simultaneously releasing antibiotics, or release growth factors that help to regenerate bone in defects where bone may no longer grow. Challenges in each of these areas include designing systems that provide the right dosing over desired time periods, and engineering the structure of these thin film systems to enable sustained release periods while maintaining the drug or biologic loading needed for the desired effect. Methods for tuning the release of various compounds and combining different types of therapeutics in these films will be discussed. These and other uses of controlled polyelectrolytes and their complexes for delivery of proteins and nucleic acids within tissues and across barriers will be addressed.
Skin inspired polymer electronics

Zhenan Bao, zbao@stanford.edu. Chemical Engineering, Stanford University, Stanford, California, United States

In this talk, I will present our decade-long effort to create skin-inspired electronics through developing skin-like electronic materials and new applications they have enabled.
**POLY/PMSE Awards and Plenary Presentation**

Hayley Brown, Organizer, The Dow Chemical Company; Andrea Kasko, Organizer, Department of Bioengineering; Robert Mathers, Organizer, Penn State University; Levi Moore, Organizer, AFRL; Sara Orski, Organizer, NIST; Sara Orski, Presider, NIST; Andrea Kasko, Presider, Department of Bioengineering; Timothy Bunning, Presider, Air Force Research Laboratory

Session Type: Oral - Virtual

**Wednesday, 04:30pm - 06:30pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 43**

**Introductory Remarks**

**Polymers and nanocomposites to treat vascular disease without a trace**

04:40pm - 05:15pm USA / Canada - Eastern - August 25, 2021 | Room: Zoom Room 43

Julia Kornfield, Presenter

**POLY Award Presentation**

**PMSE Award Presentation**
Polymers and nanocomposites to treat vascular disease without a trace

Julia A. Kornfield, kornfield@cheme.caltech.edu. Department of Chemical Engineering, California Institute of Technology, Pasadena, California, United States

A wave of bioresorbable devices are being introduced to treat vascular disease in the heart and limbs. Biodegradable semicrystalline polymers provide the structural material of leading bioresorbable scaffolds (BRSs), a credit to innovative processing methods developed to achieve new combinations of strength, toughness and hydrolysis profiles. With Abbott Vascular, we discovered the key to resilient poly L-lactide (PLLA) lies in the interaction of two manufacturing steps—tube expansion and crimping. X-ray microdiffraction revealed dramatic gradients of structure created during crimping slow hydrolysis precisely where stress is concentrated, preserving strength where it is needed most. Even after 9 months of hydrolysis in vitro, despite a 40% decrease in PLLA molecular weight, the BRS retains its initial strength. Clinical complications motivate thinner devices that are visible in x-ray radiography during and after implantation. Toward the goal of stronger, radiopaque, bioresorbable materials, we explore PLLA reinforcement by inorganic nanotubes (NT) with strong x-ray absorption, specifically, tungsten disulfide (WS2). The effects of WS2NT on PLLA crystallization reveal a new interaction between early processing steps in BRS manufacture (preform extrusion and tube expansion). Innovative processing methods developed by biomedical device manufacturers give PLLA resilience to survive crimping, deployment and months of hydrolysis, fueling optimism that scaffolds will support arteries’ ability to heal, ultimately enabling recovery from vascular diseases without leaving a trace.
POLY Graduate Student Travel Award

- Yanning Ren (University of Colorado)
  "Single Crystal of Single-crystalline Polyethylene in Solution"

- Xiaoqian Wang (Virginia Tech)
  "Solution combustion synthesis of ultrahard polymeric materials"

- Meng Zhang (Louisiana State University)
  "Understanding the Role of Chloroform in the Synthesis of Flexible Polyurethane Elastomers"

To Provide Funding for Graduate Students Studying Polymer Science at US Institutions To Attend the 2021 ACS Meetings and Present Their Results

Sponsored by POLY Industrial Advisory Board

ACS Fall 2021 RESILIENCE OF CHEMISTRY

DSM Bright Science Award for PhD Students

- Jacob Lessard (University of Florida)
  "Highly Efficient, Highly Selective Catalysts for the Hydrogenation of Ketones"

- Benjamin Puren (University of Pennsylvania)
  "Electrostatically Controlled Polymeric Micelles for Nanomedicine Applications"

- Andrea Wicke (Colorado State University)
  "Catalytic Chemical Synthesis of Ultrafine Nanoparticles: Applications in Nanotechnology and Biomedical Sciences"

To Recognize and Reward Excellence in Innovative PhD Research in Polymer Technology

Sponsored by DSM

ACS Fall 2021 RESILIENCE OF CHEMISTRY

Henkel Award for Outstanding Graduate Research in Polymer Science & Engineering

- Austin Evans (Columbia University)
  "Understanding and controlling two dimensional polymerization"

To Recognize a PhD Graduate Student or Recent Graduate who has Completed an Outstanding PhD Thesis in Research at a University in the US or Canada

Sponsored by Henkel

ACS Fall 2021 RESILIENCE OF CHEMISTRY

2021 ACS Macro Letters/Biomacromolecules/Macromolecules Young Investigator Award

- Bradley Olsen (Massachusetts Institute of Technology)
  "Innovations in the Representation and Synthesis of Polymer Networks"

- Harriet Sanders (University of the Basque Country)
  "Organically Based Macromolecular Materials: Deformation and Function in Soft Matter Systems"

To Recognize Two Individuals, Early in their Careers, Who Have Made a Major Impact on the Field of Polymer Science

Sponsored by ACS Macro Letters, BioMacromolecules

ACS Fall 2021 RESILIENCE OF CHEMISTRY

Young Industrial Polymer Scientist Award

- Victoria Plunova (IBM)
  "AI Assisted Design and Synthesis of Materials with Targeted Properties"

For Outstanding Industrial Innovation and Creativity in the Application of Polymer Science

Sponsored by POLY Industrial Advisory Board

ACS Fall 2021 RESILIENCE OF CHEMISTRY

Charles G. Overberger International Prize

- Zhenan Bao (Stanford University)
  "Skin Inspired Polymer Electronics"

To Recognize and Honor Exceptional Achievements in Polymer Science, for Researchers from Anywhere in the World

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ACS Fall 2021 RESILIENCE OF CHEMISTRY

Mark Scholars Awards

2020 Mark Senior
- Karen Winel (University of Pennsylvania)

2020 Mark Scholar
- Luis Campos (Columbia University)

To Recognize Excellence in Basic or Applied Research and Leadership in Polymer Science by Scientists of All Ages

Sponsored by ACS Fall 2021 RESILIENCE OF CHEMISTRY

Herman F. Mark Polymer Chemistry Award

- Kristi Aneesh (University of Colorado at Boulder)
  "Materials Design for 4D Biology"

For Outstanding Research and Leadership in Polymer Science

Sponsored by ACS, PMSE, Macromolecules

ACS Fall 2021 RESILIENCE OF CHEMISTRY
Structure to Function in Supramolecular Polymers & Materials
Pol Besenius, Organizer, University of Mainz; Roxanne Kieltyka, Organizer, Universiteit Leiden; John Matson, Organizer, Virginia Tech; John Matson, Presider, Virginia Tech; Rachel Letteri, Presider, Texas A&M University
Co-sponsor/Theme: Co-sponsor - Cooperative PMSE: Division of Polymeric Materials Science and Engineering

Sunday, 08:00am - 09:40am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314

Self assembled saccharide functionalized amphiphilic metallacycles as biofilms inhibitor
08:00am - 08:25am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Guosong Chen, Presenter
Withdrawn

Conditionally active electron transfer catalysts enabled by bioinspired remodeling of polymer secondary structure
08:50am - 09:10am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Tanner Hoog; Matthew Pawlak; Katarzyna Adamala; Aaron Engelhart, Presenter, University of Minnesota

Supramolecular self-assemblies of cyanine dyes for tunable excitonic properties across the visible and shortwave infrared regions
09:10am - 09:25am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Arundhati Deshmukh, Presenter; Niklas Geue; Nadine Bradbury; Austin Bailey; Ellen Sletten; Justin Caram

Hydrogen bonding indigo photoswitches as building blocks to engineer photo adaptative materials
09:25am - 09:40am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Pauline Pacquet, Presenter; Yann Bretonnière; Stéphane Chambert; Julien Bernard

Sunday, 10:30am - 12:20pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314

Supramolecular polymers from peptide assembly: From optoelectronic to therapeutic applications
10:30am - 10:55am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Prof Sebastien Perrier, Presenter, University of Warwick

Peptide stereocomplexes as supramolecular crosslinks in polymeric biomaterials
10:55am - 11:15am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Israt Dut; Emma Laudermilch; Jonathan Florian; Vincent Gray; Connor Amelung; Kyle Lampe; Rachel Letteri, Presenter, Texas A&M University

Novel materials from the co-assembly of covalent and supramolecular polymers
11:15am - 11:40am USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Samuel I. Stupp, Presenter, Northwestern University

Polyisocyanide hydrogels: Combining synthetic tailorability with biological properties
11:40am - 12:05pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Dr Paul H.J. Kouwer, Presenter, Radboud University Nijmegen

Investigating binding of polymeric cell-penetrating peptide mimics to protein cargo for intracellular delivery applications
12:05pm - 12:20pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Hazel Davis, Presenter; Nicholas Posey; Gregory Tew

Sunday, 02:00pm - 03:30pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314

Host, guest supramolecular recognition in the design of functional soft materials
02:00pm - 02:25pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Prof. Matthew J Webber, Presenter, University of Notre Dame
Highly tunable, catalyst-free dynamic covalent bonds and their incorporation into networks
02:25pm - 02:40pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Neil Dolinski, Presenter; Katie Herbert; Stuart Rowan, University of Chicago

Synthesis and application of viologen-based polymers and photoredox-responsive soft materials
02:40pm - 03:05pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
Faheem Amir; Abigail Delawder; Mark Palmquist; Tiana Saak; Jonathan Barnes, Presenter

Helical supramolecular polymers: Self-assembly, bioactivity, and catalysis
03:05pm - 03:30pm USA / Canada - Eastern - August 22, 2021 | Room: A313-A314
John Matson, Presenter, Virginia Tech; Zhao Li

Sunday, 04:30pm - 06:00pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 44
Stimuli-responsive metallosupramolecular polymer networks
04:30pm - 04:55pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 44
Dr. Christoph Weder, Presenter

Exploring the influence of hydrogen-bonding in supramolecular electronics: From a diketopyrrolopyrrole model system to state-of-the-art semiconductors
04:55pm - 05:20pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 44
Doctor Amparo Ruiz Carretero, Presenter; Nelson Avila Rovelo; Gabriel Alvarez Martinez; Ana Maria Garcia Martinez; Shu Seki; Philippe Mesini

Tuning the molecular packing of supramolecular assembly by H-bonding and impact on morphology
05:20pm - 05:35pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 44
Dr. Amrita Sikder, Presenter, University of Birmingham; Prof Rachel OReilly

Responsive polymers: Hysteresis, bistability, read/write-memory and logic gate function
05:35pm - 06:00pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 44
Joanna Michalska; Beate Förster; Stephan Hauschild; Stephan Förster, Presenter, University of Bayreuth

Sunday, 07:00pm - 08:50pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 42
"Static" and evolving supramolecular gels
07:00pm - 07:25pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 42
Dave J Adams, Presenter; Santanu Panja; Annela Seddon; Bart Dietrich

Responsive polymers: Hysteresis, bistability, read/write-memory and logic gate function
07:25pm - 07:50pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 42
Yukio Cho; Ty Christoff-Tempesta; Julia Ortony, Presenter, Massachusetts Institute of Technology

Withdrawn

Design and applications of supramolecular peptide nanomaterials
08:05pm - 08:30pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 42
Tanja Weil, Presenter, Max Planck Institute for Polymer Research

Synergies of supramolecular and dynamic covalent bonding for responsive networks
08:30pm - 08:50pm USA / Canada - Eastern - August 22, 2021 | Room: Zoom Room 42
Dominik Konkolewicz, Presenter, Miami University; Shiwanka V Wanasinghe; Nethmi De Alwis Watuthanthrige; Obed Dodo; Jafer Vakil; Jessica Sparks

