ACS Division of Polymer Chemistry
Graphical Abstracts

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

April 2021
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Thank you, POLY Program Chairs and Organizers

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ACS Award in Polymer Chemistry Sponsored by ExxonMobil Chemical Company in Honor of Ken Wagener

April 6, 2021
Prof. Brent S Sumerlin, Organizer, Presider

Look at what Ken Wagener's ADMET started
Karen Winey, Presenter

Synthesis and control of the higher-order structures of platinum-containing conjugated polymers
Fumio Sanda, Presenter

Re-examining single-chain nanoparticles
Erik Berda, (he/him/his), Presenter

Growth in all directions: the polyphenylene story
Klaus Muellen, Presenter

Discrete oligomeric materials; lessons learned from Ken Wagener
Egbert Meijer, Presenter

Elucidating the thermodynamics of polymer-metal interactions in solution
Michael Schulz, Presenter; William Archer

Reflections on metathesis polymerization: ADMET and ROMP
Robert Grubbs, Presenter

Polyolefin based anion exchange electrolytes
Geoffrey Coates, Presenter

Designing cyclic acetal monomers for re-imagined degradable thermosets
Dr. Julia Pribyl, Presenter

Creating the ADMET reaction
Dr. Kenneth B. Wagener, Presenter
Look at what Ken Wagener's ADMET started


In celebration of Ken Wagener, this talk will highlight our collaborative work. I was studying the morphologies of ionomers using a variety of random copolymers using a variety of advances characterization methods, but the inherent complexity of the polymer architecture was an impediment. Then, Ken’s group successfully used ADMET to synthesize a linear polyethylene with carboxylic acid groups precisely spaced along the backbone. Even in this first set of polymers, it was clear that the nanoscale morphologies of these precise polymers were better defined and even exhibited an ordered layered structure. By studying solution grown single crystals, we determined the crystallites were hexagonal and, by employing all-atom molecular dynamics, we established that the chain conformations adjacent to the acid groups were hairpin turns. When Ken’s group attached an imidazolium bromide group, we were surprised to identify a cubic gyroid morphology. And when a sulfonic acid group was introduced on every 21st carbon and the polymer was exposed to relative humidity, the proton conductivity was exceptional. The fascinating morphologies and properties identified in these remarkable ADMET polymers have inspired a new generation of ionomers and single-ion conductors synthesized by ROMP and step-growth polymerization. Look at what Ken Wagener’s ADMET started!
Synthesis and control of the higher-order structures of platinum-containing conjugated polymers

Fumio Sanda, sanda@kansai-u.ac.jp. Dept Chem Mtrl Eng, Fac Chem Mtrl Bioeng, Kansai University, Suita Osaka, Japan

π-Conjugated polymers with controlled higher-order structures feature molecular recognition, stimuli response, optical anisotropy, and photoelectricity. π-Conjugated polymers containing platinum (Pt)–alkynyl σ-complex moieties in the main chain exhibit intense phosphorescence due to the mixed singlet and triplet excited states. Chirally regulated π-conjugated polymers containing Pt complex moieties have great potential as chiroptically functional materials. The present study deals with the synthesis of Pt-containing novel conjugated polymers by the Sonogashira–Hagihara coupling polymerization of \([\text{Pt}(4,4′\text{-dibromo-2,2′-bipyridine})/(R,R)-2,3\text{-bis(tert-butylmethylphosphino)quinoxaline }][(\text{trifluoromethanesulfonate})_2]\) coordinated with 4,4′-dibromo-2,2′-bipyridine/(R,R)-2,3-bis(tert-butylmethylphosphino)quinoxaline [(R,R)-QuinoxP*] and 1,4-diethynylbenzene derivatives. The polymers exhibited CD signals derived from (R,R)-QuinoxP* and the conjugated main chain. The simulated CD spectroscopic pattern of a low molecular model compound agreed well with the observed spectra. The TEM images of the polymers in the solid state exhibited dispersed patterns with sizes around 10 nm. Concentrated solutions of the polymers in DMF and CHCl₃ exhibited patterns assignable to lyotropic liquid crystals.

The present study also deals with the synthesis of novel Pt-containing conjugated polymers by the dehydrochlorination coupling polymerization of dichloro(4,4′-tert-butyl-2,2′-bipyridyl)platinum and dichloro(4,4′-dinonyl-2,2′-bipyridyl)platinum with \(N\{3,5\text{-bis(4-ethynylphenylethynyl)benzoyl}\}_L\)-alanine dodecylamide, and investigation of their chiral secondary structures. The polymers exhibited bisignate CD signals assignable to the main chain chromophore in DMF/MeOH = 50/50 (v/v). The presence of particles of Z-average = 30 nm was confirmed in this solution. These results indicated that the polymers formed chirally regulated aggregates. Single-crystal X-ray analysis of the model compound and DFT calculations were carried out to examine the mode of aggregation of the polymers.
Re-examining single-chain nanoparticles

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The concept is simple: to build functional nanomaterials in the protein size regime (i.e. 2-5 nanometers in diameter), one must be able to manipulate matter on a similar length scale. Canonical synthetic organic chemistry operates on a length scale an order of magnitude too small (i.e. a few Angstroms rather than and few nanometers). Traditional polymer nanoparticle fabrication techniques (e.g. solution assembly of block copolymers or emulsion polymerization techniques) operate on a length scale that is an order of magnitude too large (i.e. a few tens of nanometers). In between the two is a vast chemical space that remains largely unexplored towards these ends, and yet sits firmly in the realm of synthetic polymer chemistry. Nature’s strategies and abilities in this regard are, regrettably, far superior to anything we can do in the laboratory. Still, using modern techniques in polymer and supramolecular chemistry it is possible to imitate Nature’s methods and in the process, fill a significant gap in technological understanding. Our group’s efforts over the past several years have focused precisely on this topic via an emergent class of materials termed “single-chain nanoparticles” (SCNP). SCNP are formed through the intramolecular cross-linking and collapse of single polymer chains in dilute solution to yield an architecturally defined network with dimensions similar to the parent linear chain. In the spirit and in celebration of Prof. Wagener’s career and style, this talk will emphasize the stories of the people that made this work possible. Congratulations Ken on your well-deserved award!
Growth in all directions: the polyphenylene story

**Klaus Muellen**, muellen@mpip-mainz.mpg.de. Max-Planck-Inst F Polymerforsc, Mainz, Germany

Benzene is a universal module of polymer chemistry occurring in linear polyphenylene chains, graphene sheets and dendrimer spheres. In each case, precision polymer synthesis is an essential tool.

Graphenes and their quasi-1D subunits, the graphene nanoribbons (GNRs), are synthesized by using a precursor protocol. They can be 600 nm long and several nm wide, but are still solution processable.

Polyphenylene dendrimers (PPDs) are obtained as unique shape-persistent 3D-particles with molecular weights as high as 1.9 MDa by way of repetitive Diels-Alder cycloadditions.

These synthetic breakthroughs open the door to unprecedented functions. GNRs are the long sought-after link between conjugated polymers and graphenes. Due to their tunable electronic band gaps, they are effective semiconductors, but can also give rise to topological insulators and are essential for new computing techniques and spintronics.

PPDs, in turn, when being decorated with patched surfaces from alternating polar and unpolar groups, are efficient vehicles for gene transfection.
Discrete oligomeric materials; lessons learned from Ken Wagener

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

Every detail counts in controlling the molecular structure of polymers, is one of the key lessons learned from Ken Wagener. We used this lesson to design, synthesize and characterize a series of discrete oligodimethylsiloxanes of different lengths and modified them to block co-oligomers (BCOs). In these discrete BCO-materials, supramolecular chemistry, crystallization and phase segregation of the blocks are in competition to arrive at the thermodynamic most stable morphology. In the lecture a variety of structures will be presented including novel functionalities as a result of long-range order in the discrete BCOs.
Elucidating the thermodynamics of polymer-metal interactions in solution

**Michael D. Schulz**, mdschulz@vt.edu, William R. 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. For example, polymer-enhanced ultrafiltration is one approach where polymers selectively coordinate specific metals and ultrafiltration membranes then filter out the polymer-metal complexes. To investigate the interplay between polymer structure and metal chelation, we used isothermal titration calorimetry to directly measure the binding affinity ($K_a$), enthalpy changes ($ΔH$), 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. These experiments will inform future work on developing chelating polymers for rare-earth element extraction.
Reflections on metathesis polymerization: ADMET and ROMP

Robert H. Grubbs, rhg@caltech.edu. Cal Tech 164-30, Pasadena, California, United States

Ken Wagener started exploring ADMET polymerization in the old days of strongly Lewis acidic metathesis catalysts that gave mixtures of products. Only with the advent of well defined catalysts could clean polymers be prepared by ADMET polymerization. We have worked together to be sure the best catalysts were available. I am disappointed that for some reason I could not convince him to change the name to DiOlefin Metathesis Polymerization in line with ROMP. He has made significant contributions to polymer science through the synthesis of polymers with precise shape and unusually functionalized systems. His latest work on high temperature catalysts is leading to high molecular weight systems and has pointed to applications in small molecule chemistry. In the ring opening area, new commercial systems have been developed, and through the design of selective catalysts, new polymer types are now available for study.
Polyolefin based anion exchange electrolytes

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

In this presentation, new advances in the synthesis of chemically stable, mechanically strong, and highly conducting anion exchange membranes will be presented.
Designing cyclic acetal monomers for re-imagined degradable thermosets

Julia Pribyl, julia.pribyl@gmail.com. Chemistry Department, US Naval Academy, Annapolis, Maryland, United States

Synthetic polyacetals have long been investigated as materials that easily degrade under acidic conditions but otherwise remain stable. The preparation of halogenated dioxepin derivatives amenable to ring-opening metathesis polymerization will be presented. After polymerization, the resulting polyacetals can be used as thermoplastics as well as precursors to ultra-violet or thermally cured thermosets. The acetal backbone, combined with the self-amplified degradation afforded by the pendant halogen creates an interesting platform for modulating polymer properties, degradation profiles, and the potential for cyclic use and recovery of precious composite fillers (e.g. carbon fiber). Preliminary results and outlook of this work will be discussed.
Creating the ADMET reaction

Kenneth B. Wagener, wagener@chem.ufl.edu. Dept. of Chemistry, University of Florida, Gainesville, Florida, United States

A group of more than 160 people created a polymerization reaction - The ADMET reaction - that has been used to examine structure of both hydrocarbon and functionalized polyolefins. Most recently the research has turned to high temperature, bulk polycondensation, similar to conditions used to synthesize polyester. Specifically the focus has been on high Mn aliphatic polysulfones. Catalyst selection has been key; well-defined catalysts must survive at temperatures greater than 160 C.
ACS Award in Pure Chemistry Sponsored by the Alpha Chi Sigma Fraternity and the Alpha Chi Sigma Educational Foundation in Honor of Rebekka Klausen
April 5, 2021
Emily Pentzer, Organizer; yuyang Ji, Presider; Qifeng Jiang, Presider

Expanding the scope of controlled self-assembly to prepare precision nanostructures
Rachel O'Reilly, Presenter

Supramolecular crosslinking strategies for polylactone-based nanocarriers
Dr. Davita L Watkins, Presenter

Silly reactions of silyl ketenes
Sarah Mitchell; Randinu Pulukkody; Yuanhui Xiang; Emily Pentzer, Presenter

From mechanism to materials in photocontrolled polymer networks
Julia Kalow, Presenter

Connecting the mechanistic chemistry of molecular silanes and silicon surfaces
Prof. Jillian M. Buriak, Ph.D., Presenter

Fragments of crystalline silicon via target-oriented synthesis
Rebekka Klausen, Presenter
Expanding the scope of controlled self-assembly to prepare precision nanostructures

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

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 precise 2D nanostructures. Using these we have further explored the design rules for the synthesis of such 2D nanomaterials and demonstrated their epitaxial growth, which highlights their potential as biocompatible nanomaterials.
Supramolecular crosslinking strategies for polylactone-based nanocarriers

Davita L. Watkins, dwatkins@olemiss.edu. Chemistry and Biochemistry, University of Mississippi, University, Mississippi, United States

As therapeutic carriers, polymersomes (bilayer vesicles) formed by amphiphilic polymers exhibit superior properties relative to other nanoformulations owing to their biomimetic morphologies, favorable sized, and enhanced stability. However, like other convention nanoparticles, polymersomes tend to disintegrate before reaching the disease site due to systemic dilution, ionic strength, and pH variations in the body. Crosslinking is a simple and straightforward, yet reliable method to minimize premature disintegration, thereby assuring enhanced circulation times and sustained release of a therapeutic agent. Here we use pi-pi stacking interactions as a noncovalent crosslinking strategy to stabilize nanoparticles and increase the uptake of NIR theranostic agents. By functionalizing lactone monomers with aryl groups, a series of block copolymers possessing self-assembling moieties were synthesized. The moieties afforded crosslinking within the nanoparticle via pi-pi stacking, resulting in improved nanoparticle stability and uptake compared to unfunctionalized derivatives. Supported by spectroscopic analysis and electron microscopy, structural information on the architectures of these well-defined block copolymers and their morphological assemblies were achieved. Cellular uptake, cytotoxicity studies, and photothermal assessment attest to the potential of these polymeric materials as promising candidates in theranostic nanomedicine.
Silly reactions of silyl ketenes

Sarah Mitchell¹, Randinu Pulukkody¹, Yuanhui Xiang², Emily Pentzer¹, emilypentzer@tamu.edu. (1) Chemistry, Texas A&M University College Station, College Station, Texas, United States (2) Chemistry, University of Notre Dame, Notre Dame, Indiana, United States

Cumulated double bonds are curious functional groups of two double bonds sharing a central carbon in which the pi systems are not conjugated; examples include ketenes (C=C=O), allenes (C=C=C), and the more ubiquitous isocyanates (N=C=O). Of these, ketenes in which the terminal carbon bears hydrogen, alkyl, or aryl groups, are highly reactive moieties that are commonly prepared in situ and used immediately without isolation due to their propensity to undergo dimerization and trimerization reactions. In contrast, silyl ketenes, in which the terminal carbon contains a trialkyl(aryl) silyl group are isolable due to stability provided by hyperconjugation (e.g., the beta silicon effect). This presentation will address our efforts to polymerization silyl ketenes and control regioreactivity to give polyketone, polyketene acetal, and polyesters. Secondary reactions, including the production of highly functionalized small molecules will be discussed.
From mechanism to materials in photocontrolled polymer networks

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

In polymer networks based on dynamic covalent bonds, changes in reactivity can be translated into macroscopic responses. Light offers precise, tunable, and noninvasive spatiotemporal control over molecular reactivity. In polymer networks based on dynamic covalent bonds, these changes in reactivity can be translated into macroscopic responses. The Kalow lab has designed crosslinks that allow us to tune the thermodynamics and kinetics of dynamic covalent bonds with light, including visible light, based on the conformation of an adjacent photoswitch. When incorporated into polymer networks, the stability or lifetime of these dynamic covalent bonds can be tuned with light. I will discuss our efforts to elucidate the molecular mechanism underlying these macroscopic changes, as well as rational optimization of the photoswitch to enable applications in 3D cell culture.
Connecting the mechanistic chemistry of molecular silanes and silicon surfaces

Jillian M. Buriak, jburiak@ualberta.ca. Department of Chemistry, Univ of Alberta, Edmonton, Alberta, Canada

Integrating molecules with silicon is of great interest for applications in molecular electronics, for passivation of silicon surfaces for solar fuel generation, and yet further miniaturization of feature sizes of transistors on silicon into the sub-10 nm regime. The formation of silicon-carbon bonds via hydrosilylation is a practical and commonly used approach to chemically functionalize the surface of silicon due to the stability of the Si-C bond. There is a surprisingly diverse array of distinct mechanisms, and hence reaction conditions, that can be harnessed to enable this chemistry. Research over the past two decades has shown, however, that the mechanisms in operation are far more diverse, and the chemistry much richer, than initially believed. The underlying electronics of the silicon play an important role in enabling the chemistry of the surface, and under many circumstances, can dominate. We will discuss the latest developments in the surface chemistry of silicon that provide practical avenues for exquisitely precise integration of molecules with silicon surfaces. From the use of surface plasmons to bonding via exotic elements (such as Si-S, Si-Se, Si-Te bonds), silicon continues to surprise.
Fragments of crystalline silicon via target-oriented synthesis
Rebekka S. Klausen, klausen@jhu.edu. JHU/Chemistry Dept., Baltimore, Maryland, United States

In the Silicon Age, daily life revolves around tools made from this ubiquitous semiconductor: computers, solar cells, and many more. Yet silicon synthesis relies on top-down, high-temperature approaches that yield only the most thermodynamically stable forms of silicon. Uncovering vast new swatches of structure-function space demands a new synthetic vision. This talk will describe the synthesis of molecular and polymeric silanes via approaches inspired by the complexity and selectivity of target-oriented organic synthesis. Topics include the chemoselective polymerization of novel bifunctional silane monomers, the selective preparation of linear and cyclic polycyclosilanes, and the stereocontrolled synthesis of cis- and trans-siladecalin. The structural characterization of novel silane architectures and the emergence of new structure-property relationships will also be discussed.