IN-PERSON POSTER SESSION
Sunday, 07:00pm - 09:00pm USA / Canada - Eastern - August 22, 2021 | Room: B2 - EXHIBIT HALL
Single crystals of mechanically entwined helical covalent polymers
07:00pm - 07:25pm USA / Canada - Eastern - August 22, 2021 | Room: B2 - EXHIBIT HALL
Yiming Hu, Presenter; Simon Teat; Wei Zhang

Session Type: Poster - In-person
Withdrawn

Withdrawn
Synergism between rifampicin and cationic polyurethanes overcomes intrinsic resistance of E. coli
Chinnapatch Tantisuwanno, Presenter; Francis Dang; Kristin Bender; John Spencer; Matthew Jennings; Hazel Barton; Abraham Joy
Session Type: Poster - In-person

Monday, 08:00am - 09:55am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312

Supramolecular polymers for biomedical applications
08:00am - 08:25am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Egbert Meijer, Presenter, Eindhoven University of Technology

Multicomponent supramolecular polymers as a platform for the design of glycoconjugate vaccines
08:25am - 08:50am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
David Straßburger; Moritz Urschbach; Natascha Stergiou; Edgar Schmitt; Pol Besenius, Presenter, University of Mainz

Designing optically transparent photo-crosslinked peptoid nanosheets for imaging applications
08:50am - 09:05am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Elizabeth A. Holman, Presenter, California Institute of Technology; Dong Li; Paul Ashby; Dr. Ronald Zuckermann, Lawrence Berkeley National Laboratory; Paul Sternberg

Controlling supramolecular assembly and dynamics for advanced tissue engineering hydrogels
09:05am - 09:30am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Matthew Baker, Presenter, Maastricht University

Withdrawn

Monday, 10:30am - 12:20pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44

Influence of light, acid and metal coordination on hierarchical self-assembly processes
10:30am - 10:55am USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 44
Gustavo Fernández, Presenter
Enhanced gene delivery and CRISPR/Cas9 homology-directed repair in serum by minimally succinylated polyethylenimine
02:50pm - 03:05pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 48
Md Nasir Uddin, Presenter, University of Kentucky; Logan Warriner; Daniel Pack; Jason Derouchey

Formation of Sequence-Defined Nanothreads through Solid-State Design
03:05pm - 03:20pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 48
Margaret C Gerthoffer, Presenter; Sikai Wu; Bo Chen; Bohan Xu; Jordan Cox; Tao Wang; Steven Huss, The Pennsylvania State University; Shalisa Oburn; Steven Lopez; Vincent Crespi; John Badding; Prof. Elizabeth Elacqua, The Pennsylvania State University

Competing hydrogen bonding supramolecular polymers allow thermo thickening effect
03:20pm - 03:45pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 48
Dr. Laurent Bouteiller, Presenter

Effect of pH and functionalisation of self-assembled Naphthalene-diimides for smart window applications
03:45pm - 04:00pm USA / Canada - Eastern - August 23, 2021 | Room: Zoom Room 48
Miss Rebecca Randle, Presenter; Leide Cavalcanti; Stephen Sproules; Emily Draper

Constrained supramolecular polymerization within linear polymer melts at equilibrium and under strain
Christopher B. Cooper, cbcooper@stanford.edu, Zhenan Bao.Chemical Engineering, Stanford University, Stanford, California, United States

Complexation of poly(β-CD) and bis-adamantyl poly(2-hydroxyethyl acrylate) to create supramolecular polymeric networks
09:05am - 09:20am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Mohammed Alaboalirat, Presenter; John Matson, Virginia Tech

Understanding the role of block sequence on the solution aggregation of polypeptoid multi-block copolymers
09:20am - 09:35am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Meng Zhang, Presenter, Louisiana State University; Yun Liu; Donghui Zhang

Tri-block copolymer thermoplastic elastomer thermosets achieving orthogonal working/healing conditions
09:35am - 09:50am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Ryan Clarke, Presenter, Colorado State University; Eugene Chen

VIRTUAL POSER:
Tuesday, 07:00pm - 09:00pm USA / Canada - Eastern - August 24, 2021 | Room: Row 17

Programming self-assembly of minimalistic heterochiral peptides: from simplicity to complexity
08:00am - 08:25am USA / Canada - Eastern - August 24, 2021 | Room: A311-A312
Ana M. Garcia; Michele Melchionna; Ottavia Bellotto; Slavko Kralj; Sabrina Semeraro; Evelina Parisi; Daniel Iglesias; Paola D’Andrea; Rita De Zorzi; Attilio V. Vargiu; Silvia Marchesan, Presenter

Transition path dynamics in protein-protein interaction
Masoumeh Ozmaeian, Presenter; Dmitrii Makarov

RAFT polymerization of star polymers with ortho-phenylene cores
Kate Georgia Elizabeth Bradford, Presenter, Miami University; Dominik Konkolewicz, Miami University; Christopher Hartley

Regulating the self-assembly of light emitting conjugated polymer spherulites via side alkyl chain branching
Lili Sun, Presenter; Lu Bai; Jin Lin
Engineering positive kinetic cooperativity between supramolecular and dynamic covalent bonds within self-healing polyurethane thermosets
Raphaël Pauchet, Presenter; Simon McKie; Vasyl CHUMACHENKO; Georges FORMON; Pierre Lutz; Eric BUHLER; Remi PERRIN; Christian GAUTHIER; Emilie Moulin; Nicolas Giuseppone

Creating a dynamic covalent peptide system by reversible native chemical ligation for dynamic combinatorial chemistry
Nicolas Capit, Presenter; Pierrick Petitnicolas; Emilie Moulin; Nicolas Giuseppone

Selenophene and thiophene based conjugated polymer gels
Sheng Li, Presenter; Keqiang He; Elisabeth Prince; Yuning Li; Dwight Seferos

Covalent organic frameworks based on porphyrin and cucurbit[n]uril for electrocatalytic water splitting
Donus Tuncel, Presenter
Self assembled saccharide functionalized amphiphilic metallacycles as biofilms inhibitor

Guosong Chen, guosong@fudan.edu.cn. Fudan University, Shanghai, Shanghai, China

Bacterial biofilms are troublesome in the treatment of bacterial infectious diseases due to their inherent resistance to antibiotic therapy. Exploration of alternative antibiofilm reagents provides opportunities to achieve highly effective treatments. Herein, we propose a strategy to employ self-assembled saccharide-functionalized amphiphilic metallacycles ([2+2]-Gal, [3+3]-Gal, and [6+6]-Gal) with multiple positive charges as a different type of antibacterial reagent, marrying saccharide functionalization that interact with bacteria via “sweet talking”. These self-assembled glyco-metallacycles gave various nanostructures (nanoparticles, vesicles or micron-sized vesicles) with different biofilms inhibition effect on Staphylococcus aureus (S. aureus). Especially, the peculiar self-assembly mechanism, superior antibacterial effect and biofilms inhibition distinguished the [6+6]-Gal from other metallacycles. Meanwhile, in vivo S. aureus pneumonia animal model experiments suggested that [6+6]-Gal could relieve mice pneumonia aroused by S. aureus effectively. In addition, the control study of metallacycle [3+3]-EG5 confirmed the significant role of galactoside both in the self-assembly process and the antibacterial efficacy. In view of the superior effect against bacteria, the saccharide-functionalized metallacycle could be a promising candidate as biofilms inhibitor or treatment agent for pneumonia.
Here we will discuss recent results from our work in which we show conditionally active electron transfer catalysts can be constructed from DNA. The catalysts are comprised of two strands, one of which can be selectively switched between a G-quadruplex and duplex or single-stranded conformations. This switching ability arises from our recent discovery that perchlorate, a chaotropic Hofmeister ion, selectively destabilizes duplex over G-quadruplex DNA. By varying perchlorate concentration, we show that the device can be operated as a switch or signal amplifier. State switching can be achieved in three ways: thermally, by dilution, or by concentration. In each case, when operated in the presence of the cofactor hemin, the device catalyzes electron transfer in only the G-quadruplex state. Examples of secondary-structure remodeling are observed in life as well. Nucleic acids exhibit considerable polymorphism in biological systems, particularly in sequences that can form G-Quadruplexes. Several proteins can remodel G-quadruplexes, and both energy-dependent (i.e., helicases) and energy-independent systems that can do so have been reported. ATP-dependent helicases are known to unwind G-quadruplex structures, and the RNA-binding protein Lin28 has been shown to unfold G-quadruplexes without the requirement for ATP. The structure switching performed by Hofmeister ions in this work thus amounts to a bioinspired means of performing such remodeling, which in turn enables a functional behavior (electron transfer).
Supramolecular self-assemblies of cyanine dyes for tunable excitonic properties across the visible and shortwave infrared regions

Arundhati P. Deshmukh, arundhatipd@ucla.edu, Niklas Geue, Nadine Bradbury, Austin D. Bailey, Ellen M. Sletten, Justin R. Caram. Chemistry & Biochemistry, University of California Los Angeles, Los Angeles, California, United States

Cyanine dyes self-assemble into distinct architectures (sheets, nanotubes or bundles) facilitated by an interplay of solubility, sterics and π-π stacking. We modulate the supramolecular packing and topologies of these self-assemblies in order to tune and explore new photophysical behaviors that are conventionally inaccessible. Photophysical properties of these assemblies are determined by the nature of long range transition dipole coupling that is highly sensitive to geometric arrangement and topology. In linear chains, cofacial arrangement leads to blue shifts in optical transitions whereas head-to-tail arrangements lead to red shifts, called as H- and J-aggregates respectively. Here, we describe an unusual situation that arises from 2-dimensional (2D) transition dipole coupling in sheet-like aggregates that extend upto micron scale. In addition to traditional H- and J-aggregation, we find a new case of I-aggregation which shows intermediate characteristics of both aggregates. We provide mechanistic insights into the self-assembly of extended sheet-like structures using a thermodynamic equilibrium model and lay down general principles for selectively stabilizing an H- or J-aggregated structure, providing a supramolecular avenue for tuning photophysical properties across a broad spectral range. We demonstrate this by stabilizing six different dyes into extended 2D structures with absorptions spanning the visible and shortwave infrared (SWIR) wavelengths. Further, we relate the packing geometries within the extended 2D aggregates to their excitonic band structures ultimately providing supramolecular control over photophysical properties such as absorption/emission wavelengths and quantum yields. Overall, this work establishes molecular aggregation as a new avenue for tuning photophysical properties and thus, opens up supramolecular chromophoric systems to new functionalities including SWIR imaging, plexitonics, and telecommunications.

![Diagram of cyanine dyes and their aggregation states](image-url)
Hydrogen bonding indigo photoswitches as building blocks to engineer photo adaptative materials

Pauline Pacquet¹², pauline.pacquet@insa-lyon.fr, Yann Bretonnière³, Stéphane Chambert², Julien Bernard¹. (1) IMP, UMR 5223, Institut National des Sciences Appliquées de Lyon, Villeurbanne, Auvergne-Rhône-Alpes , France (2) ICBMS, UMR 5246, Institut National des Sciences Appliquées de Lyon, Villeurbanne, Auvergne-Rhône-Alpes , France (3) Laboratoire de chimie, UMR 5182, Ecole normale superieure de Lyon, Lyon, Rhône-Alpes, France

Generating molecular tools displaying supramolecular interactions enable to build materials with properties that can evolve in response to different stimuli. Association/dissociation of these supramolecular systems can indeed be triggered by changing conditions (e.g. temperature, addition of polar solvent, pH...). Among them, light is of great interest owing to its selective and non-invasive nature. In this work, we aim to design photo-adaptive materials relying on hydrogen bonding patterns undergoing association/dissociation through a light-induced molecular movement. We choose to develop such systems using N,N'- modified indigos as photo-switch and an Ureidopyrimidinone (Upy) derivative as hydrogen bonding unit. In comparison to other photoswitches, indigo is attractive because of the large spatial change involved during its isomerization, the red light used in the process and the tunable thermal stability of the Z isomer (modulated by the nature of the N,N'-substituents). In order to build relevant supramolecular systems from indigoid derivatives, we first explored several synthetic pathways to modify indigo scaffolds with different N,N'-substituents and investigated the photophysical properties of the resulting adducts. Efforts were specifically devoted towards the preparation of functionalizable N,N'- or N-mono substituted indigo that could be engaged in amide coupling reactions in order to insert the Upy moieties. The results presented will encompass studies on the synthetic pathways that allow the obtention of such photoswitches as well as the chemical modification’s influence on the photophysical properties and notably on the thermal half-life of the Z isomer which could be tuned from a few seconds to several hours.