Silicon-Inspired Conjugated Polymers

Building Blocks

Poly(cyclosilane)s
Carl S. Marvel Creative Polymer Chemistry Award in Honor of Richard Hoogenboom  
01:00pm - 04:00pm USA / Canada - Pacific - April 9, 2021  
Craig Hawker, Organizer, Presider  
University of California, Santa Barbara, Santa Barbara, California, United States

Encoding information into polymers: A supramolecular approach  
Roeland Nolte, Presenter

Poly(2-oxazoline) hydrogels and related structures: towards injectable drug delivery systems  
A/Prof Tim R Dargaville, Presenter

Chemistry, structure and applications of poly(2-oxazoline)s on surfaces  
Dr. Edmondo Maria Benetti, Presenter

Solute-solvent interactions in supramolecular polymerizations; chirality as a muse  
Egbert Meijer, Presenter

Host-guest chemistry for the elaboration of multi-stimuli “colourful” polymeric materials  
Khaled Belal; Aurélien Vebr joel lyskawa; François Stoffelbach; Alba Marcellan;  
Dominique Hourdet; Prof. Richard Hoogenboom; Patrice Woisel, Presenter

Functional materials based on responsive polymers, poly(2-oxazoline)s and supramolecular interactions  
Prof. Richard Hoogenboom, Presenter
Encoding information into polymers: A supramolecular approach

Roeland Nolte, r.nolte@science.ru.nl. Organic Chemistry, Radboud Universiteit Faculteit der Natuurwetenschappen Wiskunde en Informatica, Nijmegen, Gelderland, Netherlands

The amount of information trafficking internet nowadays is enormous and we can foresee that in the next decennia the current technologies to process data will no longer suffice. Hence, we have to consider other strategies of handling information. One approach is to explore chemical routes, which nature has also followed during evolution: our brain can store and handle very large amounts of data and process them in a way silicon-based computers cannot do. Although brain-like chemical computers are still far beyond reach, it is of interest to explore how we can design and construct atom- and molecule-based systems for processing information.

In this lecture, I will discuss our efforts to develop technologies to write and store information into single polymer chains with the help of “molecular machines” that are inspired by the hypothetical device (Turing machine) proposed by the mathematician Alan Turing in 1936 as the general basis for the operation of a computer. We use synthetic machines that are derived from chiral porphyrin cages, which thread onto synthetic polymers (e.g. polybutadiene) and glide along it while encoding it with chiral epoxide functions, i.e. (R,R)-epoxide = digit 0 and (S,S)-epoxide = digit 1. The realization of this encoding process, which we control by light, is in progress.¹

¹ Catalytic motor (green and blue) gliding along a polymer chain (yellow) while printing digital information (red and purple spheres)
Poly(2-oxazoline) hydrogels and related structures: towards injectable drug delivery systems

Tim Dargaville, t.dargaville@qut.edu.au. Chemistry and Physics, Queensland University of Technology, Kelvin Grove, Queensland, Australia

Several recent examples in the literature have highlighted the potential of poly(2-oxazoline)s (PAOx) in polymer-drug conjugate applications. PAOx has a distinct advantage in that comparatively high drug loadings can be achieved because of the possibilities of functionalizing the repeat unit side chains. Compare this to other polymers such as polyethylene glycol which can only be loaded at the end groups.

Like other soluble drug delivery systems, however, PAOx-drug conjugates may suffer from low drug delivery efficiencies if it is cleared for the body before all the drug has been cleaved. To address this we hypothesize that crosslinking PAOx-drug conjugates may allow for implantable drug delivery devices with good efficiencies and sustained drug release for days to weeks.

Several systems exploiting the side-chain chemistry of PAOx will be presented, including a homologous series of poly(2-oxazoline) networks with varied hydrophobicities, in situ gelling systems based on SPAAC crosslinking, and thermoresponsive copolymers based on 2-propyl-2-oxazoline. To examine how PAOx hydrogels perform when implanted into animals a 28-day murine model was used to examine the foreign body response and compared to the gold standard, polyethylene glycol.
Chemistry, structure and applications of poly(2-oxazoline)s on surfaces

Edmondo Maria Benetti, edmondo.benetti@mat.ethz.ch. Eidgenossische Technische Hochschule Zurich, Zurich, ZH, Switzerland

Poly(2-alkyl-2-oxazoline)s (PAOXAs) have been emerging as one of the most promising non-ionic alternatives to poly(ethylene glycol)s (PEGs) in the design of biointerfaces. In comparison to PEGs, PAOXAs are chemically more robust, as they do not undergo oxidative degradation within physiological media, while their composition and structure can be precisely and easily adjusted in order to tune technologically relevant, interfacial physicochemical properties.

Especially the most hydrophilic poly(2-methyl-2-oxazoline) (PMOXA) and poly(2-ethyl-2-oxazoline) (PEOXA) have been applied through different surface functionalization strategies on medical devices, sensors and cell-sensitive platforms, attaining both biopassive and bioactive surfaces. In addition, the unique properties of PAOXAs are paving the way for their use in the design of nanomaterials, especially those that are developed as nanomedicine and bioimaging tools.

In this contribution, the most advanced surface-functionalization strategies involving PAOXAs will be described, specifically highlighting how chemical and topological modulation of molecularly designed PAOXA-based adsorbates can be exploited to generate polymer interfaces with a wide range of properties, and for an array of diverse applications.
Solute-solvent interactions in supramolecular polymerizations; chirality as a muse

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

Interactions between solvents and solutes are a cornerstone of physical organic chemistry and have been a continued focus of investigations over the last century. In recent years, a renewed interest in fundamental aspects of solute-solvent interactions has been sparked in the field of supramolecular polymers. Although solvent effects in supramolecular chemistry have been recognized for a long time, the unique opportunities that supramolecular polymers offer to gain insight into solute-solvent interactions have become clear only relatively recently. The multiple interactions that hold the supramolecular polymeric structure together are similar in strength as those between solute and solvent. The cooperativity found in ordered supramolecular polymers leads to the possibility of amplifying these solute-solvent effects and will shed light on extremely subtle solvation phenomena. As a result, many exciting effects of solute-solvent effects in modern physical organic chemistry can be studied using supramolecular polymers. In the lecture, recent progress is presented towards a more comprehensive understanding of solvents in multicomponent supramolecular polymer systems.
Host-guest chemistry for the elaboration of multi-stimuli “colourful” polymeric materials

Khaled Belal¹, Aurélien Vebr¹,⁶, joel lyskawa³, François Stoffelbach², Alba Marcellan⁴, Dominique Hourdet⁵, Richard Hoogenboom⁶, Patrice Woisel¹, patrice.woisel@centralelille.fr. (1) Univ. Lille, CNRS, INRAE, Ecole Centrale, UMR 8207 - Unité Matériaux Et Transformations, Ingénierie des Systèmes Polymères (ISP) team, Lille, France (2) Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Paris, Finland (4) Soft Matter Sciences and Engineering, ESPCI Paris, PSL University, Sorbonne University, CNRS, Paris, France (6) Ghent University, Terneuzen, Netherlands

Recently, architectures where the individual polymer blocks are connected through supramolecular interactions such as hydrogen bonding, metal–ligand and pseudorotaxane like interactions have received significant attention. The inherent features of the molecular recognition-driven self-assembly confer significant advantages over their covalently linked brethren in terms of facilitating modularity and self-healing properties. Moreover, through careful design smart polymeric systems have been developed with stimuli-responsive structures and properties. Here, we report the successful engineering of new multi-stimuli responsive and coloured macromolecular assemblies based on well-defined functionalized polymer building blocks incorporating both electro-deficient cyclobis(paraquat-p-phenylene) (CBPQT⁴⁺) and electron-rich units (tetraphiafulvalene, naphthalene) moieties. The architectures of these materials have been constructed by holding together complementary well-defined polymer building blocks featuring either host or guest motifs attached in specific locations on polymer backbones. The inherent reversibility of supramolecular architectures has allowed “on demand” modular and tunable modification of structures and properties of materials. More particularly, we have exploited the presence of coloured CBPQT⁴⁺ based interactions i) to create (re)programmable supramolecular temperature and pH sensors showing a thermal memory function, i) to control the swelling/shrinking processes of hydrogels by applying different stimuli (T, V, competitive macromolecules) and to impart both thermal and temporary memory function to the mats, and iii) to develop polymeric hydrogel systems capable of swelling via a supramolecular transmission. An important practical aspect of these new functional materials is that all relevant phenomena (self-assembly and disassembly processes, reading/reprogramming of temperature, memory function) have an associated visible readout, thereby affording convenient and quantifiable systems with applications spanning the physical and biological sciences.
Functional materials based on responsive polymers, poly(2-oxazoline)s and supramolecular interactions

Richard Hoogenboom, richard.hoogenboom@ugent.be. Ghent University, Terneuzen, Netherlands

The research of the Supramolecular Chemistry group is inspired by the beauty of natural self-assembly processes. Nature exploits a limited number of building blocks in combination with non-covalent and hydrophobic interactions to build complex functional assemblies, such as proteins and cells. Our research aims to develop well-defined synthetic structures with controlled ordering and/or self-assembly resulting in functional systems. The use of synthetic building blocks allows a higher level of complexity when compared to the limited diversity in Nature. Moreover, the combination of well-defined ‘smart’ polymer structures with supramolecular interactions provides an ideal platform to develop functional systems for, e.g., sensors and diagnostics, drug delivery and responsive hydrogels. The research of the group can be subdivided in three main research directions, namely poly(2-oxazoline)s, responsive polymers and supramolecular materials. In this lecture, I will present recent highlights from our research on functional materials through development of novel polymer chemistry. More specifically, I will present recent work on poly(2-oxazine)s and poly(2-oxazepine)s as well as the use of poly(2-iso-propenyl-2-oxazoline) as platform for responsive polymers and supramolecular hydrogels.
Celebrating Underrepresented Groups in Polymer Science
05:00pm - 07:40pm USA / Canada - Pacific - April 8, 2021
Christopher Hobbs, Organizer, Presider; Reni Joseph, Organizer

Photo-responsive polymer nanoplexes for gene therapy and wound healing applications
Thomas Epps, Presenter

Polymer science and inspiration: career perspectives and principles
Dr. Paula T. Hammond, Presenter

Celebrating first generation college students
Emily Pentzer, Presenter

Exploration of photo-responsive materials
Javier Read De Alaniz, Presenter

Eumelanin is more than just a skin pigmentation: Organic semiconductors to antimicrobials
Toby Nelson, Presenter

Nonviral gene delivery with cationic glycopolymers
Craig Van Bruggen; Joseph Hexum; Zhe Tan; Rishad Dalal; Theresa Reineke, Presenter
Photo-responsive polymer nanoplexes for gene therapy and wound healing applications

Thomas H. Epps, thepps@udel.edu. Chemical Engineering, University of Delaware, Newark, Delaware, United States

Vascular bypass grafting is a routine treatment for cardiovascular diseases; however, nearly 50% of bypass grafts fail within a few years following surgery due to cellular inflammatory responses at the suture sites. To overcome this problem, we synthesized novel diblock polymers to deliver nucleic acid therapeutics capable of promoting healing in a spatiotemporal manner. A key component of our design is a monomer containing photocleavable o-nitrobenzyl moieties linking cationic groups to the polymer backbone so that light irradiation can induce polymer hydrolysis and charge reversal. The polymers self-assemble with anionic nucleic acids in solution to form nanoparticle complexes with a PEG “stealth” coating. Application of a photo-stimulus disrupts the electrostatic interactions to trigger the release of bound nucleic acids, such as siRNA, from the nanocomplexes. More significantly, our soft nanoparticles maintained stability in serum, exhibited robust cellular uptake, facilitated nanocarrier imaging, and were capable of photo-responsive on/off control over gene expression. These formulations enabled the knockdown of two key functional genes, IL1β and CDH11, that are implicated in inflammatory responses in human aortic adventitial fibroblasts. The complete knockdown of both genes, in combination, resulted in significant attenuation of TGF-β1-triggered fibroblast proliferation and differentiation into myofibroblasts, two of the primary hallmarks of fibrosis. Further attenuation over clinically relevant time scales was achieved by modulating the polyplex dosing regimen by taking input from a recently developed kinetic model, whose creation was enabled by our polymer design.
Polymer science and inspiration: career perspectives and principles

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Scientific and engineering careers provide some of the greatest outlets for creativity, discovery, and fulfillment, and a career in polymer science is particularly enabling because macromolecular species can be designed or modified to achieve such a wide variety of functions, leading to applications that span multiple fields. The ability to create new materials systems through synthetic modification or the generation of self-assembled structures and blends can lead to new interactions with collaborators and research sponsors to establish materials that meet new and interesting challenges. The role of such interactions and collaborations in shaping my own career, and perspectives on working in this exciting field will be shared.
Celebrating first generation college students

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Our life experiences impact, if not dictate, how we approach problem solving, research, and the language we use when talking about our results and their impact. The diversity of thought afforded from different backgrounds can help research teams work better and be more creative and innovative. We like to think of education as a great equalizer, giving opportunities to individuals from any background to have successful careers—especially within the objectivity of the sciences; however, entering academia can feel like navigating a whole new culture for some. In this presentation, I will address the culture differences I felt entering the world of academia as near first generation student (really generation 1.5) and how those have shaped my career.
Exploration of photo-responsive materials

Javier Read De Alaniz, javier@chem.ucsb.edu. Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California, United States

Photons have multiple enabling advantages to control stimuli-responsive materials. In this seminar, I will discuss our group’s effort to design and develop a new class of negative photochromic molecules termed DASA, their incorporation into materials and subsequent effort to unlock their potential to convert light directly into mechanical work.

Donor Acceptor Stenhouse Adduct (DASA)
Functional polymers from biorenewable sources

Megan L. Robertson, mlrobertson@uh.edu. Chemical and Biomolecular Engineering, University of Houston, Houston, Texas, United States

A great challenge to overcome is the replacement of traditional petroleum-based plastics with polymers derived from sustainable, alternative resources. Though there are many facets to the design of truly sustainable materials, including the raw material source, energy demands of processing, and fate of the material post-consumer use, utilization of a more eco-friendly raw material source is an important first step. Of particular interest is the design of structured polymers from sustainable, plant-derived sources with well-defined molecular characteristics and competitive properties to conventional, petroleum-derived materials. We are developing a diverse array of polymers derived from plant sources spanning many classes of materials. Three project areas will be discussed. First, long-chain polyacrylates derived from vegetable oil-based fatty acids were investigated as components of thermoplastic elastomers. Vegetable oils are an attractive source for polymers, due to their low cost, abundance, annual renewability, and ease of functionalization. Though the long alkyl side-chains on the polyacrylates provide tunability of the polymer physical properties, these polymers are unentangled. Specific interactions such as hydrogen bonding and ionic interactions were incorporated into these materials to generate a transient network. Second, functional vegetable oils were investigated as additives to modify the toughness of the bioplastic polylactide. Finally, sustainable and non-toxic components were explored for epoxy resins, to replace bisphenol A-derived monomers. The presence of hydrolytically degradable groups was investigated as a means to engineer additional end-of-life options for thermosets.