Fig. 1 a) E/Z photoisomerization process b) Model system combining Indigo/Upy.
Supramolecular polymers from peptide assembly: From optoelectronic to therapeutic applications

Sebastien Perrier, s.perrier@warwick.ac.uk. University of Warwick, Coventry, West Midlands, United Kingdom

We describe the synthesis, characterisation and both optoelectronic and therapeutic applications of cyclic peptides covalently attached to well-controlled polymeric chains. The conjugates assemble into short nanotubes (20 to 200nm) through the stacking of the cyclic peptide motives, with functionality imparted by the polymeric chains. The resulting constructs show remarkable biological properties, including cell penetration and in vivo biodistribution, and in optoelectronic as light harvesting systems.
Peptide stereocomplexes as supramolecular crosslinks in polymeric biomaterials

Israt Dut, Emma Laudermilch, Jonathan Florian, Vincent Gray, Connor Amelung, Kyle Lampe, Rachel A. Letteri, rl2qm@virginia.edu. Chemical Engineering, University of Virginia School of Engineering and Applied Science, Charlottesville, Virginia, United States

Blending complementary stereoregular macromolecules brings about remarkable transformations in the thermomechanical properties, stability, and morphology of materials, ranging from synthetic semi-crystalline polymers to biomolecules like peptides and proteins. For example, blending d- and l-peptides markedly increases stiffness and proteolytic stability of hydrogel-forming peptide fibers. Hypothesizing that stereochemistry-driven supramolecular interactions between enantiomeric peptides would facilitate gelation of peptide-functionalized polymers, we appended d- and l-peptides to 4-arm poly(ethylene glycol). Whereas the d-peptide conjugates and l-peptide conjugates individually remained soluble or formed soft gels in aqueous solution, blends of the conjugates gelled instantly. Rheology showed higher storage moduli from the blends than those from individual conjugates. Going forward, we look forward to using peptide stereocomplexation to impart a myriad of biomimetic properties to polymer biomaterials, including self-healing and shear thinning behaviors, useful for 3D printing-based manufacturing processes and targeting biological proteins, among other applications.
Supramolecular polymers offer the opportunity to design assemblies of monomers with tunable degrees of order and a broad range of dynamics that optimize their functions. The possibility of programming interactions in these systems through enables design of materials that respond rapidly to external stimuli or to biological structures, dissolve or melt into monomeric liquids for limited life cycles that avoid pollution, and reversible changes in hierarchical structure and function. On the other hand, covalent polymers form mechanically robust soft materials but only with limited dynamics and order since the structural units are attached through primary bonds and they are therefore dominated by entropy. For this reason recycling capacity and life-like behaviors for advanced materials are greatly limited. This lecture reports on novel materials formed by co-assembly of covalent and supramolecular polymers to integrate functions in novel soft materials. Thus, the concept of “hybrid bonding polymers” (HBPs) in which both components coexist is proposed in this lecture and illustrated with several specific examples that offer novel functions. HBPs have led our laboratory to discover strategies to catalyze covalent polymerization, novel biomaterials, robotic materials that emulate living matter, and photocatalytic materials to synthesize solar fuels.
Polyisocyanide hydrogels: Combining synthetic tailorable properties with biological properties

Paul H.J. H. Kouwer, p.kouwer@science.ru.nl. Institute for Molecules and Materials, Radboud Universiteit, Nijmegen, Gelderland, Netherlands

Fibrous hydrogels are omnipresent in the human body. At very low protein concentrations, they form stable, porous networks that are the basis for mechanical characteristics of cytoskeleton and the extracellular matrix. The network gels in our bodies are not static; they respond to physical, chemical and cellular cues that adapt their properties. Such architecture and behavior is not readily realized in synthetic materials. Recently, however, we developed a hydrogel that closely mimics the fibrous structure as well as the linear and nonlinear mechanical properties of cytoskeletal and extracellular matrix materials. The synthetic nature of the material allows us to tune the (mechanical) properties by changing straightforward parameters, like polymer length, concentration and environmental conditions, which can be applied in situ. In this presentation, we will discuss the application of these synthetic materials for cell culturing experiments.
Investigating binding of polymeric cell-penetrating peptide mimics to protein cargo for intracellular delivery applications

Hazel Davis, hcdavis@mail.pse.umass.edu, Nicholas D. Posey, Gregory N. Tew. Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States

There is significant potential in exploiting antibody specificity to develop new therapeutic treatments. However, the intracellular delivery of proteins is a paramount challenge due to the difficulty of transporting large, polar molecules across the impermeable cell membrane. Cell penetrating peptide mimics (CPPMs) include synthetic polymers that are versatile materials for intracellular delivery of biological molecules, including nucleic acids and proteins, often with superior performance to their natural peptide and protein counterparts. Unlike many other commercial reagents, CPPMs do not require a covalent linkage between the protein and carrier. While studies have demonstrated that complexation with a carrier is necessary for delivery of proteins, the nature of CPPM-protein complexes is not well understood. Herein, critical interactions that dominate CPPM-protein complexation were explored. Fluorescence quenching assays revealed the lack of hydrogen bonding interaction between CPPMs and model protein bovine serum albumin and antibody Immunoglobin G. These assays were also used to decouple the effect of electrostatic and hydrophobic interactions between amphiphilic CPPMs and proteins. In addition, competition assays with other proteins and surfactants were conducted and the reversibility of CPPM-protein complexes demonstrated in order to provide insight on mechanisms of protein release. This work offers a promising way to gain insight on how carrier and cargo binding can promote delivery efficacy and intracellular activity. A fundamental understanding of CPPM-protein complexation will enable more robust methods for intracellularly delivering proteins that do not require covalent conjugation and will provide for new therapeutic opportunities.
Host, guest supramolecular recognition in the design of functional soft materials

Matthew Webber, mwebber@nd.edu. Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana, United States

The recognition afforded by macrocycle hosts in binding to a suite of different guests enables routes to rationally design materials from the molecular scale so as to empower specific and tunable functionality. In the context of their use as biomaterials and drug delivery devices, the modularity of these interactions facilitates opportunities to combine multiple bioactivities or therapeutic payloads within a single delivery platform, as well as routes to the facile incorporation of targeting motifs for functional delivery even in the complex biological milieu. A subset of macrocyclic host–guest chemistries are able to achieve affinities approaching that for biotin-avidin, offering a non-covalent approach to enable recognition in complex environments. Whereas conventional ligation reactions can be kinetically limiting, the association of host–guest motifs occurs near the diffusion limit. Accordingly, these interactions form quickly, and at high-affinities may have considerable lifetime. In this work, we describe our efforts to use supramolecular chemistry to facilitate crosslinking in three-dimensional networks of macromers and colloids. In this use, the molecular features of the specific interaction can be translated to the bulk material properties. This approach is also useful in the context of protein modification as a means of altering the stability and pharmacokinetics of therapeutics drugs. Finally, we demonstrate the use of supramolecular recognition to facilitate homing and retention of systemically administered small molecules at desired sites in the body, and in the process overcome dilution and physiologic competition to achieve site-specific accumulation. Supramolecular “click” chemistry thus affords a new tool in the suite of bioconjugation reactions to afford improved design of polymeric soft materials.
Highly tunable, catalyst-free dynamic covalent bonds and their incorporation into networks

Neil Dolinski, dolinski@ucsb.edu, Katie M. Herbert, Stuart J. Rowan. Pritzker School of Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Dynamic covalent networks (DCNs) are polymeric networks that incorporate dynamic chemistries as bonding motifs to enable the formation of a functional, responsive systems. While a range of dynamic chemistries (transesterification, Diels-Alder, disulfide, etc) have been utilized in the synthesis of DCNs, the use of external catalysts or high processing temperatures limit the potential application scope of these materials systems. Recently, the reversible (and low temperature) thia-Michael reaction has received growing interest from researchers as a potential dynamic bond for application in polymeric materials. In this presentation, benzalcyanoacetate/acetamide Michael acceptors are discussed as promising catalyst-free, room temperature dynamic bonds for bulk polymeric materials. Their electronic tunability, phase separation characteristics, and application in a variety of polymeric systems (tunable networks, adhesives, and particle suspensions) are highlighted.

![Dynamic Covalent Networks](image-url)
Synthesis and application of viologen-based polymers and photoredox-responsive soft materials

Faheem Amir¹², Abigail O. Delawder¹, Mark S. Palmquist¹, Tiana M. Saak¹, Jonathan C. Barnes¹, jcbche3@yahoo.com. (1) Chemistry, Washington University in St Louis, St Louis, Missouri, United States (2) Materials Science and Engineering, University of California Los Angeles, Los Angeles, California, United States

Different forms of molecular recognition – such as hydrogen bonding or π-π stacking for example – have proven to be powerful tools in biology and play a major role in mediating communication across cellular membranes and controlling the conformation and function of nature’s biopolymers. Chemists have traditionally designed synthetic polymers that adopt similar forms of molecular recognition as a way to enhance the properties of a material. The Barnes group at Washington University in St. Louis is interested in programming precision polymers with non-natural forms of molecular recognition to obtain new materials with unique functions. Specifically, my group has developed a library of well-defined main-chain polyviologens that undergo chain folding (intramolecularly) in response to reduction of each viologen subunit (aka, N,N’-dialkyl-4,4’-bipyridinium) from its dicationic oxidation state to the corresponding radical cation (i.e., V²⁺ to V●⁺). The molecular recognition process is driven by thermodynamically favorable radical-radical pairing interactions, the extent of which we hypothesize can be tuned depending on the linker units that are installed in between each viologen subunit. Conversion of the polyviologens into macrocrosslinkers through end-capping reactions that place a styrene or an acrylate group at each terminus allows for polymer networks to be established using free radical polymerizations. These polymer networks (hydrogels) can be induced reversibly to undergo large amplitude changes in volume (contraction/expansion) and mechanical properties (higher Young’s modulus, tensile strength, and elasticity) when the constituent polyviologens are reduced in situ. We have demonstrated the versatility of this new mechanism for actuating soft materials by introducing photocatalysts into the hydrogels and irradiating with different wavelengths of visible light, depending on the photocatalyst employed. In my talk, I will describe my laboratory’s progress in these areas, and I will discuss new polyviologen designs and other applications currently being pursued in my group.