Biorenewable Polymers

Thermoplastic Elastomers

Thermoplastics and additives

Thermosets
Eumelanin is more than just a skin pigmentation: Organic semiconductors to antimicrobials

Toby L. Nelson, tobylnelson@gmail.com. Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

Most of my life I have defined by the color of my skin. In this presentation, I will share that the black-brown pigment, Eumelanin is so much more.
Nonviral gene delivery with cationic glycopolymers

Craig Van Bruggen¹, Joseph Hexum¹, Zhe Tan¹, Rishad Dalal¹, Theresa M. Reineke², treineke@umn.edu. (1) Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States (2) Chemistry, University of Minnesota, Vadnais Heights, Minnesota, United States

The field of gene therapy, which aims to treat patients by modulating gene expression, has come to fruition and has landed several landmark FDA approvals. The full potential of polymer-based delivery systems has yet to be realized, however, due to the fact that most polymeric transfection reagents are either too inefficient or too toxic for use in the clinic. Developments in carbohydrate-based cationic polymers, termed glycopolymers, for enhanced nonviral gene delivery will be described. As ubiquitous components of biological systems, carbohydrates are a rich class of compounds that can be harnessed to improve the biocompatibility of non-native polymers, such as linear polyamines used for promoting transfection. We have developed a new class of carbohydrate-based polymers called poly(glycoamidoamine)s (PGAAs) by integrating linear monosaccharides with polyamines via step-growth polymerization to drastically improve the biocompatibility of the polymer without sacrificing its ability to transfect cells. Systematic modifications of the structural components of the PGAA system revealed structure-activity relationships important to its function, including its ability to degrade in situ. Expanding upon the development of step-growth glycopolymers, monosaccharides and disaccharides, such as glucose and trehalose, were functionalized as vinyl-based monomers for the formation of diblock copolymers via radical addition-fragmentation chain-transfer (RAFT) polymerization. Upon complexation with plasmid DNA, the carbohydrate-containing block creates a hydrophilic shell that promotes colloidal stability as effectively as PEG functionalization. An N-acetyl-D-galactosamine variant of this diblock polymer yields colloidally stable particles that show increased receptor-mediated uptake by liver hepatocytes in vitro and promotes liver targeting in mice. The aforementioned series of glycopolymers use carbohydrates to promote effective and safe delivery of nucleic acid cargo into a variety of human cells types by promoting vehicle degradation, tissue-targeting, colloidal stabilization, and stability towards lyophilization to extend shelf life.
**Excellence in Graduate Polymer Research**

Organizer/Presiders: Dr. H.N. Cheng, Christine Coltrain, Christopher Ellison, Timothy Long

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**Excellence in Graduate Polymer Research: Nanotech and Supramolecular Structures**
09:00am - 12:00pm USA - April 12, 2021

**Graphene oxide-montmorillonite nanocomposite films with exceptional barrier properties from scalable, one-step coassembly**
Anna LaChance, Presenter; Luyi Sun

**High-temperature performance cyanate ester composites with carboranes**
SHAILJA GOYAL, Presenter; Michael Forrester; Prof. Eric W Cochran

**Nanoscale patterning of carbon nanotubes in polyacrylonitrile fibers**
Weiheng Xu, Presenter; Dharneedar Ravichandran; Sayli Jambhulkar; Yuxaing Zhu; Kenan Song

**Carbon dioxide responsive miktoarm polymer based soft nanoparticles for drug delivery**
Hui Wen Yong, Presenter; Ashok Kakkar

**Kinetics and thermodynamics of polymer grafted nanoparticle composites**
Shawn M Maguire, Presenter; Russell Composto

**Robust laboratory procedures for the determination of microplastics and nanoplastics in tissues of humans and animals**
Varun Kelkar, Presenter; Sangeet Adhikari; Rolf Halden

**Unraveling mechanisms of filler reinforcement with in-situ x-ray photon correlation spectroscopy**
Dillon Presto, Presenter; Suresh Narayanan; Sergio Moctezuma; Mark Sutton; Roderic Quirk; Mark Foster

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**Random copolymers form crystalline structures with supramolecular polymers**
Eric Bruckner, Presenter; Tine Curk; Luka Dordevic; Ziwei Wang; Ruomeng Qiu; Adam Dannenhoffer; Hiroaki Sai; Liam Palmer; Erik Luijten; Samuel Stupp

**Synthesis of electron-deficient borinic acid polymers and their applications in supramolecular assembly and as catalysts in amide bond formation**
Monika Baraniak, Presenter; Roger Lalancette; Dr. Frieder Jaekle

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**Excellence in Graduate Polymer Research: 3D Printing, Self-Healing and Mechanochemistry**
01:00pm - 04:00pm USA - April 12, 2021

**Design of functionalized polyarylene ether sulfones for stereolithographic printing**
Cody Weyhrich, Presenter; Katherine Heifferon; Clay Arrington; Justin Sirrine; Viswanath Meenakshisundaram; Nicholas Chartrain; Christopher Williams; Timothy Long

**Self-extinguishing additive manufacturing filament from a unique combination of polylactic acid and a polyelectrolyte complex**
Thomas Kolibaba, Presenter; Chin-Cheng Shih; Simone Lazar; Bruce Tai; Jaime Grunlan

**Multiphysics modeling and machine learning to determine light irradiation pattern in grayscale digital light processing (DLP) 3D printing**
Mr. Stuart Macrae Montgomery, Presenter; Craig Hamel; Robert Caraway; H. Jerry Qi

**Dynamic bottlebrush polymer networks: self-healing in supersoft networks**
Jeffrey Self, Presenter; Javier Read De Alaniz; Christopher Bates
Highly compliant and self-healable 3D architected polyelectrolyte complexes via projection stereolithography
Amylynn Chen, Presenter; Daryl Yee; Widianto Moestopo; Julia Greer

Self-healable Fluorinated copolymers governed by dipolar interactions
Siyang Wang, Presenter; Marek Urban

Enamine-based vitrimers through thiol-ene photopolymerization
Logan Dugas, Presenter; William Walker; Rahul Shankar; Keely Hoppmeyer; Sarah Morgan; Robson Storey; Derek Patton; Yoan Simon

Generation of an usually stable merocyanine via a unique mechanochemical reaction pathway
Molly McFadden, Presenter; Maxwell Robb

Mechanochemical generation of redox species in Polyacrylamide hydrogels due to osmotic swelling
Ashray Parameswar, Presenter; Andrew Goodwin; Karan Dikshit; Sanli Movafaghi; Carson Bruns

Excellence in Graduate Polymer Research: Energy Storage and Semiconductors
09:00am - 12:00pm USA - April 13, 2021

Rational design of conjugated triazole-based polymers for organic solar cells based on structure-property relationships
Jeromy Rech, Presenter; Wei You

Understanding the molecular weight dependence of photophysics, charge transport, morphology, and performance of all-polymer solar cells
Duyen Tran, Presenter; Amélie Robitaille; Xiaomei Ding; Mario Leclerc; Samson Jenekhe

Design and synthesis of all organic polymer dielectrics for high temperature and high electric field application through molecular engineering approach
Ajinkya Deshmukh, Presenter; Chao Wu; Zongze Li; Lihua Chen; Abdullah Alamri; Yifei Wang; Rampi Ramprasad; Yang Cao; Gregory Sotzing

Understanding the impact of polymer chain rigidity on the assembly, structure, and photo-physical processes
Alex Balzer, Presenter; Mark Weber; Parker Sommerville; Elizabeth Gutiérrez-Meza; Christine Keiko Luscombe; Carlos Silva; Natalie Stingelin

Quantifying charge carrier localization and charge transport properties in chemically doped semiconducting polymers
Shawn Gregory, Presenter; Riley Hanus; Amalie Atassi; Joshua Rinehart; Jamie Wooding; Akanksha Menon; Mark Losego; GJeffery Snyder; Shannon Yee

Designing functional polymeric electrode/electrolyte interphases for high energy density lithium metal batteries
Sanjuna Stalin, Presenter

Structure-property-relationships of network ionic polymer electrolytes and their applications to electrochemical devices
Chengtian Shen, Presenter; Christopher Evans

POmAC-based circuit board with biocompatible, biodegradable, and elastomeric properties
Brendan Turner, Presenter; Stefano Menegatti; Michael Daniele

Advances in polybenzimidazole (PBI) polymerization techniques and application in high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs)
Laura A. Murdock, Presenter; Brian Benicewicz
Spontaneous fragmentation of block copolymer micelles
Julia T Early, Presenter; Alison Block; Kevin Yager; Timothy Lodge

Harnessing core chain mobility in tuning small molecule release rates from polymer micelles
Ryan Carrazzone, Presenter; Jeffrey Foster; John Matson

Design of PLGA-based drug delivery systems through a molar mass-dependent sustained release model
Stijn Koshari; Xutao Shi, Presenter; Debby Chang; Nathan Wang; Isidro Zarraga; Purnendu Nayak; karthik rajagopal; Abraham Lenhoff; Norman Wagner

Tailorable, ultra-thick hyaluronan polymer brushes: A novel class of interfaces
Jessica Faubel, Presenter; Wenbin Wei; Hemaa Selvakumar; Riddhi Patel; Jennifer Washburn; Paul Weigel; Blair Brettmann; Jennifer Curtis

Gluten and zein interactions: A vibrational and fluorescence spectroscopy study
Azin Sadat, Presenter; Maria Corradini; Iris Joyce

Multidimensional mass spectrometry of multicomponent nonionic surfactant blends
Jason O’Neill, Presenter; Chrys Wesdemiotis

Surface modification of titanium implants for improved tendon adhesion
Hannah Feinberg, Presenter; Timothy Hanks

From diapers to adhesives: Open-loop recycling of post-consumer sodium poly(acrylate) via chemical modification
Paul Chazovachii, Presenter; Michael Robo; Martin James; Dr. Dimitris I Collias; Paul Zimmerman; Neil Marsh; Anne McNeil

Exploring degradation as a viable end-of-life process for thermoset polymers
Minjie Shen, Presenter; Rawan Almallahi; Zeshan Rizvi; Eliud Gonzalez-Martinez; Guozhen Yang; Megan Robertson

Photoredox mediated cross metathesis for molecular weight control in ring-opening metathesis polymerization
Rachel Tritt, Presenter; Victoria Kensy; Farihah Haque; Daniel Knorr; Scott Grayson; A. J. Boydston

Active machine learning for new monomers for frontal ring-opening metathesis polymerization
Morgan Cencer, Presenter; Pikee Priya; NARAYANA ALURU; Rajeev Surendran Assary; Jeffrey Moore

Functional materials from living ring-opening polymerizations
You-Chi Wu, Presenter; Francesco Benedetti; Sharon Lin; Zachary Smith; Timothy Swager

Development of advanced hybrid polymer/inorganic nanoparticles using surface-initiated ring-opening metathesis polymerization
Jacob LaNasa, Presenter; Robert Hickey

Mechanistic insight into the neodymium-catalyzed polymerization of dienes and ?-caprolactone
John Michael Cue, Presenter; Erika Calubaquib; Dr. Md Muktadir Talukder; Gregory McCandless; Chunqing Zhao; Michael Biewer; Mihaela Stefan
Controlled/living branching polymerization enabled by polymerization-induced activation: mechanistic study assisted development of catalytic systems
Mengxue Cao, Presenter; Yutong Liu; Xiaowei Zhang; Feng Li; Mingjiang Zhong

Novel strategies for constructing polyolefin-containing block copolymers
Tianwei Yan, Presenter; Damien Guironnet

Directed network structure through controlled radical photopolymerization
Huayang Fang, Presenter; Allan Guymon

Influences on deactivation in organocatalyzed atom transfer radical polymerization
Daniel Corbin, Presenter; Blaine McCarthy; Zach van de Lindt; Garret Miyake

Excellence in Graduate Polymer Research: New Synthetic Methodologies
01:00pm - 04:00pm USA April 15, 2021

Degradable polymers from thionolactone radical ring-opening copolymerization
Mr. Ronald A. Smith, Presenter; Owen McAteer; Mizhi Xu; Will Gutekunst

Redox-switchable catalysts for the controlled polymerization of cyclic esters
Alicia Doerr, Presenter; Lauren Brown; Justin Burroughs; Nicholas Legaux; Prof. Brian Long

Multicomponent polymerization for the synthesis of degradable polymers with a thermal-activated dynamic covalent behavior
Hongxu Liu, Presenter; Jiaming Zhuang; Sankaran Thayumanavan

Photo-responsive polymeric nanoreactors for compartmentalization and photo-regulation of incompatible tandem catalysis
Peiyuan Qu, Presenter; Marcus Weck

Novel synthesis, activation, and transformation strategies for the preparation of covalent organic framework powder, foams, and films
Dongyang Zhu, Presenter; Rafael Verduzco

Full circle recycling of polysiloxanes via room temperature fluoride catalyzed depolymerization to repolymerizable cyclics
Joseph Furgal; Buddhima Rupasinghe,

Unconventional conjugation via vinylMeSi (O-)2 siloxane bridges may imbue semiconducting properties in double-decker and ladder silsesquioxane copolymers
Jun Guan, Presenter; Richard Laine

Programmable electromechanical deformation of liquid crystal elastomers
Hayden Fowler, Presenter; Philipp Rothemund; Christoph Keplinger; Timothy White

Investigating the stimuli-responsive and morphological properties of dye incorporated liquid crystalline polymers within unique polymeric templates
Samiksha Vaidya, Presenter; Meenakshi Sharma; Rajeswari Kasi; Christian Bruckner
Graphene oxide-montmorillonite nanocomposite films with exceptional barrier properties from scalable, one-step coassembly

Anna M. LaChance¹, amlachance18@gmail.com, Luyi Sun². (1) Chemical & Biomolecular Engineering, University of Connecticut, Willimantic, Connecticut, United States (2) Institute of Material Science, University of CT, Storrs, Connecticut, United States

Often used in packaging material, polylactic acid (PLA) has only moderate water vapor transmission rate (WVTR) and high oxygen transmission rate (OTR), thus limiting its applicability. In a facile, scalable dip coating process, a coating layer consisting of graphene oxide (GO) and montmorillonite (MMT) nanosheets were co-assembled with a polyvinyl alcohol (PVA) matrix was applied to PLA film. The resulting coating layer had vastly improved water vapor and oxygen barrier properties over the previous literature, owing to the combination of nanosheets of differing mechanical properties and aspect ratio to create a tortuous path for gas transport. The interfacial chemistry of the coating materials was verified with XRD, XPS, FTIR, and Raman spectroscopy. This technique should have unique implications for thin film vapor barrier technology, such as food packaging material, wearable electronics, biomedical devices, construction material, and anti-corrosives.
High-temperature performance cyanate ester composites with carboranes

SHAILJA GOYAL, sgoyal@iastate.edu, Michael J. Forrester, Eric W. Cochran. Chemical and Biological Engineering, Iowa State University, Ames, Iowa, United States

Cyanate ester (CE) is an important class of materials among high-temperature performance thermosets due to their high glass transition temperatures (>220°C), excellent thermal stability, and low flammability. In this work, we demonstrate carborane-filled CE nanocomposites that have an exceptionally high oxidative thermal stability as compared to the pristine resin. Carborane fillers were solvent blended at various mass loadings in the resin and cured to study their effect on thermal properties. Our TGA experiments show that the ultimate char yield of the resin can be increased from 0% to as high as 76 and 82.1% with 30 wt.% PD and EP carborane loading respectively at 1000 deg C in air. We interrogated the degradation mechanism of these carborane-CE composites through FTIR, Elemental Analysis, TGA-Mass Spectroscopy (TGA-MS), and solid-state 11B and 12C NMR. We have discovered that the iminocarbonate and oxazolidinone linkages between CE and carboranes are labile, producing a moderate temperature (ca. 450 deg C) initial degradation in TGA. Howbeit, at higher temperatures (> 650 deg C) the carborane structure disintegrates and is oxidized to boronic acid and boroxine structures.

In further studies, we are now working to translate these mechanistic insights to design other thermally protected thermoset matrices such as epoxies. Additionally, we are elucidating the effect of boron-based fillers on mechanical properties.
Nanoscale patterning of carbon nanotubes in polyacrylonitrile fibers

Weiheng Xu¹, weihengx@asu.edu, Dharneedar Ravichandran¹, Sayli Jambhulkar¹, Yuxaing Zhu¹, Kenan Song². (1) Arizona State University, Gilbert, Arizona, United States (2) Manufacturing Engineering, Arizona State University, Mesa, Arizona, United States

Polymer nanocomposites (PNCs) have been a research focus for more than a few decades due to their unique physical and chemical properties. In terms of their processing, polymer and nanoparticles are often mixed for synergistic and hybrid properties, yet, the spatial geometry and nanoscale structural features within such composite are often overlooked. In this presentation, a scalable fabrication method, combining the forced assembly process and dry-jet-wet fiber spinning technique is demonstrated for location-regulated deposition of carbon nanotubes (CNTs) within polyacrylonitrile (PAN) matrix for high mechanical performance fiber. Two polymer solutions (i.e., PAN and CNT/PAN) first entered a 3D-printed multiplier die side-by-side and then were physically separated along the horizontal direction (top-down) and repositioned along the vertical direction (right-left). In this way, a 512 layered fiber with hierarchical structures, including highly aligned nanotubes (hierarchy level 1, ~20 nm), alternatively packed nanolayers (hierarchy level 2, ~170 nm), microscale fibers (hierarchy level 3, ~80 µm) is constructed for macroscale fiber reinforcement in traditional fabrics or laminates (hierarchy level 4, ~1 m) (Figure 1a). The introduction of alternating layers facilitated the quality of CNT dispersion due to nanoscale confinement and, at the same time, enhanced their orientation due to shear stress generated at each layer interface (Figure 1b). We demonstrated an example with 0.5 wt% CNTs loading and the inclusion of 170 nm layers in composite fibers showed a 27.4% increase in modulus and a 22.2% increase in strength compared to the traditional CNT/PAN mixing method without any hierarchical structures (Figure 1c).

Figure 1. (a) Hierarchical fiber structure from macro to nanometer scale. (b) 512 layered fiber with a layer thickness of 170 nm. (c) Enhanced mechanical behaviors with increasing layer numbers.
Carbon dioxide responsive miktoarm polymer based soft nanoparticles for drug delivery

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Stimuli responsive polymers respond to changes in environment induced by physical, chemical, or biological signals, such as oxidative stress, pH, temperature, glucose levels etc. The specificity and responsiveness of such polymeric nanocarriers as well as their tunable behavior are an attractive feature for drug delivery, as they are subjected to changes only when exposed to a particular trigger, avoiding accumulation and side-effects of drug molecules at undesired sites. Miktoarm polymers continue to provide an ideal platform for developing stimuli-responsive drug delivery nanocarriers, as functional groups that can respond to a specific stimulus can be easily incorporated into the branched architecture. The nanometer size self-assemblies from these amphiphilic miktoarm stars are also known for their superior drug loading ability, while having a low critical micelle concentration. CO\textsubscript{2}-responsive polymers have been widely investigated, as the gas is benign, abundant, inexpensive, and easily reversible. These advantages have brought much attention to CO\textsubscript{2}-responsive polymers in applications such as CO\textsubscript{2}-switchable surfaces, CO\textsubscript{2}-switchable nanoreactors and CO\textsubscript{2}-responsive self-assemblies. It is, however, less studied as a stimulus in drug delivery. Numerous studies have shown that cancerous sites have elevated levels of CO\textsubscript{2}, resulting in impaired respiration in lung cancer patients and threatening the growth of healthy cells. Therefore, CO\textsubscript{2}-targeting nanocarriers are needed for delivering drugs to such targeted sites and increasing the drug release rate. We will discuss the design of biocompatible CO\textsubscript{2}-responsive AB\textsubscript{2}-type amphiphilic miktoarm stars, with a combination of hydrophilic and amine-incorporated hydrophobic segments. A 2:1 ratio of hydrophilic to hydrophobic segment greatly enhances the aqueous solubility. A detailed evaluation of the design, self-assembly, drug loading and release characteristics of these miktoarm star-based assemblies will be discussed.