This Work: Multimodal Activation (Two Wavelengths of Visible Light and/or Heat)

Summary:
- Blue + Red Light Responsive
- Thermally Responsive
- Bimodal Activation Results in Faster Contraction

[Diagram of multimodal activation process]
Helical supramolecular polymers: Self-assembly, bioactivity, and catalysis

John B. Matson, jbmatson@gmail.com, Zhao Li. Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

A family of synthetic supramolecular polymers has been developed that self-assembles into well defined helical structures. Based on tetrapeptides of the general structure $K_SXZK_S$ ($K_S =$ lysine modified with an S-aroylthiooxime [SATO]; $X$ and $Z$ are variable amino acids), some form nanocoil assemblies spontaneously in water, while others initially form nanoribbons that transform into helical ribbons upon addition of salt. Coarse-grained molecular dynamics simulations revealed that helix formation is driven by a preferred collapsed conformation combined with specific directional interactions. The nanocoils are capable of releasing hydrogen sulfide ($H_2S$), a biological signaling gas, in response cysteine-triggered degradation of the SATO units. Small changes to the order of the amino acids in the peptides lead to formation of other nanostructures, including nanoribbons and toroidal structures. We incorporated histidine residues into these peptides and found that the nanostructure had a dramatic effect on their ability to catalyze hydrolysis of a model analyte.
Stimuli-responsive metallosupramolecular polymer networks

Christoph Weder, christoph.weder@unifr.ch. Adolphe Merkle Institute, Universite de Fribourg, Fribourg, Fribourg, Switzerland

Supramolecular polymers (SMPs), in which the monomer units are connected by directional secondary interactions instead of covalent bonds, offer properties that merge the characteristics of conventional polymers with the reversible and dynamic nature of supramolecular interactions. The possibility to reversibly disassemble SMPs and shift the equilibrium from macromolecules to oligomers or monomers facilitates their processing and recycling, imparts stimuli-responsive properties, and enables functions such as reversible adhesion, healing, and mechanical morphing. However, most supramolecular polymers exhibit mechanical properties that are inferior to those of conventional commodity plastics. We show here that this problem can be overcome in semicrystalline metallosupramolecular polymer networks. These materials combine attractive mechanical properties, notably high stiffness and strength, with high thermal stability. Such materials can be toughened by creating blends that micro-phase separate into hard and soft domains and optional plasticization. The mechanical properties of these materials can be tuned over a large range by simple variation of the ratio of the two constituents. The option to combine the supramolecular monomers in any ratio further allows the creation of compositionally graded objects in which the mechanical properties can be varied in a spatially controlled manner.
Exploring the influence of hydrogen-bonding in supramolecular electronics: From a diketopyrrolopyrrole model system to state-of-the-art semiconductors

Amparo Ruiz Carretero¹, ruizcarretero@unistra.fr, Nelson R. Avila Rovelo¹, Gabriel S. Alvarez Martinez¹, Ana Maria Garcia Martinez¹, Shu Seki², Philippe Mesini¹. (1) Universite de Strasbourg, Strasbourg, Grand Est, France (2) Kyoto Daigaku Kogakubu Daigakuin Kogaku Kenkyuka, Kyoto, Japan

The presence of noncovalent interactions in organic semiconductors has been demonstrated to be beneficial in several applications, resulting in the enhancement of charge transport and device efficiency. Particularly, semiconducting supramolecular polymers resulting from hydrogen-bonding interactions have been proven to increase solar cell efficiency by 50%. Nevertheless, the race for achieving efficiency records, has hampered research focused on solving other fundamental issues. Regarding hydrogen-bonding, no comparative studies have been performed, finding scattered examples in literature with different semiconductors, hydrogen-bonding units and without complete studies including both, the optoelectronic and self-assembly properties. The main goal of our research is to understand the role and impact of hydrogen bonds in supramolecular electronics in order to apply them efficiently in devices.

Here we show a comparative study using diketopyrrolopyrrole (DPP) as a model electroactive segment and how the results obtained are translated into state-of-the-art materials, such as quinquethiophene-rhodanine and isoindigo derivatives. Different families of hydrogen-bonded DPP supramolecular polymers displaying different hydrogen-bonding parameters (position, number, function, chirality) will be discussed, including photoconductivity measurements, charge transport and spin state correlation in real devices. Finally, the results obtained with DPP will be expanded to the state-of-the art semiconductors, showing the results obtained in rhodanine-based systems.
Tuning the molecular packing of supramolecular assembly by H-bonding and impact on morphology

Amrita Sikder, A.Sikder.1@bham.ac.uk, Rachel K. OReilly. School of Chemistry, University of Birmingham, Birmingham, Birmingham, United Kingdom

Self-assembly is one of the most fundamental characteristics of life. Nature uses self-assembly to build supramolecular materials that possesses fascinating properties (self-healing, adaptive, reconfigurable and responsive) which are fundamental for many complex biological functions. Understanding the self-assembly processes of biological systems facilitates the fabrication of novel supramolecular materials and vice versa. Although significant work has been done in the field of supramolecular self-assembly to develop innovative materials, still it remains a challenging task to precisely control the morphology of a particular self-assembled system and mostly depends on trial and error method. Scientists have long endeavored to develop alluring nanostructures by introducing various noncovalent forces to the constituting building blocks of the amphiphile. Hydrogen-bonding is one of the important noncovalent interaction that can be utilized to generate elegant nanostructure by imparting directionality in the self-assembled systems and DNA double helix, folding of proteins are to name a few that exist in nature. Therefore, exploration of H-bonding mediated self-assembly is of fundamental interest. Here we have demonstrated the impact of H-bonding on supramolecular assembly of structurally near identical -amphiphiles (Scheme 1) by systematically varying the number of H-bonding units. NDI-1 with two H-bonding units formed nanotubes in aqueous medium. Interestingly, when the amide bond was replaced by an ester group, the amphiphile NDI-2 revealed nano-ribbon morphology. Whereas, NDI-3 lacking any H-bonding functionality formed cylindrical micelles. Spectroscopic measurements revealed that H-bonding plays a crucial role in molecular packing which was reflected in the fluorescence properties of the self-assembled systems as well. Highlights of these results will be described in the presentation.
Responsive polymers: Hysteresis, bistability, read/write-memory and logic gate function

Joanna Michalska, Beate Förster, Stephan Hauschild, Stephan Förster, s.foerster@fz-juelich.de. Forschungszentrum Julich GmbH, Julich, Nordrhein-Westfalen, Germany

Stimuli responsive materials change their state in response to external stimuli. Switching between different states enables to read and write information, and to perform logical operations. This requires reversibility and bistability, which for responsive materials so far has been realized by triggering chemical reactions to drive phase transition between the respective two states.

Here we successfully demonstrate bistability, remanence, reversible write/read information storage and logic gate function for a responsive linear polymers and block copolymers based on the intrinsic hysteresis of the volume phase transition, without chemical reactions. Information can be written by thermal writing on a reflective display using a laser, or simply manually by using heated or cooled pen tips. We furthermore demonstrate a memory function and an AND-logic gate function, which is based on temperature and pH-values as input. We show that the hysteresis is related to cluster domain formation occurring at the volume phase transition, which is a very common phenomenon for thermally responsive polymers such that this principle is applicable to a broad range of responsive materials.
"Static" and evolving supramolecular gels

Dave J. Adams¹, dave.adams@glasgow.ac.uk, Santanu Panja¹, Annela Seddon², Bart Dietrich¹. (1) University of Glasgow, Glasgow, Glasgow, United Kingdom (2) University of Bristol, Bristol, Bristol, United Kingdom

Supramolecular gels can be formed by the self-assembly of certain molecules into fibrous structures which form a network. Depending on how these are prepared, the gels form essentially static systems whereby their properties do not change with time, at least over a significant period of time. Other gels can be pre-programmed such that their properties change with time. This can be induced by bringing about changes in the underlying fibrous structures, the network or by generating phase changes. Here, we will describe how we have been generating such systems to allow interesting materials to be formed.
Reactive supramolecular nanostructures

Yukio Cho, Ty Christoff-Tempesta, Julia Ortony, ortony@mit.edu. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Self-assembly of amphiphilic small molecules in water leads to well-defined nanostructures with a remarkable degree of internal organization. The nanostructures exhibit high surface areas and can be designed to present a range of functional groups at their surfaces. However, by definition, the amphiphilicity and packing requirements of the constituent molecules limit the diversity of surface groups achievable. This limitation reflects that self-assembly is generally harnessed as the final step in the construction of supramolecular nanostructures. In this talk, I will describe how we generate nanostructures with domain-specific reactivities. I will then show how we carry out post-assembly reactions to form supramolecular nanostructures that are otherwise unobtainable. Finally, I will outline some new capabilities and applications enabled by this approach.

A self-assembled nanostructure with domain-specific reactivities undergoes a thermally induced reaction.
Design and applications of supramolecular peptide nanomaterials

Tanja Weil, weil@mpip-mainz.mpg.de. Synthesis of Macromolecules, Max-Planck-Institute for Polymer Research, Mainz, Germany

Polyeptide nanostructures are ubiquitous in Nature and play a crucial structural and functional role. Within cells, they form the fibrous part of the extracellular matrix as well as the cytoskeleton. Amyloid peptide nanostructures, which are rich in ordered β-sheet structures, display rich bioactivities as they are involved in melanin biosynthesis, hormone storage and several severe proteinopathies. We have identified peptide sequences through rational design that assemble into ordered peptide nanostructures that can capture virions and bind to cellular membranes. The self-assembling peptides were optimized in terms of their sequences and morphologies in order to achieve efficient gene transduction and pH-controlled local drug release. Certain sequences also stimulated the growth of neuronal cells in an in vivo model for nerve regeneration. Peptide nanostructures can also be formed inside living cells through multistage chemical reactions that occur in different cellular compartments and based on different intracellular stimuli. The formation of synthetic nanostructures in the cytosol of cancer cells affects cell viability, which opens new opportunities for applications in oncology.
Synergies of supramolecular and dynamic covalent bonding for responsive networks

Dominik Konkolewicz, d.konkolewicz@gmail.com, Shiwanka V. Wanasinghe, Nethmi De Alwis Watuthanthrige, Obed Dodo, Jafer Vakil, Jessica Sparks. Miami University, Oxford, Ohio, United States

Polymer networks containing consist of long polymer linked together using crosslinking points. Introduction of dynamic linkers, such as non-covalent or dynamic covalent linkers into a polymer material can give materials with properties such as self-healing, increased toughness and shape memory characteristics. However, there is a delicate tradeoff between desirable dynamic characteristics and also undesirable mechanical instability under load or susceptibility to creep. Therefore, designing dynamic linkers with optimized for dynamic character and performance under ambient conditions is critical to applications of these materials. This contribution will focus on polymer materials that contain both dynamic covalent and dynamic non-covalent bonds in a single material. Distinct dynamic covalent chemistries will be explored, leading to a synergy of dynamic character from the fast exchanging bond and stability from the tunable slow exchanging bond. In particular, engineering of the dynamic chemistry exchange rate and equilibrium bonding will be explored to enhance materials mechanical performance and adaptability. Polymer architecture is a further tool that can be used to enhance and tune material properties, with both macromolecular and network architecture explored.
Single crystals of mechanically entwined helical covalent polymers

Yiming Hu¹, yiming.hu@colorado.edu, Simon Teat², Wei Zhang¹. (1) Chemistry, University of Colorado Boulder, Boulder, Colorado, United States (2) E O Lawrence Berkeley National Laboratory, Berkeley, California, United States

Double helical conformation of polymer chains is widely observed in biomacromolecules and plays an essential role in exerting their biological functions, such as molecular recognition and information storage. It has remained challenging however to prepare synthetic helical polymers, and those that exist have mainly been limited to single stranded polymers or short oligomeric double helices. Here, we report the synthesis of covalent helical polymers, with high molecular weight, from the achiral monomer hexahydroxytriphenylene through spiroborate formation. Polymerization and crystallization occurred simultaneously under solvothermal conditions, forming single crystals of the resulting helical covalent polymers. Characterization by single-crystal X-ray diffraction shows that each crystal consists of pairs of mechanically entwined polymers. No strong non-covalent interactions are observed between the two helical polymers forming a pair; instead, each strand interacts with neighbouring pairs through hydrogen bonding. Each individual crystal is made up of helical polymers of the same handedness, but the crystallization process produces a racemic conglomerate, with equal amounts of right-handed and left-handed crystals.
Synergism between rifampicin and cationic polyurethanes overcomes intrinsic resistance of E. coli

Chinnapatch Tantisuwanno¹, ct75@uakron.edu, Francis Dang¹, Kristin Bender², John D. Spencer², Matthew E. Jennings³, Hazel A. Barton⁴, Abraham Joy¹. (1) Polymer Science and Polymer Engineering, University of Akron, Akron, Ohio, United States (2) Center for Clinical and Translational Research, Abigail Wexner Research Institute at Nationwide Children’s Hospital, Columbus, Ohio, United States (3) Biology Department, Centenary College of Louisiana, Shreveport, Louisiana, United States (4) Department of Biology, University of Akron, Akron, Ohio, United States

Antibiotic-resistant Gram-negative bacteria are an emergent pathogen, causing millions of infections worldwide. While there are several classes of antibiotics that are effective against Gram-positive bacteria, the outer membrane (OM) of Gram-negative bacteria excludes high molecular weight hydrophobic antibiotics, making these species intrinsically resistant to several classes of antibiotics, including polyketides, aminocoumarins, and macrolides. The overuse of antibiotics, such as b-lactams has also promoted the spread of resistance genes throughout Gram-negative bacteria, including the production of extended spectrum b-lactamases (ESBL). The combination of innate and acquired resistance makes it extremely challenging to identify antibiotics that are effective against Gram-negative bacteria. In this study, we have demonstrated the synergistic effect of outer membrane permeable cationic polyurethanes with rifampicin, a polyketide that would otherwise be excluded by the OM, on different strains of E. coli, including a clinically isolated uropathogenic multidrug resistant (MDR) E. coli. Rifampicin combined with a low dose treatment of a cationic polyurethane reduced the MIC in E. coli of rifampicin by up to 64-fold. The compositions of cationic polyurethanes were designed to have low hemolysis and low cell cytotoxicity, while maintaining high antibacterial activity. Our results demonstrate the potential to rescue the large number of available OM-excluded antibiotics to target normally resistant Gram-negative bacteria via synergistic action with these cationic polyurethanes.
The striking resemblance between biological one-dimensional structures and supramolecular polymers assembled in water inspired many chemists to study these artificial mimics for possible biomedical applications. In our research we use water-soluble 1,3,5-benzene-tricarboxamides (BTAs) that from one-dimensional fibers in aqueous solution. By modifying the periphery of these BTAs, we can create biological relevant copolymers that can use their dynamic nature to adapt their structure to rearrange the ligands accordingly to the receptors at the cell membrane. In the lecture, we will show that fundamental insights into the dynamic nature of these copolymers are essential to create function.
Multicomponent supramolecular polymers as a platform for the design of glycoconjugate vaccines

David Straßburger¹, Moritz Urschbach¹, Natascha Stergiou², Edgar Schmitt², Pol Besenius¹, besenius@uni-mainz.de. (1) Department of Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany (2) Institute of Immunology, Johannes Gutenberg-University Mainz, Mainz, Germany

Peptide secondary structures can be harnessed to design monomers capable of self-assembling into supramolecular polymers in aqueous media. Decorating the surface with immunogenic molecular patterns results in pathogen-mimicking entities and potential vaccine candidates. In the context of antitumor vaccines, the challenge is to overcome self-tolerance mechanisms to enforce an immune response against endogenous, tumor-associated glycopeptide motifs. To this end, a co-stimulation of B cells with Th cells is mandatory, which we aim to achieve using a co-presentation of different epitopes and immunostimulating agents at the surface of multicomponent supramolecular polymers. Mucin 1 (MUC1) is well-known for undergoing alterations in O-glycosylation during tumorigenesis, and is thus an excellent tumor-associated target structure for immunotherapy. In this contribution I focus on the use a fully synthetic glycopeptide from the MUC1 tandem repeat sequence. As T cell epitope we chose a small fragment from highly immunogenic tetanus toxin (p30). Additionally, an imidazoquinoline as potent TLR7/8 agonist, was synthesized. These epitopes were conjugated to supramolecular monomers and mixed in aqueous solution to yield a polymeric vaccine formulation. High antibody titers of the IgG type were observed in C57BL/6 mice and FACS analysis confirmed the high binding affinity of the antibodies to T47D tumor cells. These results support the potential of this modular supramolecular platform approach for the development of glycoconjugate vaccines.
Designing optically transparent photo-crosslinked peptoid nanosheets for imaging applications

Elizabeth A. Holman\textsuperscript{1,2}, holman.ea@gmail.com, Dong Li\textsuperscript{2}, Paul D. Ashby\textsuperscript{2}, Ronald N. Zuckermann\textsuperscript{2}, Paul Sternberg\textsuperscript{3}. (1) Chemistry, California Institute of Technology, Pasadena, California, United States (2) Molecular Foundry, E O Lawrence Berkeley National Laboratory, Berkeley, California, United States (3) Biology and Bioengineering, California Institute of Technology, Pasadena, California, United States

Peptoid bilayer nanosheets are a new class of biocompatible 2D nanomaterial with broad applications, including sensing, membrane mimicry and pathogen binding. They are formed from the self-assembly of sequence-defined peptoid chains and can be readily functionalized to tune their properties. In order to broaden their utility, there is a need to improve their mechanical stability. Here, we create nanosheets that can function as a mechanically robust, optically transparent interfacial barrier for covering microfluidic channels, microscopy grids and other sample chambers. This barrier would increase hydration control in otherwise open-channel environments, permitting water-sensitive, non-destructive infrared spectroscopy to be incorporated into multimodal imaging platforms. Therefore, we explored new peptoid analogs containing photo-crosslinkable side chains that can form intra-monolayer as well as inter-layer covalent bonds. These constructs can be co-assembled in various ratios to achieve a range of desirable mechanical properties to provide a new route to ultrathin, mechanically robust, 2D nanomaterials that serve as optically transparent interfacial barriers for a variety of imaging techniques.
Controlling supramolecular assembly and dynamics for advanced tissue engineering hydrogels

Matthew B. Baker, m.baker@maastrichtuniversity.nl. Complex Tissue Regeneration, Universiteit Maastricht Faculty of Health Medicine and Life Sciences, Maastricht, Limburg, Netherlands

Mimicking the complex environment of a cell in 3D remains a challenge in tissue engineering. Both engineering biomimetic hydrogels and biofabrication of complex 3D shapes provide avenues to create complex tissues. Synthetic supramolecular hydrogels provide the opportunity to recreate the fibrous self-assembled structure of the native ECM; however, the control of the hydrogel properties and their translation to advanced fabrication technologies has remained a challenge. Recently, we have created a small library of hydrogels based on the supramolecular polymerization of 1,3,5-benzenetricarboxamide (BTA) macromers. Via molecular engineering, we can alter the self-assembly, mechanical properties, and functional behavior of cells in these hydrogels. In this talk, I will focus on the tuning of the dynamic and viscoelastic properties of the hydrogels, the effect of these properties on cellular behavior, and the translation of these materials for use in 3D bioprinting as bioinks. With careful control over the (supra)molecular structure, we can move from soft, liquid-like supramolecular polymers to highly functional materials for tissue engineering.

Moving from supramolecular fibers in water, careful control of the viscoelastic properties of the self-assembled hydrogels can facilitate applications in advanced cell culture and 3-D bioprinting.
Influence of light, acid and metal coordination on hierarchical self-assembly processes

**Gustavo Fernández**, fernandg@uni-muenster.de. Organisch-Chemisches Institut, Westfalische Wilhelms-Universität Münster, Münster, Nordrhein-Westfalen, Germany

Understanding the influence of various external stimuli on the hierarchical organization of p-systems is key to develop smart functional materials. Herein, the self-assembly of a small p-conjugated molecule (L₁) as well as its responsiveness towards light, TFA addition (L₁:TFA) and complexation of metal ions (Pd²⁺ and Pt²⁺) have been elucidated via mechanistic studies. Target ligand L₁ undergoes complex time-, temperature- and concentration-dependent self-assembly pathways driven by H-bonding leading to fiber-like associates. Irradiation with UV light (365 nm) leads to a reversible transition from long to short fibers. On other hand, addition of trifluoroacetic acid (TFA) causes the transformation of the anti-parallel H-bonded fibrillar assembly of L₁ in MCH into superhelical fibers stabilized by H-bonding of parallel-stacks of L₁:TFA. Light irradiation causes a strain-driven disassembly and subsequent aggregate reconstruction that ultimately leads to short fibers. In contrast, complexation of Pd and Pt(II) ions (complexes C₁ and C₃) leads to a slight attenuation of the supramolecular growth into short thin fibers. Interestingly, the long thin fibers of C₁ transform reversibly into short thin fibers upon irradiation with UV light. Surprisingly, the fibers formed by C₃ show no changes upon light irradiation, but they undergo coordination isomerism. The mechanism of self-assembly and photo responsive behavior of all these species have been elucidated using UV-Vis, 1D and 2D NMR and AFM investigations.
Transfer and amplification of asymmetry in supramolecular polymers: From kinetic effects to CPL-emitter materials

Cristina Naranjo¹, Yeray Dorca¹, Elisa E. Greciano¹, Goutam Ghosh², Rafael Rodríguez³, Rafael Gómez¹, Katsuhiko Maeda³, Gustavo Fernández², Luis Sanchez¹, lusamar@ucm.es. (1) Química Orgánica, Universidad Complutense de Madrid, Madrid, Comunidad de Madrid, Spain (2) Organisch-Chemisches Institut, Westfalische Wilhelms-Universität Münster, Münster, Nordrhein-Westfalen, Germany (3) WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa Daigaku, Kanazawa, Ishikawa, Japan

Helical structures have inspired scientists due to the relevant functionalities displayed for these chiral entities in living organisms. Macromolecules and small molecules have been thoroughly utilized to achieve this fascinating, chiral topology. Of special interest is the process of transfer and amplification of asymmetry reached in supramolecular polymers from the molecular to the supramolecular level that finally yields helical aggregates. In this communication, we will show two different examples on chirality in supramolecular polymers. In the first one, the kinetic, chain-capper effect provoked by the metastable monomeric species (M*) formed from the trisbiphenylamine tricarboxamides (S)-1 and (R)-1 in the corresponding majority rules (MR) experiments will be presented. In the second example, the formation of homochiral helical aggregates from self-assembled N-annulated perylene tetracarboxamides 3-5, capable to emit circularly polarized light (CPL) with remarkable |glum| values, will be illustrated as an example of the achievement of functional, supramolecular polymers.

Figure 1. (a) Chemical structure of the trisbiphenylamine tricarboxamides (S)-1 and (R)-1; (b) schematic illustration of the chain-capper effect exerted by the M* species in the MR experiments; (c) chemical structure of the N-annulated perylene tetracarboxamides 3-5; (d) schematic illustration of the formation of supramolecular CPL-emitters from chiral 3 and 4.
Squaramides as versatile binding units for the development of supramolecular polymers

Bartolome Soberats, b.soberats@uib.es. Dpt. of Chemistry, Universitat de les Illes Balears, Palma de Mallorca, Illes Balears, Spain

Squaramides are a family of compounds based on a cyclobutenedione ring with two directly bonded amino groups. This molecular configuration confers them versatile non-covalent interaction possibilities by means of hydrogen bonds, dipolar interactions and \( \pi-\pi \) stacking. Accordingly, squaramide derivatives have been increasingly used in supramolecular chemistry to develop molecular receptors and sensors, catalysts, and more recently supramolecular polymers and gels. Our research focuses on the study of the self-assembly patterns of squaramide units and its capacity to generate pathway complexity and supramolecular polymorphism. On the one hand, we developed a new macrocycle self-assembling via hydrogen bonds into two different polymorphs depending on the Z,E conformation of the squaramide units. On the other hand, we prepared a family of amphiphilic aryl-squaramides that aggregate in water via uncommon dipolar \( \pi-\pi \) interactions, while no hydrogen bonds are formed. These latter compounds have been applied for the preparation of thixotropic hydrogels for the controlled release of zwitterions. We believe that the versatility of squaramides to form supramolecular aggregates through different interactions makes them interesting compounds for the development of novel supramolecular materials.

Figure 1. a) Schematic illustration of self-assembly behavior of two different squaramide-based systems. The aggregation in organic solvents is driven mainly by hydrogen bonding and leads to supramolecular polymorphism. In water environments, other interactions such as \( \pi-\pi \) interactions play an important role on the self-assembly.
Modeling of the effects of addition of zinc on morphology and rheology of xanthan gum polysaccharide solutions

Kolattukudy P. Santo¹, santotheophys@gmail.com, Andrei Potanin², Alexander V. Neimark¹. (1) Chemical and Biochemical Engineering, Rutgers The State University of New Jersey, Piscataway, New Jersey, United States (2) Colgate Palmolive Co, Piscataway, New Jersey, United States

We study the effects of metal complexation on the morphology and rheology of Xanthan gum (XG) polysaccharide aqueous solutions containing Zn ions, by multi-scale computational modelling. XG is the most widely used exopolysaccharide in food, cosmetic and health care products and in many cases, contains metal salts like ZnCl₂. Here, we perform extensive atomistic molecular dynamics (MD) and mesoscale dissipative particle dynamics (DPD) simulations of XG-Zn aqueous solutions at different Zn and polymer concentrations. The conformational effects of Zn on the level of individual chains are studied by MD simulations employing the cationic dummy atom model of Zn ion. DPD simulations are performed by developing original coarse-grained models, to analyze the rheological and conformational changes induced by Zn ions in multichain systems with and without shear flow. MD simulations reveal that Zn dramatically affects conformations of single chains, by forming various loop/hairpin structures (Fig. 1) via crosslinking the side chains, the extent of which depends on the pyruvate content in the chain, while the radius of gyration of the chains is found to decrease with increased pyruvate content. Multichain systems, exhibit Zn-induced inter-chain crosslinking, and undergo a sol-gel transition upon increase of polymer and Zn concentrations. With shear flow, the chains undergo an orientational transition to a nematic phase, aligning in the flow direction, which leads to a bundling transition accompanied by a gel-sol transition at high Zn content and shear rate. While the orientational and bundling transitions decrease XG viscosity, at low shear rates, the interchain crosslinking increases viscosity (Fig.1). We find that the morphological behavior of the chains is strongly dependent on the pyruvate content, which may have practical implications for the choice of the XG compositions for specific applications.