Proposed drug release mechanism of micelle upon exposure to CO\textsubscript{2}. 
Kinetics and thermodynamics of polymer grafted nanoparticle composites

Shawn M. Maguire, shawnmag@seas.upenn.edu, Russell J. Composto. Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

In this work, model binary and ternary polymer nanocomposites (PNCs) of poly(methyl methacrylate) grafted silica nanoparticles (PMMA-NP), poly(styrene-ran-acrylonitrile) (SAN), and PMMA homopolymers are examined to probe thermodynamic and kinetic parameters underlying phase behavior and nanoparticle assembly. Using complimentary techniques, the addition of PMMA to the binary PMMA-NP/SAN composite is observed to increase the miscibility in off-critical compositions of the ternary blend. This compatibilization is attributed to interfacial segregation of PMMA and supported by polymer reference interaction site model theory calculations and molecular dynamics simulations. Knowing the phase diagram, the interplay between phase separation and wetting is then studied by quenching the binary PNC films into the two-phase region. The PNC morphology exhibits symmetric wetting layers of PMMA-NPs at the surface and substrate, separated by “pillars” of PMMA-NPs that span the thickness. This composite morphology enhances the film modulus and hardness, as measured by nanoindentation, as well as the films thermal stability. The growth of this PMMA-NP surface excess increases rapidly with time and reaches a plateau that is dependent on quench depth. The diffusion coefficients of PMMA-NPs are measured and compared with prevailing models. Overall, these results highlight the complex parameter space in PNCs and provide new insights and control over both the bulk and surface morphologies of PNCs.
Robust laboratory procedures for the determination of microplastics and nanoplastics in tissues of humans and animals

Varun Kelkar, Vpkelkar@asu.edu, Sangeet Adhikari, Rolf U. Halden. Environmental health engineering, Arizona State University, Tempe, Arizona, United States

The presence of microplastics (MPs) and nanoplastics (NPs) in commodities of daily use and is a human health concern. Polyethylene terephthalate (PET) and polycarbonate (PC) are among the most widely used plastics, made from monomers of terephthalic acid (TPA) and bisphenol A (BPA), respectively. The present work aimed to perform a literature analysis of PET and PC exposures in humans and to assess the potential for analytically demonstrating potential human exposures to MPs and NPs against a potentially significant background of environmental plastics that may cross-contaminate samples during sample acquisition, handling, storage, processing and analysis. For the literature review, peer-reviewed data on the presence of plastic monomers and polymers in human tissues were obtained and analyzed from scientific databases. To assess the feasibility and limits of plastic exposure determination in human tissues, a multi-step analytical approach was outlined, (1) solubilization of tissue using an alkaline agent, (2) determination of BPA/TPA in tissue extracts using liquid chromatography tandem mass spectrometry (LC-MS/MS), (3) depolymerization of MPs and NPs putatively present in the form of PET and PC polymers, (4) concentration and analysis by LC/MS-MS of monomers liberated by the depolymerization step, and (5) comparison of the mass of plastic monomers determined to be present before and after the tissue solubilization and plastic depolymerization. Study results demonstrate that a significant body of literature on human exposure to plastic monomers exist, whereas authoritative reports of the presence of plastic polymers in human tissues are still scarce. Overall, this study highlights the significant challenges associated with the qualitative and quantitative determination of plastics that are ubiquitous and thus pose a high risk of unwanted cross-contamination during analysis. Recommendations are provided on how to minimize the risk of erroneous conclusions about the type and extent of polymers present in animals and human study subjects. Opportunities for interpreting obtained results in the context of lifetime exposure metadata also are discussed.
Unraveling mechanisms of filler reinforcement with in-situ x-ray photon correlation spectroscopy

Dillon Presto¹, dgp15@zips.uakron.edu, Suresh Narayanan², Sergio Moctezuma³, Mark Sutton⁴, Roderic P. Quirk¹, Mark D. Foster¹. (1) School of Polymer Science and Polymer Engineering, University of Akron, Akron, Ohio, United States (2) Advanced Photon Source, Argonne National Lab, Argonne, Illinois, United States (3) Dynasol Elastómeros, Altamira, Mexico (4) Physics, McGill University, Montreal, Quebec, Canada

The interfacial chemistry between elastomer matrix and reinforcing filler are key for the design of reinforced rubbers which meet goals for both performance and sustainability. Despite the broad commercial utility of reinforced rubbers to technologies such as tires, the crucial connections between chemistry at the elastomer/filler interface and the resulting mechanical properties at the macroscale remain poorly understood. We have elucidated, using X-ray photon correlation spectroscopy (XPCS), important relationships between the chemistry at the silica surface and the microdynamics of filler particles when the interfaces are modified by silane coupling agents. We have performed XPCS on silica-filled styrene-butadiene rubber (SBR) containing different silane coupling agents under both static strain and dynamic strain. Static strain (stress relaxation) XPCS measurements reveal differences in the disaggregation and subsequent ballistic motion of filler structures. Meanwhile, dynamic strain XPCS measurements allow us to probe the microscale breakdown and reformation of the filler network, which are responsible for the fuel efficiency and traction of tire tread compounds. From these experiments we have drawn connections between filler microdynamics and mechanical performance which provide new perspectives for understanding how the chemistry at the elastomer/filler interface give rise to the remarkable properties of reinforced rubbers.
Random copolymers form crystalline structures with supramolecular polymers

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The ordering of polymer chains into well-defined crystal lattices remains a challenge due to kinetic barriers during crystallization and the difficult synthesis of structurally precise macromolecules. We report here on a strategy where monomers of a supramolecular polymer can be used to promote the crystallization of covalent polymers that lack the sequence and stereochemical control to crystallize on their own. Synchrotron X-ray scattering, absorbance spectroscopy, and coarse-grained molecular dynamics (CG-MD) simulations reveal that the supramolecular monomers co-crystallize with complementary motifs on the covalent polymer to form nanoscale structures under aqueous conditions. Transmission electron microscopy and CG-MD simulations show that this method can also be used to tune the size and shape of these nanostructures through a competition between the entropy of polymer chain folding and the formation enthalpy of an extended crystalline lattice. When these hybrid covalent-supramolecular polymers are used as photosensitizers in aqueous catalysis, we observe an unexpected enhancement in catalysis linked to their structure.
Synthesis of electron-deficient borinic acid polymers and their applications in supramolecular assembly and as catalysts in amide bond formation

Monika K. Baraniak¹, monika.baraniak86@gmail.com, Roger Lalancette², Frieder Jaekle².  
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The enhanced Lewis acidic character of borinic acid-functionalized polymers suggests broad potential applications in supramolecular materials, chemo- and biosensors, as well as supported catalysts. This presentation will discuss the synthesis of a new class of more electron-deficient borinic acid polymers, studies on their supramolecular assembly, and investigations into their use as catalysts in amide bond formation.

We synthesized two electron-deficient borinic acid copolymers poly(styrene-co-2,4-dichlorophenyl borinic acid) and poly(styrene-co-3,5-dichlorophenyl borinic acid). Due to the less bulky and more electron-withdrawing group at the boron center these polymers are able to form supramolecular assemblies via Lewis acid–Lewis base interactions and reversible covalent B-O-B bond formation. The dynamic processes were studied in detail by variable temperature (VT) NMR using 2,4- and 3,5-substituted (dichlorophenyl)(tert-butylphenyl)borinic acids as molecular model compounds and the respective pyridine-complexed boroxanes, R'RB-O-BRR'(Py). The polymers and their corresponding model compounds were also examined as catalysts in the amide bond formation reaction between phenylacetic acid and benzylamine. The 3,5-dichlorophenyl borinic acid derivatives proved to be the more effective catalysts. Mechanistic studies suggested that the borane Lewis acid-catalyzed coupling involves initial acid-induced protodeboronation to release the dichlorophenyl boronic acid as the active catalyst.
Design of functionalized polyarylene ether sulfones for stereolithographic printing

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Vat photopolymerization (VPP) is an advanced additive manufacturing technique that allows for the production of intricate 3D assemblies that are unable to be matched by traditional manufacturing methods. VPP was targeted as the preferred method for 3D printing high temperature thermoplastics due to its high modularity and selectivity of UV exposure. In this work, modifications of polyarylene ether sulfones (PSU) formulations allow for VPP processing. Telechelic functionalization with acrylates across various molecular weights (6KDa, 10KDa, 15KDa) of PSU yielded photo-crosslinkable polymers. Addition of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) photo-initiator to the solution of PSU in N-methylpyrrolidone (NMP) at 20 wt % produces a vat photopolymerizable resin. The relationship between photoinitiator concentration and acrylate conversion along with the storage/loss modulus crossover time was investigated through variations of the photoinitiator concentration. These studies displayed that the concentration of photoinitiator and crossover time share an inverse relationship therefore the highest loadings of TPO yield the fastest crossover times, which is important for determining the viability of a materials use for VPP as a fast crossover time is essential for the printed parts to retain their shape. Photorheology studies of the molecular weight and TPO loading series identified the 6KDa PSU as the best sample for VPP. The addition of 0.5 wt% of avobenzene photoblocker produced a well-defined print with 6KDa PSU. For higher molecular weights (>12KDa), a small molecule crosslinker was added to increase the acrylate concentration thereby producing an organogel with a modulus sufficient for stereolithography.
Self-extinguishing additive manufacturing filament from a unique combination of polylactic acid and a polyelectrolyte complex

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Additive manufacturing, also known as 3D printing, has quickly become a widely used tool for rapid prototyping of complex parts. Most of the common filaments for the fused filament fabrication form of 3D printing are inherently flammable thermoplastics, which has led to numerous fires that pose a serious danger to lives and property. In an effort to improve the safety of these filaments, a unique composite of polylactic acid (PLA) and a flame-retardant polyelectrolyte complex, consisting of polyvinylamine and poly(sodium phosphate), was developed. This composite filament can be printed using an ordinary 3D printer under identical conditions to neat PLA. The filament and its printed parts are self-extinguishing in an open flame tests and exhibit a 42% lower peak heat release rate, as measured by microscale combustion calorimetry. This unique filament concept solves a major safety problem for 3D printing and could be extended to other commonly used polymer filaments.
Multiphysics modeling and machine learning to determine light irradiation pattern in grayscale digital light processing (DLP) 3D printing

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Additive manufacturing (AM) is a rapidly growing field that continues to find new applications and reach new heights of structure fabrication as the technology continues to improve. Digital light processing (DLP) is one of the most promising AM technologies due to its fast build speed, high accuracy, and material versatility. In this approach, a light pattern is shone onto a build platform submerged in a vat of photopolymerizable resin. The resin is cured in the shape of the light pattern, and then the platform sinks further into the resin so that a new layer can be cured on top of the previous one. In this way, parts can be built very rapidly in a layer-by-layer manner. Moreover, the brightness of each pixel can be tuned within each layer, which allows the final modulus of the printed structures to vary throughout the part. This is known as grayscale DLP (g-DLP). While this is a very powerful fabrication method, there are still several factors that can limit the quality of the prints. The light used to cure each new layer of resin will also penetrate previous layers, which causes the curing reaction to continue. This can cause errors in the final properties of regions designed to be softer (lower degree of cure). There can also be property errors within each layer, known as over-curing, which is mainly caused by overlapping Gaussian light distributions from each pixel and the diffusion of free radicals generated during the curing process. This work presents a platform that integrates multiphysics modeling with machine learning to determine correct light irradiation dose to overcome overdose issues. First, a model that couples light propagation in resin, chemical reaction kinetics, and diffusion of chemical species is developed. This tool can be used to optimize the individual pixel intensities along property boundaries in order to sharpen the transition between regions. Separately, a neural network is used to determine the sequence of light intensities that will most-accurately produce the desired property pattern in the printing direction. This work not only provides a better understanding of the curing kinetics of DLP printing, but also provides a path toward unlocking the full potential of the g-DLP method.
Dynamic bottlebrush polymer networks: self-healing in supersoft networks

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Dynamic polymer networks are of research interest for various applications where self-healing and reprocessability are advantageous. We describe a design strategy for expanding the scope of mechanical properties of these materials by selective crosslinking of bottlebrush polymers. Well-defined bottlebrush polymers with poly(4-methylcaprolactone) side chains were cured into networks via reaction with a bis-lactone crosslinker catalyzed by a strong Lewis Acid (tin ethylhexanoate). At elevated temperatures (160 to 180 °C), residual hydroxy groups undergo transesterification reactions with sidechain esters as evidenced by stress relaxation experiments. The crosslinking density can be varied by both changing the stoichiometry of crosslinker as well as the backbone degree of polymerization, resulting in supersoft and tunable shear moduli ca. 10 – 100 kPa. The ability of these materials to self-heal was demonstrated by the re-molding of a tensile bar after rupture, with the sample recovering >85% of its original toughness over 2 cycles. In summary, design of the molecular architecture of dynamic polymer networks creates new opportunities to tailor the mechanical properties of CANs in ways that are otherwise difficult to achieve.
Highly compliant and self-healable 3D architected polyelectrolyte complexes via projection stereolithography

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Additive manufacturing (AM) has been demonstrated as an efficient method to produce high-accuracy and isotropic parts with complex geometries. Projection micro-stereolithography (PµSL) is a rapid AM technique based on photo-induced polymerization of liquid photoresin, which is capable of fabricating complex 3D structures in a layer-by-layer fashion. Currently, the established photolithography-compatible materials are high crosslinked brittle and inert polymers, which limits their applications. There has been a growing effort to seek compliant materials for AM with advanced functionalities, such as stimuli-responsiveness, self-healing, deformability, degradability, and recyclability.

Polyelectrolyte complexes (PECs) are a class of supramolecular polymers that consist of oppositely charged polyions interconnected by electrostatic interactions. Generally, the synthesis of PECs involves multiple steps, such as polyanion/polycation synthesis, purification and mixing of the polymer components to achieve desirable properties. These systems are notable for their high compliance and rapid self-healing at the hydrated state but require multistep processes that are unsuitable for AM. To maintain their properties, these materials are often stored in water. This raises concerns for the consistency of the mechanical properties and long-term stability in ambient environment and limits the potential applications. In this work, we demonstrate the a “one-pot” approach to fabricate 3D structures of PECs via PµSL, where the material obtains >450% strain at break and ~3MPa failure strength through tensile testing. After equilibrating in ambient environment for more than 20 days, our ASTM D638 standard type-V tensile specimens still exhibit 100% of the original strain. We have also investigated the tunability, cyclability, reproducibility, strain-rate dependency and self-healing properties of the additively manufactured PECs. This simple and versatile approach opens up a new space for 3D printing of self-healable and responsive polymers with tunable properties.
Self-healable Fluorinated copolymers governed by dipolar interactions

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We developed a route to obtain self-healable properties in thermoplastic copolymers that rely on non-covalent dipolar interactions present in essentially all macromolecules, and particularly fluorine-containing copolymers. The combination of dipolar interactions between C-F and C=O bonds as well as CH₂/CH₃ entities facilitates self-healing without external intervention. The presence of dipole-dipole, dipole-induced dipole, and induced-dipole induced dipole interactions lead to a viscoelastic response that controls macroscopic autonomous multicycle self-healing of fluorinated copolymers under ambient conditions. Energetically favorable dipolar forces attributed to monomer sequence and monomer molar ratios induces desirable copolymer tacticities, enabling entropic energy recovery stored during mechanical damage. The use of dipolar forces instead of chemical or physical modifications not only eliminates additional alternations enabling multiple damage-repair cycles but also provides further opportunity for designing self-healable commodity thermoplastics.