Figure 1. (Left) XG chain extended conformation without Zn and loop structure formed with 20 Zn ions in atomistic simulations. (Right) XG viscosity at different shear rates as function of Zn concentration in DPD (with units scaled).
Intramolecular cyclization induced crystallization driven self-assembly

Hui Sun¹, sunhui@nxu.edu.cn, Jianzhong Du². (1) Ningxia University, Yinchuan, Ningxia, China (2) Tongji University, Shanghai, Shanghai, China

Macromolecular self-assembly is a powerful tool to fabricate multifunctional nanomaterials. Highly crystalline nano-objects have unique optical, electrical, and magnetic properties, and have received widespread attention. However, it is quite challenging to prepare highly crystalline nano-objects through traditional self-assembly strategies. The crystallization-driven self-assembly is an efficient method to solve this problem, but the nucleation segment is limited to crystalline or semi-crystalline polymers such as polyferrocenylsilane (PFS), poly(lactic acid) (PLA), polycaprolactone (PCL) and so forth, restricting the development of this filed. Based on our previous study, we creatively used amorphous poly(amic acid) (PAA) as building blocks, and proposed a new concept of intramolecular cyclization-induced crystallization-driven self-assembly (ICI-CDSA). Upon thermo-induced intramolecular cyclization, rigid and crystalline polyimide segments are introduced into the backbone of PAA to drive the self-assembly, leading to the formation of nanobundles, nano-flowers with controlled number of petals, and nanowires with high crystallinity. The critical degree of imidization for the occurrence of crystallization-driven self-assembly was determined to be 92%, below which only amorphous nano-objects were obtained. When the initial concentration was low, nanobundles were formed. As the initial concentration increases, the nanobundles underwent hierarchical self-assembly to form nano-flowers with controlled number of petals. The proposed ICI-CDSA opens a new avenue to prepare highly crystalline nano-objects using amorphous polymers as building blocks. Considering the diversity and the structural designability of PAA, the ICI-CDSA will promote the rapid development of crystallization-induced self-assembly and is an important supplement to the theory of macromolecular self-assembly.
POLY – Structure to Function in Supramolecular Polymers & Materials

Elucidating dynamic behavior of synthetic supramolecular polymers in water

Anja Palmans, a.palmans@tue.nl. Chemical Engineering and Chemistry, TU Eindhoven, Eindhoven, Netherlands

We present a generally applicable approach to elucidate the structure, self-assembly mechanism and dynamics of one-dimensional supramolecular polymers in water, which is essential for their application as biomaterials. Although a plethora of techniques is available to study the first two properties, there is a paucity in possibilities to study dynamic exchange of monomers between supramolecular polymers in solution. Thus, for the latter we apply hydrogen/deuterium exchange mass spectrometry (HDX-MS) to characterize the dynamic nature of synthetic supramolecular polymers with only a minimal perturbation of the chemical structure. The technique is applicable to a diverse library of assemblies. The only requirements are that there are exchangeable hydrogen atoms protected from direct contact with the solvent and that the monomer concentration is sufficiently high to ensure the presence of supramolecular polymers during dilution. We observe that the kinetic behaviour as probed by HDX-MS is influenced by the internal order within the supramolecular polymers and by the self-assembly mechanism. HDX-MS is extremely useful to assist in the rational design of building blocks able to form supramolecular polymers in water. Our results demonstrate that the structure, self-assembly mechanism and dynamics of supramolecular polymers are not independent variables and are best evaluated simultaneously.
It remains a challenging task to control the functional group display at the inner or outer surface of a vesicle at will. We have recently solved this classical problem by H-bonding functional group attached π-Amphiphiles. Basically, driven by the motivation to form extended H-bonding, both A-1 and A-2 undergo unidirectional orientation and furthermore the propensity of the H-bonded chain to remain at the inner wall ensures display of the functional group attached to the H-bonded arm at the inner wall while the functional group attached with the other arm are displayed at the outer surface. This has been tested with a series of unsymmetric bolaamphiphiles having different anionic head groups. Subsequent studies demonstrate the possibilities of precisely tuning the size and surface charge density of such vesicles by systematic variation of the structure of the ionic head groups which was reflected in their ability to inhibit the enzymatic activity of ChT. Most recently, H-bonding regulated functional group display has also been verified by the glycol-cluster effect exhibited by sugar-functionalized similar π-amphiphiles. Hydrazide containing bolaamphiphile produces unsymmetric membrane leading to effective display of the sugar moieties at the vesicular surface which enables much efficient binding with ConA compared to control molecule lacking any H-bonding group. Interestingly when the hydrazide group was replaced by amide, the amphiphile revealed cylindrical micellar structure which showed even better multivalent effect for interaction with biological targets owing to the more adaptable nature of cylindrical structure than vesicle. Very recently we have explored such directional assembly with cationic derivatives and shown strong impact in their antimicrobial activity. We also have used such self-assembly motifs for protein assembly, supramolecular protein-polymer conjugation and stimuli responsive activity tuning. Highlights of these results will be described in the presentation.
Enhanced gene delivery and CRISPR/Cas9 homology-directed repair in serum by minimally succinylated polyethylenimine

Md Nasir Uddin¹, nud223@uky.edu, Logan Warriner², Daniel Pack²,³, Jason E. Derouchey¹. (1) Chemistry, University of Kentucky College of Arts and Sciences, Lexington, Kentucky, United States (2) Chemical and Materials Engineering, University of Kentucky College of Engineering, Lexington, Kentucky, United States (3) Pharmaceutical Sciences, University of Kentucky College of Medicine, Lexington, Kentucky, United States

Gene therapy aims to treat patients by altering or controlling gene expression. The field of gene therapy has had increasing success in recent years primarily using viral-based approaches, however, there is still significant interest towards the use of polymeric materials due to their potential as flexible, low-cost scaffolds for gene delivery that do not suffer the mutagenesis and immunogenicity concerns of viral vectors. To address the challenges of efficiency and biocompatibility, a series of zwitterion-like polyethylenimine derivatives (zPEIs) were produced via the succinylation of 2-11.5% of PEI amines. With increasing modification, zPEI polyplexes exhibited decreased serum protein aggregation and dissociate more easily in the presence of a competitor polyanion when compared to unmodified PEI. Surprisingly, the gene delivery mediated in the presence of serum showed that even succinylation of as few as 2% of PEI amines resulted in transgene expression 260- to 480-fold higher than that of unmodified PEI and 50- to 65-fold higher than that of commercial PEI-PEG2k in HEK293 and HeLa cells, respectively. Remarkably, the same zPEI also produced 16-fold greater efficiency of CRISPR/Cas9 gene knock-in compared to unmodified PEI in the presence of serum. In addition, we show that 2% succinylation does not significantly decrease polymer/DNA binding ability nor reduce serum protein interaction to a significant extent, yet this small modification is still sufficient to aid a remarkable transgene expression and gene knock-in in the presence of serum.
Design strategies to synthesize sequence-defined polymers remain fairly limited for industrial-scale applications, often due to complex multi-step syntheses with low reaction tolerances. Recently, a supramolecular approach enabled the synthesis of a sequence-defined sp³-saturated copolymer, the diamond nanothread. Alternating copolymer nanothreads are synthesized by the pressure-induced polymerization of stacks of eclipsed aromatic cores to 10s of GPa. Polymerization proceeds through a one-dimensional cycloaddition with reaction outcomes dependent on monomer design. Here, we will discuss efforts to polymerize supramolecular monomers into one-dimensional sp³ architectures using guided noncovalent interactions to achieve sequence definition. The effort designed monomer pairs favoring nanothread formation through preorganizing desired external functionalities using combined aryl:perfluoroaryl synthons and intermolecular hydrogen bonding of phenol and pentafluorophenol. Our approach realized polymerization being initiated at lower pressures compared to the individual components. The polymerization of supramolecular monomers lends insight toward the further design of complex sequence-specific polymeric nanothreads, with potential toward large-scale industrial syntheses.
Competing hydrogen bonding supramolecular polymers allow thermo thickening effect

Laurent Bouteiller\textsuperscript{1,2}, laurent.bouteiller@upmc.fr. (1) Centre National de la Recherche Scientifique, Paris, Île-de-France, France (2) Sorbonne Université, Paris, Île-de-France, France

Introduction of competing interactions in the design of a supramolecular polymer creates pathway complexity. Ester–bis-ureas (see figure) contain both a strong bis-urea sticker that is responsible for the build-up of long rod-like objects by hydrogen bonding and ester groups that can interfere with this main pattern in a subtle way. Spectroscopic (FTIR and CD), calorimetric (DSC, see figure), and scattering (SANS) techniques show that such ester–bis-ureas self-assemble into three competing rod-like supramolecular polymers. The previously unreported low-temperature supramolecular polymer is stabilized by hydrogen bonds between the interfering ester groups and the urea moieties and also features a weak macroscopic alignment of the rods. The other structures form isotropic dispersions of rods stabilized by the more classical urea-urea hydrogen bonding pattern. The transition from the low-temperature structure to the next occurs reversibly by heating and is accompanied by an increase in viscosity (see figure), a rare feature for solutions in hydrocarbons.
Effect of pH and functionalisation of self-assembled Naphthalene-diimides for smart window applications

Rebecca Randle¹, 2412311R@student.gla.ac.uk, Leide Cavalcanti², Stephen Sproules¹, Emily Draper¹. (1) University of Glasgow, Glasgow, Glasgow, United Kingdom (2) b. ISIS Neutron and Muon Source, Didcot, United Kingdom

Naphthalene diimides (NDIs) have great potential for application to electrochromic Smart Windows due to their colourless native states, highly stable dark reduced states (due to a highly coloured radical anion or dianion produced both photo-and electrochemically) and fast switching times. NDIs functionalised with simple amino acids and dipeptides have advantages of facile synthesis, low cost and operating conditions (low redox potentials), and solubility in water. The effectiveness of each NDI is affected by the aggregated state used, which is affected by both functional group and the absolute pH used. We report a number of systems which demonstrate darkest colouration upon reduction and fastest electrochemical oxidation at an 'ideal' pH. We deduce that aggregation has a significant effect upon chromic properties of these systems and evaluate their long-term use within a Smart Window electrochromic device in their individual ideal aggregated states.