Chemical structure of 2,2,2-trifluoroethyl methacrylate (TFEMA) and n-butyl acrylate (nBA) as well as p(TFEMA/nBA) copolymers; (A) Optical images of p(TFEMA/nBA) copolymer films: undamaged (B1); damaged (B2) – cut size: ~50 mm; and self-healed (B3). 2D ¹⁹F NOESY NMR spectra of undamaged (C1), damaged (C2) and self-healed (C3); 2D ¹H NOESY NMR spectra of undamaged (D1), damaged (D2) and self-healed (D3) copolymer.
Enamine-based vitrimers through thiol-ene photopolymerization

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Associative exchange chemistries in network polymers have enabled the advent of vitrimers, a unique class of materials likened to both thermosets and thermoplastics that possess remarkable stability while displaying healability and on-demand degradability. Herein, we describe a novel thiol-ene photopolymerized vitrimer that exchanges through enamine linkages derived from cyclic triketones. Uncatalyzed enamine chemistry exhibits low energy barrier of amine exchange and the ability to rapidly depolymerize. Accordingly, we devised an alkene-functionalized triketone, 5,5-dimethyl-2-(pent-4-enoyl)cyclohexane-1,3-dione, which was reacted with 1,6-diaminohexane in a stoichiometrically imbalanced (~85:15 mol %, enamine:primary amine) fashion. We found that ester-free tetrafunctional thiols work best as they preclude transamidation. The glass transition temperatures (T_g) of the resulting network were below room temperature (~ 3-7°C) and the topology freezing temperature (T_v) was found through frequency-sweep experiments to be 90 °C. Arrhenius fitting of the stress relaxation of the networks enabled us to measure the activation energy of the exchange process (51.45 kJ/mol). The materials readily degraded upon introduction of either strong acids or excess primary amines showing the versatility of this approach. Therefore, this work opens up new avenues for the development of tailorable next-generation multifunctional and degradable materials and their implementation in a multitude of applications, such as high-performance composites or polymer upcycling.
Generation of an usually stable merocyanine via a unique mechanochemical reaction pathway

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A wide range of force-coupled reactions have been developed since the emergence of the contemporary field of polymer mechanochemistry around 2005. Discovery of new mechanochemical transformations expands both the range of applications for force-responsive materials and the fundamental understanding of force-mediated reactivity. Naphthopyrans are mechanophores that undergo a reversible 6 electrocyclic ring-opening reaction under force to generate intensely colored merocyanines. Thermal electrocyclization often occurs under ambient conditions, resulting in loss of color. The naphthopyran mechanophore has been successfully derivatized to access mechanochromic polymers with variable colors, fading rates, and even force-dependent multicolor responses. However, to date, all naphthopyran mechanophores belong to a structural family known for particularly rapid thermal reversion. We recently discovered a new class of mechanochemically active naphthopyrans that generates an unusually stable merocyanine dye under mechanical force. Excitingly, the remarkable stability of this merocyanine is unique to the mechanochemical reaction pathway and is not accessed under photochemical activation. We discuss the elucidation of a novel force-mediated transformation and the identification of the unusual merocyanine product, and the potential impact of this new mechanochromic mechanophore in stress-reporting polymers.
Mechanochemical generation of redox species in Polyacrylamide hydrogels due to osmotic swelling

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In this talk, we report the mechanochemical production of free radicals in swelling polyacrylamide hydrogels. Osmotic swelling of hydrogels can lead to significant chain strain due to opposite forces of solvation and network integrity, resulting in bond scission at crosslink sites. We first investigated the swelling induced production of H$_2$O$_2$ due to crosslink breakage. By tuning the nature and loading of crosslinker employed in thin square hydrogels, mechano-scission of crosslink sites and subsequent production of free radicals was observed. Production of OH$\bullet$ radicals and the resultant combination to H$_2$O$_2$ was observed via colorimetric assay analysis. The assay consisting of Horseradish peroxidase and Amplex ultrared reported H$_2$O$_2$ concentrations from 5-28 μM depending on crosslinker strength in both weak (disulfide) and strong (PEG) linkages. H$_2$O$_2$ concentration was enhanced by swelling constrained gels, which is known to introduce significant biaxial stresses.

Next, we report contact separation induced radical formation of a hydrogel-glass interface to fluorescently tag the network at sites of interfacial damage. Weakly tethered hydrogels can undergo edge failure due to solvent ingress. Here, thin circular amine-doped hydrogels were swollen in aqueous solutions of a novel ketone containing fluorophore to initiate radical-mediated reductive amination between the dye and the hydrogel. After swelling and washing, fluorescent edge patterns were observed, enabling a post-swelling analysis of interfacial damage. Failure was tuned by varying monomer/crosslinker loading, swelling conditions and thickness to reveal variable fluorescent patterns. Higher crosslinker loading led to more radial penetration and higher area fraction of delamination across monomer loadings, while the length scale of delamination scaled directly with gel thickness. Currently, we are investigating the dual capability of redox specie generation to initiate versatile reactions. We also aim to control these pathways with scavengers/promoters, to design specific applications such as reductive generation of antibacterial gold nanoparticles and oxidative activation of a latent fluorophore.
Rational design of conjugated triazole-based polymers for organic solar cells based on structure-property relationships

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With the recent remarkable advances in the efficiency of organic solar cells, the need to distill key structure–property relationships for semiconducting materials cannot be understated. The fundamental design criteria based on these structure–property relationships will help realize low-cost, scalable, and high-efficiency materials. In this talk, we will systematically explore the impact of a variety of functional groups, including nitrogen heteroatoms, fluorine substituents, and cyano groups, along the conjugated polymer backbone. Each functional group and can modify the optoelectronic, photovoltaic, and morphological properties of the resulting solar cell, and we highlight the strengths and weaknesses of the functional groups and location of functionalization. Interestingly, amongst this library of polymers, there are limits to the improvements which can be made to the conjugated polymers, and a delicate balance is required to achieve the best organic solar cell. Overall, this work highlights some of the benefits, thresholds, and limitations for functionalization of conjugated polymers for organic solar cells.
Understanding the molecular weight dependence of photophysics, charge transport, morphology, and performance of all-polymer solar cells

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All-polymer solar cells (all-PSCs) is a promising next-generation photovoltaic technology due to its unique advantages, including good mechanical flexibility, excellent thermal/mechanical durability, high visible transparency, and great potential for large-scale manufacture with low production cost. I will present our study of the effects of polymer number-average molecular weight ($M_n$) on the performance of all-PSCs. We used a series of biselenophene-naphthalene diimide (PNDIBS) acceptor polymers synthesized by direct heteroarylation polymerization method with six $M_n$ values spanning 20 – 130kDa and the donor polymer PBDB-T. We found that the short-circuit current and the power conversion efficiency (PCE) of all-PSC composed of PNDIBS/PBDB-T binary blends were maximized as $M_n$ approached a critical value ($M_n = 55$kDa) but subsequently declined with further increase beyond the critical value. The blend photophysics, blend charge transport properties, and blend morphology were concurrently optimized at the critical $M_n$ value. The underlying mechanism for the observed trends was explained by the efficient charge photogeneration rate, suppressed space-charge formation, superior and symmetric charge transport, and a bi-continuous network of ordered crystalline domains with predominant face-on molecular orientations at the optimal $M_n$. Our findings provide important structure-property relationship insights while providing design guidelines that are broadly applicable to the development of high-performance semiconducting polymers with optimal properties and enhanced photovoltaic properties.
Design and synthesis of all organic polymer dielectrics for high temperature and high electric field application through molecular engineering approach

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Polymers with high electric field stability at ambient and elevated temperatures are important for various electrical and electronic applications. For capacitor applications, polymers need to have a high discharge density with high efficiency. However, at elevated temperatures, common high-temperature polymers show enhanced electrical conduction due to their low bandgap, which leads to low discharged energy density with high energy loss. At the same time, polymers with high bandgap and low loss at high electric fields cannot be used at elevated temperatures because of their low glass transition temperatures. For example, the state-of-the-art dielectric polymer that is BOPP can only be used up to 110 °C with cumbersome cooling.

To overcome this issue, we carefully studied the common polymers and explored an inverse correlation between Tg and bandgap for common polymers. Further, to break this design constraint, we developed a new polymer design strategy through a molecular engineering approach where high bandgap (~ 5 eV) and high Tg (~186 °C) can be obtained simultaneously. As a result, polymer synthesized using this new design strategy can be exposed to harsh conditions of simultaneous high temperature and high electric field. The synthesized polymer is then further characterized for capacitive energy storage purposes, and it shows a high discharged energy density of 5.7 J/cc at 150 °C, outperforming all the flexible polymer dielectrics. High bandgap, coupled with high Tg, leads to low electrical conduction loss and a combination of flexible and rigid segments in the polymer repeat unit leads to low dielectric loss. Additionally, the synthesized polymer can be processed into flexible free-standing films using a simple roll to roll process. The design strategy can be used for polymers for energy storage and for polymers for other electrical applications where low electrical conduction is desired.
Understanding the impact of polymer chain rigidity on the assembly, structure, and photo-physical processes

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The field of polymer-based electronics has witnessed major developments in the past few years that have led to systems of vastly improved charge transport- and energy-harvesting properties. This progress can be predominantly attributed to synthetic efforts in the form of the creation of new materials, which often comprise backbones of a significantly more rigid nature than the first generation polymer semiconductors and most bulk commodity plastic. Moreover, many semiconducting polymer frequently lack significant long-range order, but it is hypothesized that they may exhibit liquid-crystalline-like behavior because of their hairy-rod nature. To understand the polymer phase behavior, how it relates to chemical design and how it dictates important optoelectronic features, we use fast scanning calorimetry to identify the glass transition and possible liquid-crystalline-like transitions, as well as side-chain softening regimes, using physical aging signatures and focusing on poly(indacenodithiophene)s and other next-generation semiconducting polymers. By pairing the thermodynamic data with 2D coherent excitation spectroscopy, we can relate information of the very local polymer order (backbone torsion, structural dynamics introduced by side-chain softening) on exciton coherence and charge transport properties. This approach allows us to gain insights on the role of polymer assembly and solid-state structure on energetic disorder and photophysical characteristics towards the delivery of important structure-property interrelations for design of fourth generation semiconducting plastics for organic solar cells, plastic electronics, wearable sensors, and beyond.

We use fast scanning calorimetry to identify the glass transition and possible liquid-crystalline-like transitions, as well as side-chain softening regimes, using physical aging signatures and focusing on next-generation semiconducting polymers.
Quantifying charge carrier localization and charge transport properties in chemically doped semiconducting polymers

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Charge transport in semiconducting polymers ranges from localized (hopping-like) to delocalized (metal-like), and the transport physics can vary significantly as a function of several engineering parameters (e.g., polymer chemistry, dopant chemistry, dopant quantity, and processing.) Despite the increasing ubiquity of semiconducting polymers, there is not a succinct transport model that captures this wide spectrum of transport physics nor its dependency on carrier densities and these engineering parameters. To inform the development of an improved transport model, we collected temperature-dependent thermoelectric measurements on poly(3-hexylthiophene) chemically doped with FeCl₃. The extent of doping and carrier densities were quantified using XPS, and we observed that with increasing carrier density, the electrical conductivity increased, the thermal activation energy for electrical conductivity decreased, and the Seebeck coefficient decreased. We then used these measurements to develop the semi-localized transport model (SLoT model). The SLoT model uses a modified Boltzmann transport approach to quantify the effects of several engineering parameters and carrier densities on the observable transport properties. Additionally, the SLoT model predicts how quickly the localization activation energy decreases and how quickly the Fermi energy level increases with increasing carrier density. Furthermore, several literature studies are well modeled using SLoT, including organic field-effect transistor thermoelectrics and chemically doped single-walled carbon nanotubes. This consistency validates the SLoT model and suggests broad utility. Ultimately, for the first time, this SLoT model quantifies both localized and delocalized contributions to charge transport in chemically doped semiconducting polymers, and it enables us to design the next generation of semiconducting polymer electronics more rationally and quantitatively.

S-σ plot showing that a nominal s = 1 Kang-Snyder model cannot explain the P3HT-FeCl₃ experimental data. The SLoT model accounts for a localization energy that decreases with increasing carrier concentration.
Designing functional polymeric electrode/electrolyte interphases for high energy density lithium metal batteries

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Reactive metal anodes are known to electrodeposit in the form of irregular morphological features on planar substrates. Formed during the earliest stages of deposition, these features are thought to eventually result in non-planar, mossy structures that proliferate in the electrode spacing, hampering electrode reversibility. A growing body of work suggests that the mechanics, structure, ion transport properties, reductive stability, and interfacial energy of interphases formed spontaneously on the metal electrode play important, but separate roles in regulating nucleation, growth, and reversibility of these non-planar structures. In this study, we examine the effect of polymeric interphases on the early stages of lithium metal deposition and subsequent growth rate of the deposit front. By performing a theoretical linear stability analysis of metal electrodeposition across elastic interphases, we find that interphase thickness, mechanics, ion transport and interfacial properties all play precise and differentiated roles in setting the optimal interphase design. Motivated by this analysis, we focus specifically on thermosetting polymer interphases because their mechanical and chemical properties can be readily manipulated. Our goal is to develop design rules that can be implemented without adding substantially to the weight or volume of the metal electrode. By systematically varying the physical and chemical properties by manipulating monomer chemistry at the molecular level, we try to elucidate the effect of the properties of the polymer on the morphology of electrodeposited lithium. Using characterization techniques that include electroanalytical tools and operando visualization of the metal deposition, we find that parameters like polymer thickness, metal-polymer interfacial energy and elasticity have a profound effect on the morphology of electrodeposited lithium and correlate that with the theoretical results. These findings can potentially guide the design of artificial interphases as well as electrolyte components that lead to specific compositions of the SEI.
Structure-property-relationships of network ionic polymer electrolytes and their applications to electrochemical devices

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Next generation applications such as roll up displays, wearable electronics, and tactile communication require safe and flexible solid-state electrolytes with diverse functionalities. We have investigated how molecular design controls key properties (e.g. glass transition, ion transport, modulus) of network ionic polymers which also influence their performance as electrolytes in a range of applications. We first systemically showed, in ammonium networks, ion exchange with 1.5 equiv. of the new counterion was insufficient and lead to 10 times lower in ionic conductivity, 50 K decrease in thermal stability, with minimal change in glass transition temperature (Tg). This points to the importance of preparation for fundamental investigations of charge transport in polymers. Next, imidazolium cation was used to synthesize low Tg, electrochemically stable electrolytes. Polar ethylene oxide linkers were found to increase the ionic conductivity and lower the modulus compared to identical length hydrocarbon counterparts. In response to a 3 V stimulus, both decreased crosslinking and increased polarity of the electrolyte improved the bending strain of actuators which scaled inversely with modulus. These materials were also used as electrolytes for flexible supercapacitors with a reduced graphene oxide composite electrodes. They showed stability up to 120 °C, flexible and 3 V, as well as high capacitance (> 300 F/g) exceeding that of existing polymer or ionic liquid systems. In the final investigation, a Li conducting system was prepared by tethering fluorinated anions to the backbone. We showed how systematic tuning of crosslinking density, side chain length, and ion concentration lead to a 70 K fluctuation in Tg and 3 orders of magnitude shift in ionic conductivity. Decoupling between modulus and ionic conductivity was observed at low crosslinking density showing routes towards future design of polymer electrolytes.
Biocompatible, biodegradable, and elastomeric (BBE) printed circuit boards (PCBs) are a target goal across a variety of fields from traditional consumer electronics to applications in implantable and wearable devices. A desirable PCB should provide good electrical properties, shield internal components from the environment, and should be compatible with traditional microfabrication. Poly(octamethylene maleate (anhydride) citrate) (POMaC) an elastomer with tunable degradation and stiffness, good elasticity, and biocompatible properties presents an ideal elastomer for use as substrate for a BBE PCB, thus a POMaC-based circuit board with biocompatible, biodegradable, and elastomeric (PCB3E) properties is presented and analyzed for applicability. The pre-polymer was made in-house and synthesis optimized for desired molecular weight, monomer composition, and porosity. Boards were constructed using traditional microfabrication methods (spin-coating, sputtering, and encapsulation with bioprinter). Processing methods were investigated for desired thickness of board, tensile and degradation properties, basic cytocompatibility, and electrical properties. A simple LED circuit was designed and fabricated on a PCB3E and monitored in physiological conditions. The easy synthesis of the pre-polymer allows for large batch sizes and reproducibility. Various board thicknesses were obtained by varying spin speed and time during coating – thicknesses between 50-300 µm were achieved here. Multilayers can be deposited for further control of thickness or for variable tensile properties between layers. Post processing curing conditions and introduction of porogen can be used to select for desired tensile and degradation properties. The results indicate that the presented PCB3E can serve as a bioelectronic platform to be applied across a variety of fields by nature of the tunable tensile properties and degradation rate, simple manufacturing, and good electrical properties. Further work will investigate the functionality of more complex circuit types and direct integrations with cell cultures.
Advances in polybenzimidazole (PBI) polymerization techniques and application in high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs)

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Polybenzimidazoles (PBIs) membranes have been investigated for their application in various electrochemical devices, including high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs). The most common method of PBI membrane synthesis involves dissolving the polymerized PBI in an organic solvent followed by casting and removal of the solvent, and finally doping the membrane in phosphoric acid. The Benicewicz group developed an alternative method, called the polyphosphoric acid (PPA) process, in which PBI is polymerized in PPA and cast directly from solution. A sol-to-gel phase transition is induced, resulting in PBI gel membranes that are imbibed in phosphoric acid. Advantages of the PPA process include higher acid uptake, greater conductivity, and better fuel cell performance. The main degradation mode of the PBI gel membranes in fuel cells was found to be from mechanical creep of the highly swollen gel membrane over time. A recent processing technique has been discovered in which a gel PBI membrane made in the PPA process undergoes a physical transformation into a dense PBI film, leading to unique properties. This presentation will highlight the advances with this recent technique in terms of structure-property relationships. In particular, the key membrane properties of tensile, creep and ionic conductivity will be discussed, as well as fuel cell performance.
Spontaneous fragmentation of block copolymer micelles

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Block copolymers (BCPs) self-assemble into various micellar nanostructures in selective solvents, and can be applied in a host of diverse technologies including drug delivery, viscosity modification, and nanoreactor design. To fully realize these practical uses, the mechanisms for micellization and equilibration must be elucidated. Micelle fragmentation, fusion, and chain exchange are all possible relaxation mechanisms. To date, fragmentation has not been studied in any detail. We use temperature-jump dynamic light scattering (T-jump DLS), synchrotron small-angle X-ray scattering (SAXS), and liquid-phase transmission electron microscopy (LP-TEM) to develop a quantitative understanding of micelle fragmentation kinetics in ionic liquids (ILs). The use of non-volatile IL solvents enables high-temperature annealing and direct use of TEM. Fragmentation of one molecular weight of 1,2-polybutadiene-b-poly(ethylene oxide) (BO) was studied in five ILs to determine the effect of solvent selectivity. Then, fragmentation of BO was visualized for six molecular weights in one IL using LP-TEM. The fragmentation kinetics were also quantified by time-resolved SAXS and T-jump DLS. By combining these experimental techniques, a detailed analysis of micelle fragmentation kinetics, along with the direct observation of intermediate structures during fragmentation events, was achieved.