(a) Schematic diagram of the FTO window setup (b) Images of the neutral and reduced colouration of buffered NDI-I at 10 mg/mL adjusted to pH 9.2. Colouration occurred as a result of application of -2.5 V for 120 seconds
Programming self-assembly of minimalistic heterochiral peptides: from simplicity to complexity

Ana M. Garcia¹, Michele Melchionna¹, Ottavia Bellotto¹, Slavko Kralj², Sabrina Semeraro¹, Evelina Parisi¹, Daniel Iglesias¹, Paola D’Andrea³, Rita De Zorzi¹, Attilio V. Vargiu⁴, Silvia Marchesan¹, marchesan.silvia@gmail.com. (1) Chemical and Pharmaceutical Sciences, Universita degli Studi di Trieste, Trieste, Friuli-Venezia Giulia, Italy (2) Materials Synthesis, Institut Jozef Stefan, Ljubljana, Slovenia (3) Life Sciences, Universita degli Studi di Trieste, Trieste, Italy (4) Physics, Universita degli Studi di Cagliari, Cagliari, Sardegna, Italy

Self-assembling peptides are being widely studied for applications both in health and nanotechnology. Their uses are closely linked to their modes of self-organization, which determine the functional nanostructures that they form. Research in this area stemmed from the ability of hydrophobic (tri)peptides to stack into anisotropic structures (e.g., fibrils) with an amphipathic architecture that provides gelling ability and stability in water. Recent developments included a more diverse set of amino acids with interesting chemical features and functional groups on the side chains to program the supramolecular behaviour of heterochiral short peptides in new ways. As an example, two structural elements that direct supramolecular behavior in divergent directions were combined in one sequence: proline as a β-breaker and the β-structure-associated diphenylalanine motif. The inherent tension due to these conflicting self-assembly instructions could be resolved by amino acid chirality. Stereoconfiguration determined the ability of each stereoisomer to self-associate into diverse nanostructures, including nanoparticles, nanotapes, or fibrils, which yielded hydrogels with gel-to-sol transition at a physiologically relevant temperature. Single-crystal structures and all-atom molecular dynamics simulations elucidated the ability of each peptide to establish key interactions to form long-range assemblies (i.e., stacks leading to gelling fibrils), medium-range assemblies (i.e., stacks yielding nanotapes), or short-range assemblies (i.e., antiparallel dimers or trimers that further associated into nanoparticles). Importantly, diphenylalanine is known to serve as a binding anchor for pathological amyloids, potentially allowing to use these heterochiral peptides to inhibit the fibrillization of pathological amyloids, as demonstrated in vitro on the Alzheimer’s disease-associated Aβ(1–42) peptide.

Overall, this line of research is evolving from simple hydrophobic structures to a more diverse set of functional groups to enable a wide variety of functions and expand the supramolecular level of complexity that can be attained from very simple building blocks based on biomolecules.
Squaramide-based supramolecular materials: From self assembly to biomedical application

Roxanne Kieltyka, r.e.kieltyka@chem.leidenuniv.nl. Universiteit Leiden, Leiden, Zuid-Holland, Netherlands

The application of adaptive materials in areas from biomedicine to electronics has invigorated the development of new supramolecular materials with specific function. Due to the non-covalent interactions that hold them together, these polymers show great potential because of their easy preparation with tailororable compositions, environmental responsiveness, self-healing upon damage, and recyclability. In the biomaterials field, their easy processing permits the mixing of functionalized monomers with biomolecular cargo such as peptides, and their responsiveness to different stimuli opens the door to designer materials that can be used to deliver therapeutic cargo or as scaffolds for tissue engineering. In order to realize these end-stage applications, there is a need for structurally simple monomers with high synthetic accessibility that can robustly self-assemble into polymeric architectures in the presence of complex molecular cargo. Squaramides, structurally minimal ditopic hydrogen-bonding units, show tremendous potential in this regard due to their high synthetic accessibility from commercially available precursors and robust self-assembly into supramolecular polymers. In this talk, I will share our exploration of the squaramide synthon as a building block for supramolecular polymers and their application to nanoparticles and hydrogel materials for biomedical applications such as drug delivery and 3D cell culture.
Constrained supramolecular polymerization within linear polymer melts at equilibrium and under strain

Christopher B. Cooper, cbcooper@stanford.edu, Zhenan Bao. Chemical Engineering, Stanford University, Stanford, California, United States

Polymer networks formed through dynamic noncovalent or covalent bonds exhibit robust and tunable mechanical properties (e.g., tough, elastic, self-healable, stimuli-responsive, and reconfigurable). Here, we present our work on linear, flexible polymer chains with periodically-placed and directional dynamic bonds that collectively assemble into secondary supramolecular networks of nanorods and nanofibers under various conditions. We show that when the overall molecular weight (Mₙ) is below the polymer’s critical entanglement molecular weight (Mₑ), robust self-assembly of a secondary network of supramolecular nanofibers within the linear polymer melt occurs. However, for Mₙ > Mₑ, fiber formation is restricted, despite identical chemical composition of the chains (i.e., dynamic bond concentration). The formation of nanofibers increases the bulk film modulus by over an order of magnitude and delays the onset of terminal flow by more than 100°C. We expand upon the key aspects of polymer molecular design learned through this model system to design a novel shape memory polymer with record-high recovery stress (12.8 MPa) and energy density (18.9 MPa) based on the formation of strain-induced supramolecular nanostructures. While polymer chains initially adopt an amorphous structure (Mₙ > Mₑ), the polymer chains align during strain and form strong directional dynamic bonds, which trap the stretched polymer chains in a highly elongated state. The formation of ordered supramolecular structures from building blocks constrained onto the backbone of linear polymers offers an exciting mechanism to enhance and control material properties.
Complexation of poly(β-CD) and bis-adamantyl poly(2-hydroxyethyl acrylate) to create supramolecular polymeric networks

Mohammed Alaboalirat, liratium@gmail.com, John B. Matson. Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

The controlled synthesis of polymers containing densely grafted cyclodextrin units has proven challenging due to the steric hindrance of cyclodextrins. In this study, we report the controlled synthesis of poly(β-cyclodextrin) (PβCD) through ring-opening metathesis polymerization (ROMP) using Grubbs third-generation catalyst (G3). Molecular weights of >10^5 g/mol were obtained with a controlled dispersity of ≤ 1.2. In aqueous solutions, β-cyclodextrin forms a complex with adamantane through host-guest interaction. This interaction was utilized to prepare a supramolecular polymer network (SPN) made by adding PβCD to bis-adamantly poly(2-hydroxyethyl acrylate) (PHEA) in an aqueous solution and dried to make a homogenous film. The ratios of the two components were varied to study the structure-property relationship via tensile measurements.
Ionic block copolymers (BCPs) containing non-charged hydrophobic segments and charged hydrophilic segments can self-assemble into aggregates with varying morphologies in solution. The aggregate morphology is influenced by several factors, such as the polymer composition, pH and, the ionic strength. Polypeptoids are structural mimics of polypeptides. They are largely free of hydrogen bonding and have a flexible backbone whose conformation is determined by the molecular characteristic of N-substituent via steric and stereo-electronic interactions. These attributes make polypeptoids a suitable model system to study the effects of the sequence-encoded electrostatic interactions on the aggregate structures. The hypothesis of this study is that the electrostatic interactions encoded in the block sequence of the polypeptoid BCP chains will influence their equilibrium aggregate structures. Earlier studies were mainly focused on ionic BCPs aggregates in which the ionizable monomers are randomly distributed in the coronal chains. As such, how the charge pattern (i.e., the position of ionizable monomers along the amphiphilic polymer chain) influences the aggregate structure in solution is poorly understood. In this study, two ionic polypeptoid triblock copolymers comprised of different ionizable group positions (the chain end or the junction of hydrophobic and hydrophilic segment) were synthesized by controlled ring-opening polymerization method. The SANS (Small-Angle Neutron Scattering) and cryo-TEM analysis revealed notable difference in the aggregate structures of ionic polypeptoid BCPs with different block sequences. These two polymers formed 1D nanostructures (core-shell cylindrical structure) in aqueous solution and the geometry/dimension of the core-section of these two elongated aggregates is not significantly different between them. Importantly, the solvation level both in the micellar core and shell decreased as the ionizable group is moved towards the junction of the hydrophobic and hydrophilic segment.
Tri-block copolymer thermoplastic elastomer thermosets achieving orthogonal working/healing conditions

Ryan Clarke, r.clarke@colostate.edu, Eugene Y. Chen. Chemistry, Colorado State University, Fort Collins, Colorado, United States

Conventional thermosets and rubbers are highly regarded in thermal, mechanical, and chemical durability but fail to achieve practical recyclability. In an effort to merge performance and recyclability, the emergence and rapid development of covalent adaptable networks (CANs) has established various methods of installing thermal-, photo-, chemical-, and mechanical-responsive components within crosslinks capable of triggering topology-altering dynamic bond exchange. Despite achieving broad reprocessing conditions in numerous CAN systems, trace exchange events during working conditions often lead to pronounced creep and poor mechanical performance while requiring external crosslinkers, exchange agents, and catalysts. To address these challenges, we have applied simple carbonyl chemistry to generate high-performance tri-block copolymers (tri-BCPs) that can be converted to active CANs in the absence of any external reagents or catalysts. Discrete self-assembly of these tri-BCPs to well-defined inter-domain-crosslinked nanostructures has led to observations on the principal requirement for inter-domain bond exchange in phase-separated networks to access productive or intentional deformation. This presentation will discuss a unique activation mechanism that fulfills the orthogonality between working/healing conditions in CANs with high-performance mechanical profiles, facile scalability in the BCP synthesis, and broad applicability in other polymer systems.
Association of biopolymers is a ubiquitous process in living systems. Recent single-molecule measurements probe the dynamics of association in unprecedented detail by measuring the properties of association transition paths. In an effort to develop a model to interpret the dynamics of experimental observables, here we report a simulation study of the association dynamics of two oppositely charged, disordered proteins. We mimic experimental measurements by monitoring intermonomer distances, which we treat as “experimental reaction coordinates.” While the dynamics of the distance between the centers of mass of the molecules is found to be memoryless and diffusive, the dynamics of the experimental reaction coordinates displays significant memory and can be described by a generalized Langevin equation with a memory kernel. We compute the most commonly measured property of transition paths, the distribution of the transition path time, and show that, despite the non-Markovianity of the underlying dynamics, it is well approximated as one-dimensional diffusion in the potential of mean force provided that an apparent value of the diffusion coefficient is used. This apparent value is intermediate between the slow (low frequency) and fast (high frequency) limits of the memory kernel.
RAFT polymerization of star polymers with ortho-phenylene cores

Kate G. Bradford, bradfokg@miamioh.edu, Dominik Konkolewicz, Christopher Hartley. Miami University, Oxford, Ohio, United States

ortho-Phenylenes, which adopt helical geometries, are one of simplest classes of aromatic foldamers. Due to the rotations from one or more internal torsional angles, this helical geometry can change to give a misfolded structure. These folding and misfolding conformational changes are slow on the NMR timescale at or below room temperature, therefore allowing us to detect changes in folding via $^1$H NMR spectroscopy. Herein, we synthesize hexamer o-phenylenes that are coupled with a RAFT chain transfer agent (CTA) on each repeat unit. These CTA functionalized o-phenylenes are polymerized using different acrylate monomers via PET-RAFT to give fully functionalized star shaped polymers with o-phenylene cores. The steric bulk on the acrylate monomer units is varied systematically, and we assess the twisting of the o-phenylene backbone using $^1$H NMR spectroscopy to see whether the folding state of the polymeric core changes.
Regulating the self-assembly of light emitting conjugated polymer spherulites via side alkyl chain branching

Lili Sun², 18325767556@163.com, Lu b. Bai¹, Jin y. Lin². (1) Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University, Xi'an, Shaanxi, China (2) Institute of Advanced Materials (IAM), Nanjing Tech University, Nanjing, Jiangsu, China

The morphology of the active layer is a critical factor that determines the electronic behavior between molecular chains and device performance. Chain conformation and chain orientation are two microstructures that cannot be ignored for controlling the film's morphology. Herein we advance a strategy that side-chain engineering to control the morphology of the active layer. Solvent Vapor Annealing (SVA) is used to achieve self-assembly of supramolecular spherulites. We studied the growth of spherulites via polarized optical microscopy (POM). We found that the introduction of a high degree of branching can promote the growth of spherulites. The width of a single nanowire that composes spherulites is about 35 nm through atomic force microscopy (AFM). Meanwhile, The luminescence of spherulites is more stable compared to thin-film via spectral stability test. Finally, a highly ordered molecular arrangement is formed, which improves the luminescence stability of polyfluorene light-emitting semiconductors, inhibited the formation of green bands, and provides a feasible strategy for efficient and stable deep blue light emission.
Engineering positive kinetic cooperativity between supramolecular and dynamic covalent bonds within self-healing polyurethane thermosets

Raphaël Pauchet¹, raphael.pauchet@etu.unistra.fr, Simon McKie¹, Vasyl CHUMACHENKO¹, Georges FORMON¹, Pierre J. Lutz¹, Eric BUHLER², Remi PERRIN³, Christian GAUTHIER¹, Emilie Moulin¹, Nicolas Giuseppone¹. (1) Institut Charles Sadron, Strasbourg, Alsace, France (2) Matiere et Systemes Complexes, Paris, Île-de-France, France (3) Soprema SAS, Strasbourg, Grand Est, France

The incorporation of dynamic chemical moieties into polymer networks has led to the development of responsive and adaptive materials. At the interface between traditional thermosets and thermoplastics, research has been focused on two main avenues for innovation: 1) the enhancement of physical cross-links by incorporating directional non-covalent supramolecular interactions into polymeric systems; and 2) the substitution of irreversible covalent chemical cross-links for reversible and exchangeable alternatives. One step further in the direction of smart and adaptable material is the use of a combination of two different dynamics to trigger stimuli responsiveness along with desired mechanical properties, combining the best of thermosets and thermoplastics. In our work we developed thermoset polyurethane elastomers reversibly cross-linked by a combination of labile supramolecular hydrogen bonds and of more stable dynamic covalent imine bonds. We show quantitatively that kinetic cooperative synergies take place within such double-dynamic networks, endowing these materials with higher mechanical performances together with superior self-healing efficiency. Additionally, we demonstrated the recycling potential of such polyurethane thermosets.

![Graph showing tensile test results before and after healing](image)

**Fig. 1** Tensile test of the material before and after healing
Creating a dynamic covalent peptide system by reversible native chemical ligation for dynamic combinatorial chemistry

Nicolas Capit, nicolas.capit@ics-cnrs.unistra.fr, Pierrick Petitnicolas, Emilie Moulin, Nicolas Giuseppone. SAMS research group, Institut Charles Sadron, Strasbourg, Alsace, France

Dynamic combinatorial chemistry (DCC) has proven over the recent years to be a powerful tool in the discovery of novel molecules for targeted applications. At the core of this process is the creation of a dynamic chemical library (DCL). Due to the stability of the peptide bond, creating DCLs with peptides is challenging. However, by incorporating an N-methyl-cystein in a peptide sequence, the peptide bond can evolve into a much more reactive thio-ester by N to S acyl-shift. The resulting trans-thioesterification exchange reactions can lead with the proper peptide fragments to the creation of a DCL, in one pot and in water under reducing conditions.

In this presentation we will describe the thermo-kinetics of this exchange reaction, as well as the influence of pH which directly affects the reaction through the thiol protonation equilibrium. We will also discuss the creation of a dynamic polypeptide system with the differential formation of recombining sequences as a function of experimental conditions.

Dynamic exchange reaction permitted by the N-methyl-cystein
Selenophene and thiophene based conjugated polymer gels

Sheng Li¹, sli781317885@gmail.com, Keqiang He², Elisabeth Prince¹, Yuning Li², Dwight S. Seferos¹. (1) University of Toronto, Toronto, Ontario, Canada (2) University of Waterloo, Waterloo, Ontario, Canada

Conjugated polymer gels are promising materials that are intrinsically stretchable and conductive, which may play an important role in the development of stretchable electronics. In this work, a series of thiophene and selenophene-based conjugated polymers with similar molecular weight and low dispersity were synthesized and the gelation conditions of these polymers were studied. The electrical performance of both thin and bulk films of these conjugated polymer gels was investigated. Blade coated gels that form the highest quality films can achieve a similar charge carrier mobility as a spin-coated sample, showing that gels are indeed promising electronic materials. The most promising gels were studied as a stretchable device. The initial application of strain appears to lead to lower mobility, however, the device stabilizes, and retains the same mobility from 18-40% strain. Finally, a new cycle-doping method was developed to successfully dope the bulk gels to yield conductive films. This method allows one to monitor the changes in conductivity as a function of doping to ultimately achieve the highest conductivity. The cycle-doping method appears to be superior to the commonly used dip-doping method. Overall this work expands on the types of conjugated polymers gels that are useful for electronics, stretchable electronics, and conductive materials.
Covalent organic frameworks based on porphyrin and cucurbit[n]uril for electrocatalytic water splitting

Donus Tuncel, dtuncel@fen.bilkent.edu.tr. Department of Chemistry and UNAM-National Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent Universitesi, Ankara, Ankara, Turkey

Here, we describe the synthesis and characterization of a novel covalent organic frameworks based on properly functionalized porphyrins and cucurbit[n]uril derivatives. These frameworks have been loaded with nickel ions and either integrated with TiO$_2$, or graphene oxide and electrochemically reduced graphene oxide to be employed as an efficient and stable electrocatalyst for hydrogen evolution reaction (HER) in alkaline medium from water splitting.
Young Industrial Polymer Scientist Award in Honor of Victoria Piunova
J Hedrick, Organizer, Presider, IBM Research
Session Type: Oral - Hybrid
Co-sponsor/Theme: Co-sponsor - Nominal PMSE: Division of Polymeric Materials Science and Engineering

Monday, 10:30am - 12:15pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312

Aliphatic polycarbonates: A new class of broadly applicable biologics
10:30am - 11:05am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
J Hedrick, Presenter, IBM Research

Polymeric hydrogels for the fabrication of engineered living materials
11:05am - 11:40am USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Alshakim Nelson, Presenter

Supramolecular biomaterials enabling innovations in drug formulation and delivery
11:40am - 12:15pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Eric A Appel, PhD, Presenter, Stanford University

Monday, 02:00pm - 04:00pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312

Hierarchical structures of star polymers produced via controlled molecular assembly
02:00pm - 02:40pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Gang-Yu Liu, Presenter; Jiali Zhang; Yunbo Zheng; Victoria Piunova; Jane Frommer

Organic photoredox catalysts for the synthesis of small molecules and polymers
02:40pm - 03:20pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Garret Miyake, Presenter

AI assisted design and synthesis of materials with targeted properties
03:20pm - 04:00pm USA / Canada - Eastern - August 23, 2021 | Room: A311-A312
Victoria Piunova, Presenter; Dmitry Zubarev; Seiji Takeda; J Hedrick, IBM Research
Aliphatic polycarbonates: A new class of broadly applicable biologics

J Hedrick, hedrick@us.ibm.com. IBM Research, San Jose, California, United States

Amongst these use cases for aliphatic polycarbonates, application to biomedicine requires the most diverse functional group arsenal. Although there exist over 700 1, 3- diols that can be transformed to 6-membered cyclic carbonates, the vast majority of reports use 2,2- bis(hydroxymethyl) propionic acid (bis-MPA) as a foundational building block owing to the cost, ease of installation of functional groups, and since the subsequent monomer is derivatized at the 5-position, distal to the polymerization site, polymerization conditions (ROP) tend to be universal. Similarly, inexpensive and readily available functional 1, 5- diols have been exploited as precursors to 8-membered cyclic carbonates. Transformation of these functional monomers and subsequent polymers have been applied to numerous applications that include drug, gene and cell delivery as well as the use of the polymer as a stand-alone therapeutic including antimicrobials, anticancer agents and antiviral therapies packaged as micelles, hydrogels or coacervates. Specifically, we address the multi-faceted problem of drug-resistance as well as other important concerns in disease treatment exploiting polymer science to develop novel macromolecular therapeutics for treating infectious disease and cancer. Overall, the field of macromolecular therapeutics offers significant promise for improving human health by applying the tools of polymer and supramolecular chemistries together with nanotechnology to create materials for precise, highly effective disease treatment that does not induce resistance.
Polymeric hydrogels for the fabrication of engineered living materials

Alshakim Nelson, alshakim@uw.edu. University of Washington, Seattle, Washington, United States

Additive manufacturing (or 3D printing) has re-emerged into the spotlight in the last 5 years driven by the rapid progress in hardware and software. Along with these advances, new materials are required to meet the demands of emerging technologies. Herein, we present multi-stimuli-responsive hydrogels designed for direct-write 3D printing. Triblock copolymers based on F127 or poly(alkyl glycidyl ethers) were developed and formulated into stimuli-responsive hydrogels that (1) underwent a reversible sol-gel transition in response to temperature, (2) exhibited shear-thinning behavior, and (3) cross-linked in the presence of UV-irradiation. The syntheses, characterization, and patterning of these materials will be presented. The application of these polymer hydrogels toward printing microbes for immobilized whole-cell catalysis will also be discussed.
Supramolecular biomaterials enabling innovations in drug formulation and delivery

Eric A. Appel, eappel@stanford.edu. Materials Science & Engineering, Stanford University, Stanford, California, United States

Supramolecular biomaterials exploiting rationally-designed non-covalent interactions can enable innovative approaches to drug formulation and delivery. For example, supramolecular interactions can be used to generate dynamically cross-linking polymer networks, yielding shear-thinning and self-healing materials that exhibit viscoelastic mechanical properties similar to biological tissues and flow properties enabling minimally invasive implantation in the body through direct injection or catheter delivery. In this talk we will discuss the preparation, characterization and application of a class of physical hydrogels generated by non-covalent interactions between modified biopolymers (BPs) and nanoparticles (NPs). Owing to the dynamic, non-covalent interactions between the NPs and BPs, the hydrogels flow under applied stress and their mechanical properties recover completely within seconds when the stress is relaxed, demonstrating the shear-thinning and injectable nature of the materials. Moreover, these interactions have been shown to be entropically driven, causing these materials to elicit alternative temperature-dependent mechanical properties than typically observed in physical hydrogels. Further, the hierarchical construction of these biphasic hydrogels allows for multiple therapeutic compounds to be entrapped simultaneously and delivered with identical release profiles, regardless of their chemical make-up, over user-defined timeframes ranging from days to months. These materials have proven to be particularly promising as controlled delivery technologies in vaccines and cancer immunotherapy - applications where precise release of complex mixtures of compounds over prolonged timeframes is crucial. Overall, this presentation will demonstrate the utility of a supramolecular approach to the design of biomaterials affording unique opportunities in the formulation and controlled release of therapeutics.
Hierarchical structures of star polymers produced via controlled molecular assembly

Gang-Yu Liu¹, gail.panda@gmail.com, Jiali Zhang¹, Yunbo Zheng¹, Victoria Piunova², Jane Frommer². (1) Chemistry, University of California Davis, Davis, California, United States (2) IBM Almaden Research Center, San Jose, California, United States

Due to dynamic spatial confinement, molecular assembly in evaporation of ultrasmall solution droplets follows a different dynamic from that of larger scales. This work reported a combination of microfluidic probe with an atomic force microscopy, used to deliver subfemtoliter liquid droplets containing star polymers. Upon solvent evaporation, star polymers form well-defined features with dimensions as small as tens of nanometers. The initial shape of the droplet and the concentration of solute within the droplet play significant roles in the final assembly of polymers due to the ultrafast evaporation rate and spatial confinement by the small droplets. The technology used could regulate those factors and thus control the final molecular assembly in terms of feature geometry and distribution and packing of individual star polymers within the features. This presentation also discusses potential application of the technology and products, such as to programmable synthesis for chemistry and materials science, and three-dimensional (3D) nanoprinting in additive manufacturing.
Organic photocatalysts for the synthesis of small molecules and polymers

Garret Miyake, garret.miyake@colostate.edu. Chemistry, Colorado State University, Fort Collins, Colorado, United States

Photoredox catalysis has emerged as a powerful methodology for the synthesis of molecules under mild reaction conditions. This presentation will discuss the development of organic photocatalysts for the synthesis of small molecules and polymers.
Al assisted design and synthesis of materials with targeted properties

Victoria A. Piunova¹, victoria@lolware.com, Dmitry Y. Zubarev², Seiji Takeda³, J Hedrick². (1) Loliware Inc, San Jose, California, United States (2) IBM Almaden Research Center, San Jose, California, United States (3) IBM Tokyo Research Laboratory, Tokyo, Japan

Materials innovation is an essential piece of driving growth and sustaining industries. However, the process of materials discovery is slow and expensive. Currently employed combinatorial approaches generate a wide range of potential candidates, far exceeding the available capabilities for human evaluation and experimental validation. In this talk, AI-driven molecular inverse-design system for materials discovery coupled with high-throughput experimental validation of predictions will be discussed. The combination of substructure-based feature encoding and molecular graph generation algorithms enables users to develop high-speed, interpretable, and customizable design processes. As an illustration of the technique in action, we apply the proposed workflow to the discovery of novel antimicrobial therapies and acrylic polymers with targeted glass transition temperature (Tg).
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