Transmission electron micrograph of BO micelle (light region) fragmenting in an IL (dark region) solvent. Fragmentation is illustrated schematically on the left.
Harnessing core chain mobility in tuning small molecule release rates from polymer micelles

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Polymer micelles have been widely studied as drug delivery agents, but methods for precisely tuning their rates of drug release are limited. We sought to develop systems with tunable drug release rates through control of polymer chain mobility. To achieve this goal, we designed systems based on amphiphilic block copolymers (BCPs) of poly(ethylene glycol) and polymethacrylates or polyacrylates. We attached H\textsubscript{2}S-releasing S-aryloxythiooxime (SATO) groups to the constitutional units of the hydrophobic block. Upon self-assembly in water, SATO groups were sequestered within the hydrophobic micelle core. SATO groups release H\textsubscript{2}S in response to reaction with thiols such as cysteine (Cys); thus, we hypothesized that controlling the rate of diffusion of triggering Cys molecules into the micelle core might impart control over the H\textsubscript{2}S release rate. To investigate this hypothesis, we prepared a series of amphiphilic BCPs with varying amounts of a plasticizing co-monomer in the hydrophobic block. H\textsubscript{2}S release rates from these micelles varied with glass transition temperature (T\textsubscript{g}) of the core-forming block, with a difference of over 20-fold (t\textsubscript{1/2} = 0.18 – 4.2h) between the two extremes, signifying a relationship between release rate and core chain flexibility. To further investigate this idea, we prepared a series of amphiphilic BCPs which incorporated varying amounts of a crosslinker into the core-forming block. We observed a 2-fold decrease in H\textsubscript{2}S release half-life, with increasing crosslinking percentages in the micelle core, supporting our hypothesis that influencing core mobility could tune the rate of H\textsubscript{2}S release. We believe these methods for tuning drug release from polymer micelles may inform future designs of polymeric drug delivery systems.

![Figure 1](image-url)  
**Figure 1.** (A) Chemical structure of the core-forming block of amphiphilic BCPs incorporating SATO groups and plasticizing comonomer, and H\textsubscript{2}S release curves relating to incorporation of comonomer. (B) Chemical structure of amphiphilic BCPs incorporating crosslinks into the core-forming block, and H\textsubscript{2}S release curves relating to crosslinking percentage.
Design of PLGA-based drug delivery systems through a molar mass-dependent sustained release model

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Improvements to a drug-release model are validated by comparing model prediction to in vitro experiments on a novel, industrially relevant PLGA controlled release system from Genentech. Combining parameter estimations from literature and comparisons to an extensive data base, this study enables a priori design of controlled drug release from a model PLGA system. Model predictions were validated against formulations of FITC-labeled dextran, a model surrogate for biopharmaceutical drugs, in PLGA rods with a broad range of parameters. While successful, deviations were noted for several model formulations with significant first-phase drug release. Supported by cross-sectional florescence microscopy images of the FITC-dextran distribution within the rods, this first-phase release was attributed to a combination of factors: (1) percolation of the drug particles and (2) swelling and pore formation due to water uptake. These observations indicate the importance of careful selection of the PLGA polymer grade when designing drug release systems. Adapting model parameters, without modifying the physical processes included in the model, enabled accurate fitting of the experimental data for all formulations, highlighting the wide applicability of the model. Areas for model improvement were identified and supplemented by X-ray computed tomography images of the PLGA spatial distribution during early stage of drug release.
Tailorable, ultra-thick hyaluronan polymer brushes: A novel class of interfaces

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Functional interfaces are crucial in many biomedical applications like biosensing, protein purification, anti-bacterial coatings, and tissue engineering. Polymer brushes, or structures of densely organized end-grafted polymers, are of particular interest for dynamic and self-healing bio-interfaces, especially when using biocompatible materials like hyaluronan (HA). We introduce a novel method to generate microns-thick HA polymer brushes using the HA synthase enzyme to synthesize the thickest polymer brushes ever, reaching ~22 µm in a matter of hours. Due to this incredible thickness, their characterization and study can be performed in a straight-forward manner with confocal microscopy. The HA brushes offer a unique platform to study surface modification and fundamental polymer physics. We have developed a method to control the topology of the brush with visible light patterning where the underlying grafting density of the HA polymers is modified. In this way, shapes and gradients can be sculpted into the brush. The brush height is tunable through not only synthesis time, but also its stimulus responsiveness. Our brushes exhibit both osmotic and salted brush regimes when exposed to varying salt concentration, as well as collapse in the presence of a poor solvent. These interfaces show promise in a variety of applications from stimulus responsive biomaterials, anti-microbial surfaces, filtration, drug delivery, and the potential for implants or bandages.
Gluten and zein interactions: A vibrational and fluorescence spectroscopy study

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The volume spanning network formed by gluten during breadmaking is crucial for the end product quality. Zein proteins are also capable of forming a protein network when mixed above their glass transition temperature and could, hence, be a high performing alternative to gluten. Vibrational (FTIR and Raman scattering) and fluorescence spectroscopy are believed to be powerful, non-invasive methods capable of assessing protein structure in complex cereal systems. The objective of this project is to explore the suitability of the above techniques to study complex zein-gluten dough systems. The dough was prepared by mixing 20 w/w% of protein (with different proportions of zein and gluten) and 80 w/w% of corn starch. The tyrosine (Tyr) fluorescence emission peak (λ<sub>exc</sub> = 280 nm) was still present even in those zein-gluten samples containing the highest gluten concentration and lowest zein concentration. This suggests that the Tyr moieties (stemming from Tyr residues in zein) are not in close proximity to tryptophan (Trp) of gluten and their fluorescence is not quenched efficiently. Raman scattering results also showed the presence of different Tyr residues, exposed and buried, in zein and gluten samples. These results indicate that two distinct network structures of gluten and zein are formed in the dough system. These two distinct networks (fibrillar and sheet-like) were observed in the SEM images as well. The presence of a variable content of secondary structures and different conformations of disulfide bridges between different dough samples have also been observed. The present work provides valuable insights into the protein conformation and interactions in zein-gluten dough systems.
Multidimensional mass spectrometry of multicomponent nonionic surfactant blends

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Ultra-performance liquid chromatography (UPLC) and ion mobility (IM) separation were coupled with mass spectrometry (MS) and tandem mass spectrometry (MS/MS) in order to characterize a commercially available complex nonionic surfactant mixture. The surfactant molecules are comprised of a glycerol core functionalized with units of poly(ethylene oxide) (PEOₙ) and esterified by caprylic or capric fatty acids. Reverse-phase UPLC separated the mixture according to polarity into four fractions corresponding to no, mono-, di- and, tri-fatty acid containing compounds. Additional separation within each fraction was achieved according to the length of the fatty acid chains. Coeluting molecules of similar polarity were further separated by collisional cross section area using IM. Performed together, UPLC and IM allow for the detection of several ions that would otherwise be superimposed by isobaric species and enable confident structural elucidation through MS² fragmentation.

Liquid Chromatography Ion Mobility Mass Spectrometry Separation of a Multicomponent Nonionic Surfactant Blend
Surface modification of titanium implants for improved tendon adhesion

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Titanium is the primary material for orthopedic implants due to its high strength and biocompatibility. Surface modifications that allow for effective osseointegration are well known, however such metal prosthetics are not conducive to soft tissue and tendon adhesion. Here, we address this problem by coating the surface of titanium or tantalum plates with polypyrrole (PPy), polydopamine (PDAm) or a combination of the two polymers (PPy-PDAm). PPy, PDAm, and PPy-PDAm surface coatings can be fabricated via chemical and/or electrochemical polymerization. The chemical polymerization requires the addition of a dopant and an oxidant, ammonium persulfate in this work. The electrochemical polymerization by way of oxidative polymerization. PDAm is formed through electrochemically induced polymerization of dopamine (DAm) and this can occur at the same potentials as the polymerization of pyrrole. Likewise, two monomers can be simultaneously polymerized chemically. This dual polymerization produces a film with both electrical conductivity and better adhesion to the metal substrate than just the PPy films. All coatings were characterized by scanning electron microscopy, contact angle measurements, and the sticky-tape method for adhesion. Biological testing was also conducted to measure cell adhesion and proliferation on each polymer film, as well as extracellular matrix production.
From diapers to adhesives: Open-loop recycling of post-consumer sodium poly(acrylate) via chemical modification

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Synthetic polymer products used in most consumer applications, like polyethylene, polyethylene terephthalate, and superabsorbent polymers (SAPs) are indispensable to our daily lives; however, their current sustainability profile requires significant improvement. Over 90% of the feedstocks used to access these types of polymers are derived from nonrenewable resources. Unfortunately, the chemical architectures that are desirable to confer high performance and durability (e.g., carbon-carbon backbones) are also responsible for the persistence of post-consumer polymers in the environment. In this work, the sodium polyacrylate based superabsorbent polymer (SAP) primarily used in disposable diapers is repurposed to make pressure-sensitive adhesives (PSAs). As a new direction, this work transitions into a novel application of these adhesives instrumental to microplastics capture in aqueous media.

Repurposing sodium polyacrylate based superabsorbent to make pressure-sensitive adhesives followed by microplastics capture in aqueous media.
Exploring degradation as a viable end-of-life process for thermoset polymers

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There is a great need to recycle polymers to minimize their environmental impact, as the majority of produced polymers end up in landfills after their useful lifetime. Linear polyesters degrade rapidly, and their degradation behavior has been well studied, establishing phenomena of surface erosion in basic media and bulk erosion in acidic media. By contrast, thermoset polymers normally require harsh degradation conditions due to their highly crosslinked structures. We have explored the incorporation of hydrolytically cleavable linkages into the crosslinked network, to enhance their degradation rates under benign conditions. Epoxy resins are widely used thermoset polymers. The standard precursor to epoxy resins, the diglycidyl ether of bisphenol A (DGEBA), is derived from petroleum and lacks functional groups which can promote degradation under benign conditions. Epoxidized vegetable oils, phenolic acids, and vanillic acid, which contain ester linkages, were investigated as sustainable sources to produce degradable epoxy resins. The resulting phenolic acid-based and vanillic acid-based epoxy resins exhibited comparable thermal and mechanical properties to conventional DGEBA-based epoxy resins. The accelerated hydrolytic degradation behavior of the ester-containing epoxy resins was explored, through monitoring of the polymer mass loss after exposure to a basic solution at moderate temperatures. The biobased epoxy resins exhibited rapid degradation in the basic solution, in contrast to the slow degradation rate of DGEBA-based epoxy resin. A solid state kinetic model, the contracting volume model, was applied to describe the degradation behavior and the mechanism was confirmed as surface erosion through ester hydrolysis in basic media. Degradation behavior under mild acidic conditions was also explored. Biobased epoxy resins exhibited bulk erosion in acidic media, in agreement with the behavior of linear polyesters. A reaction order model with autocatalysis was employed to describe the degradation behavior in acidic media and the mechanism was bulk erosion through ester hydrolysis. Various factors which affected the degradation rates were discussed.
Photoredox mediated cross metathesis for molecular weight control in ring-opening metathesis polymerization

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We have explored and established conditions for the synthesis of targeted, low molecular weight polymers in metal-free ring-opening metathesis polymerization (MF-ROMP) by utilizing the ability of terminal alkenes to do cross metathesis with the radical cation chain end. This method using alkenes as chain transfer agents has facilitated the synthesis of norbornene polymers with average molecular weights between 30 and 1 kDa. Set up and execution of the reaction are both simple and prediction of molecular weights is straightforward. The structures of final polymer end groups were successfully identified using MALDI-TOF MS and NMR spectroscopy and were shown to be consistent with efficient chain transfer and reinitiation. Furthermore, mechanistic investigations revealed high regioselectivity of the chain transfer event. This procedure has also been successfully used on multi-gram scales, as well as with functionalized norbornene copolymers for materials applications.
Active machine learning for new monomers for frontal ring-opening metathesis polymerization

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Thermoset polymers and composites are widely used in airplanes, cars, and structural components due to their strength, stiffness, and low density. However, traditional thermosets require large amounts of energy to cure. Frontal ring-opening metathesis polymerization (FROMP) only requires a small initial thermal or photo stimulus which triggers a self-propagating exothermic reaction that fully cures the monomer to polymer. Currently, there are only a small number of monomers that can sustain FROMP. We use active machine learning (ML) to identify new FROMP-able monomers. The active learning cycle uses an ML model of the small pool of currently known FROMP monomers, then predicts outcomes across a database of candidate monomers, and identifies the candidate monomer that will most improve the model’s predictions. The chosen monomer is synthesized and tested before feeding the resulting information back to the model. This process was repeated until the pool of FROMP-suitable monomers is expanded, and the uncertainty of the predictions is sufficiently low. We will also use all the data generated to build a classification ML model. This model can identify key features that determine whether a monomer is FROMP-able. This research has expanded the pool of FROMP-suitable monomers and will develop guidelines for future FROMP monomer development.
Functional materials from living ring-opening polymerizations

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The advent of living polymerization has enabled the development of novel materials with precise control over polymer architecture and functionality. In particular, the robustness of ring-opening polymerization methods has contributed to their popularity. Looking forward, continued innovation in both polymer design and polymerization methodology will broaden the impact of organic materials in addressing pressing real-world issues. Herein, we present two such developments that expand the toolbox of polymer synthesis and improve performance in membrane materials for chemical separations. First, we describe a platform for postpolymerization modification based on the living cationic ring-opening polymerization of a 2-alkylthio-2-oxazoline. The method enjoys mild activation and substitution conditions to access a diversity of polyureas and polythiocarbamates with broad functional group tolerance. Second, we use ring-opening metathesis polymerization to realize an alternative design strategy for microporous materials used in gas separation membranes, wherein the unique architecture of a flexible backbone with rigid, three-dimensional side chains engenders ultrahigh permeability and record stability at high pressure. Modifications in polymer structure and chemical functionality shed light on structure–property relationships and promise improved selectivity performance.
Development of advanced hybrid polymer/inorganic nanoparticles using surface-initiated ring-opening metathesis polymerization

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Polymer/inorganic nanoparticle hybrids are potential candidates for designing advanced materials due to the nanoparticle’s ability to reinforce or add inorganic functionality to the polymer matrix. However, thermodynamics of mixing will govern the nanoparticle dispersion state within the matrix, and can effectively dictate the degree of material performance and processability. As a solution, an effective method for tuning dispersion in hybrid materials is to graft polymer chains from the particle surface to desirably interact with the polymer matrix. Several successful surface-initiated polymerization techniques are commonly used, but their chemistries typically yield linear styrene or acrylate-based grafts that are limited in miscibility and reactivity within commercial grade materials and processes. To assess the potential of polymer-grafted nanoparticle (PGNP) components within polyolefin and other semi-crystalline materials, the synthetic toolbox of surface-initiated polymerizations needs to be expanded. The work here presents a surface-initiated ring-opening metathesis polymerization (SI-ROMP) technique that was developed to graft unsaturated backbones from silica nanoparticle surfaces. The versatility of ROMP and the resulting polyolefin grafts enable new opportunities for functionality in PGNP components. Through the use of size exclusion chromatography, dynamic light scattering, thermal analysis and transmission electron microscopy, structural and thermal properties of poly(norbornene)- and poly(cyclooctadiene)-grafted nanoparticles can be quantified. The technique can also be implemented to produce PGNPs with chemistries that can be used in in situ polymerizations, hydrogenated to achieve semi-crystalline poly(ethylene)-grafted nanoparticles, or functionalized to create non-linear bottlebrush architectures. These new graft properties present desirable chemical, thermal and structural properties in PGNPs that cannot be easily replicated with traditional methods and are useful for fundamental investigations in novel hybrid systems.
Mechanistic insight into the neodymium-catalyzed polymerization of dienes and \( \varepsilon \)-caprolactone

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Neodymium based Ziegler-Natta systems are superior to the traditional Ziegler-Natta catalysts and other lanthanide-based Ziegler-Natta systems for the polymerization of dienes and lactones. The synthesis of the polymers from these simple monomers is complex due to the wide variety of materials obtained from tuning ligands, co-catalysts, temperature, solvent, and [co-catalyst]/[catalyst] ratios. Development of neodymium catalysts to obtain a living polymerization and control over molecular weight, polydispersity, tacticity, and microstructure are desirable. We recently demonstrated the neodymium phosphate-catalyzed polymerization of myrcene and \( \varepsilon \)-caprolactone (homopolymers and block copolymers). Herein, we provide a deeper understanding of the neodymium-catalyzed polymerization of myrcene and \( \varepsilon \)-caprolactone through experimental studies (crystal structure of the active complex, end-group analyses, reaction rates, kinetics, thermodynamics, reactivity ratios). These results may guide the logical design of new catalysts to give well-defined polymer properties and expand the scope of monomer substrates.
Controlled/living branching polymerization enabled by polymerization-induced activation: mechanistic study assisted development of catalytic systems

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Polymers with branched structures exhibit superior mechanical, photonic, and electrical properties. In our previous study, site-specifically anchored branched polymers with controlled degrees of branching and molecular weights were successfully prepared via copper-mediated atom transfer radical copolymerization of conventional vinyl-based monomers and n-butyl α-bromoacrylate (BBA). BBA serves in this controlled branching polymerization as an inibramer (initiator + branching point + monomer) that, exclusively after being polymerized, can produce a double-initiating center to form a branching junction. Despite the preliminary success, challenges such as a limited monomer scope and relatively low conversion of the comonomers remained unaddressed due to the inevitable radical termination that slows down the polymerization rate more rapidly compared to linear polymerizations. Polymerization kinetics was systematically investigated by combining experiments and numerical simulation, quantitatively providing the optimal profile of radical concentration for a sustainable polymerization. Guided by the knowledge attained from the mechanistic study, polymerization conditions and setups that are able to accurately regulate the radical concentration throughout the entire polymerization process were developed accordingly for various monomers. In this development, activator regeneration atom transfer radical polymerization was applied, in which an external power such as light or electricity was employed to regulate the concentration of propagating radicals, to suppress termination reactions and achieve high monomer conversion. Monomers with different reactivities, such as acrylate, acrylamide, styrene, and acrylonitrile, were successfully copolymerized with the inibramer to synthesize branched polymers.
Novel strategies for constructing polyolefin-containing block copolymers

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Polyolefin, as by far the most commonly produced polymer worldwide, accounts for a huge fraction of the global plastics market. However, despite the promising future of block copolymer development, there is significant dissonance between the dominance of polyethylene and its under-representation as a component in block copolymers. Here, we established a complete set of methods for constructing polyolefin-containing di- and triblock copolymers. The first part is a universal one-pot synthesis strategy for accessing polyolefin-containing diblock copolymers. My approach consists of performing a series of post-polymerization strategies to first access a hydroxyl-terminated polymer that can then be used as an initiator for the ring-opening polymerization of cyclic esters and cyclic ethers. In the second part, I developed two independent methodologies that yield polyethylene- and polypropylene-containing triblock copolymers, with the polyolefin as the center block. The approach for polyethylene employs a series of post-polymerization functionalizations, while the approach for polypropylene consists of a selective copolymerization. In both cases, dihydroxyl polyolefins as macroinitiators were obtained in quantitative yields and subsequently converted into amphiphilic triblock polymers via the ROP of tert-butyl glycidyl ether and the subsequent hydrolysis of the tert-butyl ether group. The amphiphilic nature of the block polymer was established via dynamic light scattering.
Directed network structure through controlled radical photopolymerization

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Reversible addition-fragmentation chain transfer (RAFT) has shown great utility in controlled radical polymerization to synthesize monodisperse linear polymers and block copolymers. However, little is known about effects of RAFT on cross-linked materials. In this work, we investigate the effect of RAFT agents on photopolymerization behavior and ultimate polymer properties in urethane acrylate systems. Our results have shown that RAFT agent addition has a significant impact on polymerization behavior and ultimate polymer properties in model systems. When incorporating RAFT agents, the final monomer conversion of RAFT modified polymerization is approximately 80% which is very similar to systems that do not contain RAFT. However, the polymerization rate is slightly decreased with increased RAFT concentrations. This decrease in polymerization rate results from the creation of RAFT-adduct radicals during chain propagation that delay gelation and retard the termination process. Moreover, dynamic mechanical analysis shows that the RAFT-modified films exhibit narrower half width of tan (δ) profiles, indicating more homogeneous networks are generated. The effect of RAFT agents on photopolymerization kinetics and thermomechanical properties by varying R group are also investigated. Cyanomethyl dodecyl trithiocarbonate (CDT) and 2-(dodecylthiocarbonothioylthio) propionic acid (DPA) are different RAFT agents which share the same Z-group but have different R-groups. Much faster photopolymerization rates are observed from DPA-modified polymerization as the DPA R group results in more rapid RAFT-adduct radical dissociation that allows more chain propagation. Additionally, incorporating DPA and CDT RAFT into model systems enhance elongation at break by approximately 119% and 63%, respectively. These results demonstrate the impact of the RAFT agents to alter polymerization, especially for CDT-modified polymerization which leads to lower reaction rates and higher molecular weight between crosslinks.

Films strain of CDT and DPA RAFT at different concentrations.
Influences on deactivation in organocatalyzed atom transfer radical polymerization

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Organocatalyzed atom transfer radical polymerization (O-ATRP) is a controlled radical polymerization method employing organic photoredox catalysts (PCs) for the synthesis of precision polymers under mild, metal-free conditions. To control polymer growth, O-ATRP relies on reversible deactivation of the polymer, wherein reactive propagating radicals are placed in a “dormant” state. As a result, this deactivation step minimizes the concentration of radicals in solution and limits irreversible, radical-based termination reactions that would otherwise hinder polymerization control.

Despite the importance of deactivation in O-ATRP, few reports have investigated its mechanism and factors influencing it during a polymerization. Further, the species responsible for deactivation – the PC radical cations – remain poorly understood, limiting development of this polymerization method. To address these issues, this work probes the reactivity of these radical cations to understand their role in deactivation as well as their possible side reactions during O-ATRP. In addition, a number of other factors are investigated, including how the identity of the halide in O-ATRP impacts deactivation. Finally, the information gathered in these fundamental studies is applied to O-ATRP when radical cations are employed as reagents to improve a challenging polymerization. Ultimately, this work highlights the benefit of understanding the mechanism of O-ATRP, as well as the utility of radical cations as reagents in O-ATRP.

This work investigates deactivation in O-ATRP and the role of radical cations during this process.
Degradable polymers from thionolactone radical ring-opening copolymerization

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Polymers synthesized via traditional radical techniques have resulted in the creation of commonplace materials such as Styrofoam and Plexiglass. The unreactive carbon-carbon backbone of these polymers leads to their robust nature but also prohibits polymer degradation. To provide functionality into the backbone of these polymers, a new class of radical ring-opening (rRO) monomers containing a thionolactone has been developed. The radicophilic nature of the thiocarbonyl group and modular design of the thionolactone structure facilitates the tuning of monomer reactivity allowing for incorporation of thioesters into common monomer families (styrene, acrylates, and acrylamides). The resulting thioesters in the polymer backbone are stimuli responsive and can be utilized in post-polymerization modifications. One monomer, a seven-membered thionolactone, has been identified to incorporate evenly within acrylate copolymer. Therefore, only a small number of thioester responsive units is required for full polymer degradation. Further investigation into a second monomer derivative has resulted in the discovery of a six-membered thionolactone which is highly reactive with acrylamides. This reactivity has been leveraged to make precision degradable junctions in acrylamide block copolymers. Through further monomer design, a wide scope of thionolactone monomers can be synthesized to match the desired reactivity with various comonomers allowing for targeted comonomer incorporation and responsivity.
Redox-switchable catalysts for the controlled polymerization of cyclic esters

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The field of redox-switchable catalysis has gained considerable interest in recent years, enabling catalytic reactivity/selectivity to be oscillated based on the redox-state of the ligand or active metal center. Unfortunately, though a myriad of redox-switchable catalysts have been developed for the ring opening polymerization of cyclic esters, very few fundamental structure-catalytic performance studies have been conducted that ascertain how systematic changes in ligand structure affect the catalytic performance. Herein, we will describe our studies to determine how changes in the placement and number of redox-active moieties, ligand denticity, and active metal center identity impacts the catalytic performance. We will compare group IV metal centered catalysts bearing symmetric, tetradeutate [ONNO] ligands with two redox-active moieties distal to the active metal center to related catalysts bearing either symmetric, tetradeutate [ONNO] ligands with one redox-active moiety in close proximity to the active metal center or asymmetric, tridentate [ONN] ligands featuring a single redox-active moiety distal to the active metal center. The results of these studies reveal that the proximity of the redox-active moiety to the active metal center may influence both catalyst activity and redox-switchable. Conversely, the number of redox-active moieties present within the ligand scaffold may not play a crucial role in the catalysts’ switchability. Lastly, when Ti/- Zr-centered analogues of these catalysts were compared it was revealed that the choice of metal center may dramatically influence both catalyst activity and redox-switchable.
Multicomponent polymerization for the synthesis of degradable polymers with a thermal-activated dynamic covalent behavior

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Recently, multicomponent reactions (MCRs) were introduced into polymerizations which have been efficient and robust strategies for the construction of polymer architectures with unique and distinct properties. However, the number of MCRs suitable for multicomponent polymerizations (MCPs) is still limited. Herein, we report a new MCR which happens in a “Click” chemistry manner without any catalyst needed. This MCR has been applied for polymerization, generating sequence-controlled polymers with excellent degradability in phosphate buffer. More interestingly, the synthesized polymer demonstrates an interesting thermal-activated dynamic covalent behavior, which makes this chemistry a good candidate for the construction of thermal-controlled chemical switch. To the best of our knowledge, this is the first report about a polymer obtained from a multicomponent reaction, which exhibits a thermal-activated dynamic covalent behavior. We expect this chemistry can be applied into materials coating and modification in the future. The multicomponent nature of this chemistry brings opportunities to precisely tune materials properties from structural aspects.
Photo-responsive polymeric nanoreactors for compartmentalization and photo-regulation of incompatible tandem catalysis

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One of the paramount goals in modern science is to design and realize artificial nanostructures that rival biological systems in terms of complexity, functionality, and efficiency. The cell perfects the regulation of thousands of incompatible chemical transformations simultaneously using key concepts such as compartmentalization of active sites and communication between compartments.

Inspired by nature, this presentation will introduce an advanced compartmentalized polymeric nanoreactor that possesses a reversible photo-responsive feature and can photo-regulate reaction pathways for incompatible tandem catalysis. The smart nanoreactor is based on multi-functional amphiphilic poly(2-oxazoline)s-based micelles, covalently cross-linked with a bifunctional spiropyran. The smart nanostructure responds to light irradiation in a wavelength-selective manner and switches its physicochemical properties i.e. color, hydrophobicity, and size as confirmed by dynamic light scattering and cryo-transition electron microscopy. The tailor-made microcompartments within the nanoreactor render distinct yet suitable environments for two incompatible enantioselective transformations: a rhodium-diene complex-catalyzed asymmetric 1,4-addition occurs in the hydrophilic corona and a Rh-TsDPEN-catalyzed asymmetric transfer hydrogenation reaction in the hydrophobic core. A series of control experiments and kinetic studies shows that the gated behavior induced by the photo-triggered reversible spiropyran to merocyanine transition in the cross-linking layer is key to discriminate among substrates/reagents during the catalysis. The smart nanoreactor has realized photo-regulation to direct the reaction pathway to give a multi-chiral product with great conversions and perfect enantioselectivities. Our smart polymeric catalytic system, on a basic level, mimics the concepts of compartmentalization and responsiveness Nature uses to coordinate thousands of incompatible chemical transformations into a streamlined metabolic process.

Photo-Responsive Polymeric Nanoreactors for Compartmentalization and Photo-Regulation of Incompatible Tandem Catalysis
Novel synthesis, activation, and transformation strategies for the preparation of covalent organic framework powder, foams, and films

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Covalent organic frameworks (COFs) are an emerging class of organic, crystalline polymers. They have recently received significant attention for various applications including catalysis, energy storage, and remediation. However, developing materials for these applications requires addressing many fundamental challenges in COF synthesis, activation, and transformation. In this presentation, we present novel strategies for synthesis that increase crystallinity, new catalysts for the rapid synthesis of COFs under ambient conditions, activation approaches that preserve the porosity even for fragile COFs, and transformation approaches that enable the conversion of linear polymers to COFs.

First, we focus on COF synthesis and show that benzaldehyde modulators compete with multi-functional aldehyde monomers to slow down the imine-COF polymerization and growth chemistry, and thus improve their crystallinity. We also demonstrate that transition metal nitrates can rapidly produce COFs under ambient conditions. These catalysts produce crystalline COFs within 10 minutes at room temperature and could catalyze a wide range of COF targets varying in linker chemistry, linker lengths and substituents. In the second part, we demonstrate that the use of an ultralow surface tension solvent perfluorohexane enables rapid, simple and effective activation of COFs with reduced pore collapse. This approach avoids the use of supercritical CO$_2$, which is not widely accessible. Finally, we demonstrate a novel route to the synthesis of COFs through the transformation of linear polymers using reversible chemistries. Specifically, triformylphloroglucinol (TPG) first reacts through dynamic chemistry to replace linkers in the linear polymers and then undergoes irreversible tautomerism to produce ketone linkages. Additionally, we will present processing of COFs and characterization of mechanical properties. Altogether, these studies significantly advance synthetic control over COFs and processing approaches critical to the development and implementation of COFs for applications.
Full circle recycling of polysiloxanes via room temperature fluoride catalyzed depolymerization to repolymerizable cyclics

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Siloxane based polymeric materials are widely used all over the world due to their chemical, mechanical, and thermal stability, and low-toxicity. Despite their usefulness, a critical issue has been the accumulation of these materials in the environment. The need to recycle them effectively has thus far been challenging. The present methods used to recycle silicone-based materials, such as PDMS, involve high temperatures/pressures, and complicated setups. To address this issue, we have established an efficient room temperature technique for depolymerization of silicone-based polymers and resins in the presence of low catalytic amounts of fluoride in specific high swell organic solvents. The products primarily contain cyclic siloxane units (D4, D5, D6) as verified by GCMS and $^{29}$Si NMR. Nearly any silicone resin can be depolymerized quite rapidly using our methods. Silicone rich systems result in the best conversions and the highest quantity of identifiable cyclics, while complex resins resulted in complicated products alongside discernable cyclics. We have also repolymerized the products from this process to reform silicones via acid, base and fluoride catalysis. Our discovery has the potential for large scale industrial processing due to the use of mild conditions and solvent recycling ability.

TOC Image: Depolymerization of Wacker Elastosil to cyclic siloxanes

Depolymerization of Wacker Elastosil to cyclic siloxanes
Unconventional conjugation via vinylMeSi(O-)2 siloxane bridges may imbue semiconducting properties in double-decker and ladder silsesquioxane copolymers

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Silsesquioxane (SQ) based polymers are of increasing interest due to their enhanced thermal stability, high compatibility with organic materials as well as high processability. However, to our knowledge, no one has sought to explore through-chain conjugation between double decker (DD) and ladder (LL) SQs and organic linkers. We recently demonstrated that stilbene derivatives of simple DD SQs exhibit photophysical properties commensurate with formation of cage-centered LUMOs, supporting the existence of 3-D excited-state conjugation. We describe here Heck catalyzed co-polymerization of vinyl(Me)Si(O-0.5)2[PhSiO1.5]8(O-0.5)2Si(Me)vinyl (vinylDDvinyl) with Br-Ar-Br where Br-Ar-Br = multiple aromatic and heteraromatic moieties.

Apparent excited state conjugation via vinyl(Me)Si(O-)2 siloxane bridges is observed in the DD copolymers, as evidenced by 50-120 nm red-shifts in emission from corresponding model compounds. To identify minimum SQ structures that may offer such extended conjugation vinyl(Me)Si(O-0.5)2[PhSiO1.5]4(O-0.5)2Si(Me)vinyl [vinyl-ladder(LL)-vinyl] derived copolymers were also synthesized. Surprisingly, most of the resulting oligomers show 30-60 nm emission red-shifts beyond those seen with the vinylDDvinyl analogs despite lacking a true cage.

We also find that brominating DD/LL copolymer vinyl groups eliminates emission red-shifts. Zn debromination thereafter restores vinyl groups and emission red-shifts but brominated phenyls remain providing potential access to families of “hairy” conjugated SQ polymers. Further proof of semiconducting properties led to studies wherein DD/LL-co-thiophene, bithiophene and thienothiophene were doped with 10 mol% F4TCNQ resulting in integer charge transfer (ICT) behavior.
Programmable electromechanical deformation of liquid crystal elastomers

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Liquid crystal elastomers (LCEs) are stimuli-responsive materials. Programming the local orientation within LCEs is a promising route to realize 3-D deformations. Recent demonstrations have demonstrated these materials can exhibit exceptional work capacity of upwards of 40 J/kg. However, the inefficient and slow responses of LCEs to heat and light limit the functional integration of these materials in many applications. Electrical control of LCEs has and continues to be the preferred stimuli. Recently, electromechanical actuation of LCEs at ambient conditions was realized by exploiting the unique mechanical anisotropy (e.g., association of modulus with orientation) of aligned LCEs. By coating both sides of an aligned LCE with compliant electrodes and applying voltage, the LCE film is compressed in its thickness, leading to deformation in the planar area. However, due to the mechanical anisotropy, the LCE deforms preferentially in the lower modulus direction, leading to directional mechanical response in these actuating elements. Here, we are concerned with understanding the role of materials properties on the electromechanical response of LCEs. Using a newly developed materials chemistry and employing established processing methods, reliable electromechanical actuation is realized in LCEs with high mechanical anisotropy and uniaxial actuation strains up to 17.5%. The uniaxial actuation behavior is closely predicted using previously developed theory and the physical materials properties of the LCEs. Response times of 1 Hz are demonstrated.
Investigating the stimuli-responsive and morphological properties of dye incorporated liquid crystalline polymers within unique polymeric templates

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Stimuli-responsive dyes have received significant attention due to their color changing properties upon application of mechanical force/pressure, heat or UV light. Introducing them in processable and flexible polymer matrix can lead to practical applications like mechanical damage sensors, pressure sensors, thermal sensors and crack detectors. Allowing these dyes to interact with structural color exhibiting cholesteric liquid crystalline polymers can create a new hybrid platform of multi-stimuli responsive tunable optical materials. Thermochromic properties of cholesteric liquid crystalline (LC) polymers are well established where their optical properties can be tuned with temperature. To introduce additional functionality to the cholesteric polymers, we have synthesized hybrid mechanochromic dye incorporated cholesteric LC polymers enabling heat and mechanical force/indentation responsive synergistic color response. Molecular engineering of monomers plays an integral role in coupling unique stimuli responsive properties of liquid crystals and dye molecules. Simply tweaking the structure of the monomers within the liquid crystalline polymeric framework induces cooperative interactions between liquid crystalline cholesteric phase ($N^*$ phase) and dye molecules. We have successfully shown that these materials can respond to multiple stimuli to tune the color response. These adaptive functional materials with multiple stimuli responsive functional properties can be envisioned for mirrorless lasing, actuators, thermal sensors and photonic applications.

Optimizing polymer architecture to achieve a mechano-thermochromic system
Salt doped PEDOT: PSS for thermoelectric: structure-property correlation study
Peng Zhang, Presenter; Zhen Liu; Xin Li; Zekun Zhou

2D polymers, 2D COFs, polymer nanosheets, and polymer membranes for energy storage and conversion
Prof. Xiaodong Zhuang, Presenter

Synthesis of freeform single-handed helical strips and ladder polymers
Dr. Kyle E Murphy, Presenter

Designing pi-conjugated polymers with quinonoid repeat units
Ms. Girisha Grover, Presenter; Miklos Kertesz; John Tovar

Topology and Ground State Control in Open-Shell Donor–Acceptor Conjugated Polymers
Yang Qin; kevin Mayer, Presenter

New functional and soluble polyacetylenes bearing intrinsic n- and p-doping side groups
Bruno T. Luppi, Presenter; Nils Ostermann; Shailendra Saxena; I Cheong; Michael Ferguson; Richard McCreery; Inke Siewert; Eric Rivard

New conjugated polymers based on boron element-blocks
Yoshiki Chujo, Presenter

Development of stimuli-responsive luminescent polymers based on a flexible “element-block”
Kazuo Tanaka, Presenter

Pendant-controlled fluorescent and phosphorescent conjugated solids
Samuel Thomas, Presenter

Pyrrole-based organic semiconducting small molecules for organic field-effect transistors
Mihaela Stefan, Presenter

Designing simple conjugated polymers for scalable and efficient solar cells
Wei You, Presenter; Jeromy Rech

Efforts to stabilize organic photovoltaics
Emily Mueller, Presenter; Anne McNeil

Water soluble poly(Phenylene Ethynylene)s for bio applications
Dr. Kirk Schanze, Presenter; Han Sun; Pradeep Kumar Jagadesan; Daniel Martinez

Well defined conjugated polymers
Dwight Seferos, Presenter
Investigation of (Hetero) bimetallic catalysts in the synthesis of π-conjugated polymers
Christine Keiko Luscombe, Presenter

Transition-metal-free photopolymerization of π-conjugated polymers
Julia Kalow, Presenter

Exploring the choice of boron coupling partner in Suzuki-Miyaura catalyst-transfer polymerization
Josue Ayuso-Carrillo; Michael Bautista; Kevin Noonan, Presenter

Synthetic development and optical characterization of π-conjugated poly(purine)s
Michael Kilbey, Presenter; C. Elizabeth O’Connell; Sina Sabury; Prof. Brian Long

Exploring isomeric effects on optical and electrochemical properties of red/orange electrochromic polymers
Graham Collier, Presenter; Aimee Tomlinson; Prof. John R Reynolds

π-Face taming vs. appending pendant solubilizing chains for soluble π-conjugated polymers
Nagarjuna Gavvalapalli, Presenter

Optical properties of silicon nanosheets modified with conjugated units
Joji Ohshita, Presenter

Cross-conjugated poly(thienylene vinylene)s (PTVs) and poly(selenylene vinylene)s (PSVs)
Yang Qin, Presenter

π-Conjugated polymers possessing unique element-blocks
Ikuyoshi Tomita, Presenter; Feng Zheng; Alvin Tanudjaja; Yoshimasa Matsumura; Shinsuke Inagi

Hybrid materials containing cyclosilane fragments
Rebekka Klausen, Presenter

Sulfenate anions as organocatalysts for benzylic chloromethyl coupling polymerization (BCCP)
Patrick Walsh, Presenter

Organoboranes as electron-deficient building blocks for new conjugated materials
Dr. Frieder Jaekle, Presenter

Putting “conductivity” back into conducting polymer research
Prof. John R Reynolds, Presenter

Advances in all-polymer solar cells and non-fullerene electron acceptors
Samson Jenekhe, Presenter; Duyen Tran; Sarah West; Xiaomei Ding

Structure-property studies of non-planar azadipyromethene-based macromolecules for organic photovoltaic applications
Genevieve Sauve, Presenter
Tunable conjugation topologies for fluxional macromolecular pi-electronics
John Tovar, Presenter

Going against the grain: A new design paradigm for low bandgap polymers
Evan Culver; Wyatt Wilcox; Seth Rasmussen, Presenter

Design, synthesis, and characterization of conducting plastics
Colleen Scott, Presenter; Mohammed Almtiri; Feng Daijun; Ranganath Wahalathantrige Don

Reimagining semiconducting polymers for alternative energy applications
Barry Thompson, Presenter
Salt doped PEDOT: PSS for thermoelectric: structure-property correlation study

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Recently, electronic inks have attracted widespread attention in the field of printed flexible electronics. Among them, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is recognized as the most promising candidate owing to its mechanical flexibility, biocompatibility, solution processability and good environmental stability. However, untreated PEDOT:PSS film displays poor electrical conductivity as low as about 1 S cm$^{-1}$. To solve this issue, secondary doping agents ionic salts are generally introduced into PEDOT:PSS to achieve 3 orders of magnitude improvement on the conductivity. However, the influence of the cations in salts on the structure and conductivity of PEDOT:PSS films has not been explored yet.

In this report, we study the electrical conductivity of PEDOT:PSS films with salts that have various cations but the same bis(trifluoromethanesulfonyl)amide (TFSI) anion. Doping salts of small-sized cations led to higher conductivity because of the improved crystalline order and p-doped level of PEDOT, as revealed by the grazing-incidence wide-angle X-ray scattering (GIWAXS) and UV–vis spectrum, respectively. We understand this phenomenon with the fact that small-sized cations with stronger Coulombic interactions can lead to rearrangement of PEDOT:PSS and thus high doping. These findings help us to develop recipes based on the PEDOT:PSS/salt hybrid for the applications of thermoelectric.

Salt induced structural reorganization of PEDOT:PSS
2D polymers, 2D COFs, polymer nanosheets, and polymer membranes for energy storage and conversion

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The rapid development of two-dimensional (2D) materials triggered the polymers with in-plane dimensionality at the beginning of this century. Although the concept of 2D polymers is much earlier than graphene, the most famous 2D material, the development in this field is not satisfied. The main reasons include concept confusion, synthesis challenge and reliable application. In principle, 2D polymers are the polymers with single molecular layer and repeating units. However, the layered and bulk 2D covalent organic frameworks (COFs) and metal 2D organic frameworks (MOFs) entered into this field as more impact species. Inspired by such big progress, more and more polymers with 2D morphology have been developed, e.g., sandwich-like polymer nanosheets, self-assembled polymer nanosheets, polymer films with large area and uniform nano-scale thickness, etc. In this presentation, we will briefly present our contribution in this field in this past five years and then focus on two cases reported in 2020 from our group. The two cases are semiconductive polypyrrole film-based micro-supercapacitors and ionic polyimide nanosheets-derived 2D hybrid catalysts for water splitting.
Synthesis of freeform single-handed helical strips and ladder polymers

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In nature, shape defines function, and as such scientists have long since attempted to mimic nature in a pursuit to reach a similar level of fidelity. Complex macromolecular structures and shapes have been developed with interesting and unique functionalities—such as the design and synthesis of molecular machines. However, macromolecular structures such as these are difficult to synthesize. The work herein addresses this challenge and presents a strategy to precisely control the shape of macromolecules to generate well-defined structures. This synthetic technology leads to controlled growth of a molecular structure with precisely predictable shapes. In particular, the work involves the generation of short molecular strips, both linear and with a helical bend, as well as ladder polymer helices of different pitches which were probes for their spring-like motions. The development of these three-dimensional building blocks, their affinity for coupling in a controllable fashion, and their ability to be functionalized with through-space directed aromatic nitration methodology, has laid the foundation for much of the research related to chirality-assisted synthesis (CAS).
Designing \( \pi \)-conjugated polymers with quinonoid repeat units

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Mixing of aromatic (A) and quinonoid (Q) units has not only proved to be an effective synthetic strategy in designing polymers with delocalized electrons, it often yields a low band gap system as well.[1] While many conjugated polymers display A-ground state, only a few examples of Q-ground state are known. In our approach, in designing low band gap polymers, we have computationally studied more than two dozen heteroaromatic molecules with repeat units (up to \( n = 5 \)) of potential polymers with a Q-ground states which are synthetically attainable. Among various monomer repeat units explored, eight systems which energetically favors Q-ground states compared to their A isomeric structures were successfully obtained using density functional theory (DFT); one is illustrated below. Some of these systems are found to possess low band gaps. These Q-ground states systems were further characterized using inter-ring bond lengths parameters. The systems with 6-membered ring forming a \( \pi \)-conjugated backbone failed to energetically stabilize the Q-ground states while many examples of stable Q-ground states of 5-membered ring in the backbone were obtained.[2] Quinonoid systems often show unusual open-shell diradical characteristics exhibiting interesting electronic and optical properties.[3] From unrestricted open-shell DFT calculations on quinonoid repeat units of polymers under study, terminated with hydrogen atoms at both ends, we computed \( \gamma_0 \), a measure of diradical character. Only the Q-ground states systems and a few A-systems showed diradical character. Further, the diradical character increases with increasing size (typically converging for \( n > 10 \)). Mixing the Q-ground state systems with the A-ground state systems under study will be the next step with the expectation that some of these combinations will yield Q-ground state polymers with high diradical characters and very low band gaps.

![Optimized geometry of the n=5 oligomer of thieno-3,4-[b]pyrazine in the (a) aromatic structure terminated by -H and the (b) quinonoid structure terminated by =CH\(_2\) (distances in Å).](image)

Optimized geometry of the \( n = 5 \) oligomer of thieno-3,4-[b]pyrazine in the (a) aromatic structure terminated by -H and the (b) quinonoid structure terminated by =CH\(_2\) (distances in Å).
Topology and Ground State Control in Open-Shell Donor–Acceptor Conjugated Polymers

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Donor–acceptor (DA) conjugated polymers (CPs) with narrow bandgaps and open-shell character represent an emerging class of materials whose rich categories of behavior emanate from the collective properties of π-electrons and diminished intramolecular electron pairing. However, the structural and electronic heterogeneities that define these materials complicate bandgap control at low energies, and connections linking topology, exchange interactions, and (opto)electronic functionality remain nascent. We synthesized open-shell donor–acceptor copolymers comprised of a solubilizing thia-diazoloquinoxaline (TQ) acceptor and alternating cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) or dithieno[3,2-b:2',3'-d]thiophene (DTT) donors, which exhibit highly rigid backbones. Electron paramagnetic resonance and magnetic susceptibility measurements, complemented by quantum chemical calculations, demonstrate dramatic differences in the structural, electronic, topological, and magnetic structure as a result of atom-specific substitution. The CPDT–TQ copolymer demonstrates extensive π-conjugation with a quinoidal bonding pattern, a very narrow optical bandgap of less than 0.1 eV, and a high-spin ground state singlet-triplet splitting (ΔEST) of 7.17 × 10⁻³ kcal mol⁻¹. Substitution of electron-rich sulfur at the donor bridgehead position in DTT–TQ results in diminished π-conjugation, an aromatic bonding pattern, and a low-spin ground state with ΔEST of −5.24 kcal mol⁻¹. This work provides a framework to rationally understand the evolution of the electronic structure in open-shell DA CPs, control the ground state electronic structure, tune distance-dependent spin–spin coupling, and articulate the emergence of the novel properties of these materials.
New functional and soluble polyacetylenes bearing intrinsic n- and p-doping side groups

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While the discovery of metallic-like conductivity in doped polyacetylene provided an important foundation for the field of polymer electronics, the use of polyacetylene in modern applications has lagged since parent polyacetylene is completely insoluble and cannot be readily processed. Therefore, researchers have explored polymers with complex molecular structures and extensive synthetic protocols to obtain desirable optoelectronic performances, while enabling device fabrication to occur via spin coating or roll-to-roll printing. In this work, we report the straightforward synthesis of polyacetylenes with functional side groups that provide polymer solubility and enhanced stability to air, while concurrently leading to reduced HOMO/LUMO gaps in an undoped state. These new p- and n-type polymers bearing boryl- and amino-groups, respectively, show uniquely opposing NIR absorption behavior as a function of voltage, making these materials good candidates for the fabrication of flexible NIR photodetectors and optical switches.
New conjugated polymers based on boron element-blocks

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We have reported a wide variety of organoboron polymers including boron atoms in the main chain by means of hydroboration polymerization. These polymers exhibited various interesting properties due to the high electron affinity of boron atoms; strong fluorescence emission, n-type electronic conductivity, third-order nonlinear optical properties, and so on. We also reported other examples of photoluminescent organoboron conjugated polymers having tetracoordinated boron complexes such as poly(cyclodiborazane)s, poly(pyrazabole)s, organoboron diketone polymers, BODIPY conjugated polymers and carborane-based polymers. In these polymers, very interesting and peculiar optical properties were observed.

Recently, we proposed an advanced concept of organic-inorganic hybrid materials. A structural unit consisting of various groups of elements is called an "element-block." The design and synthesis of new element-blocks, polymerization of these blocks, and development of methods of forming higher-order structures and achieving hierarchical interface control in order to yield the desired functions are expected to encourage the creation of new polymeric materials that share, at a high level, electronic, optical, and magnetic properties not achievable with conventional organic polymeric materials as well as forming properties of molding processability and flexible designability that inorganic materials lack.

Here, our recent research results concerning these "element-block" materials are demonstrated. Especially, some examples of "luminescent organoboron element-blocks" exhibiting "aggregation-induced emission" (AIE) properties are emphasized. Such examples showed extremely high photo-emissions, fine tuning of emission colors, phosphorescence properties, near-UV fluorescence emission, near-IR photoluminescence, aggregation-induced emission behavior, crystallization-induced emission enhancement, and control of refractive indices, and so on. These performances would be the topics of the present paper and should be very important in the fields of electrical, optical, magnetical, and biomedical applications.
Development of stimuli-responsive luminescent polymers based on a flexible “element-block”

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Conjugated heteroatom complexes are a versatile “element-block”, which is defined as a minimum functional unit composed of heteroatoms, for fabricating opto-electronic devices because of their superior properties such as light absorption property, emission, and electron-carrier ability. However, their emissions in the solid states were usually spoiled by undesiredintermolecular \(\pi-\pi\) stacking interaction, called as aggregation-caused quenching (ACQ) effects. Therefore, applications of conventional complexes in the solid state are still limited by the ACQ effects. Especially, in order to obtain stimuli-responsive luminescent films, ACQ is one of critical problems to be solved. Aggregation-induced emission (AIE), which is observed only by aggregation formation, is a key phenomenon for overcoming the ACQ effect and obtaining highly-efficient light-emitting solid materials. We have found that ACQ-active organoboron dyes composed of the \(\beta\)-diketonate structure can be transformed to the AIE-active dyes by replacing the oxygen atoms to nitrogen to form the ketoiminate and diiminate structures. According to quantum calculation, it was proposed that these complexes should potentially show large degree of structural relaxation in the excited state. Furthermore, the series of AIE-active and stimuli-responsive film materials composed of conjugated polymers were able to be obtained. Therefore, we regarded as these flexible organoboron complexes as not only an AIE-inducible but also a stimuli-responsive luminescent “element-block”. In this presentation, recent progresses of the stimuli-responsive luminescent materials based on flexible boron “element-blocks” will be demonstrated. In particular, we mention the regulation of luminescent properties by the external stimulus in the film. In these studies, flexible complexes showed luminescent chromism triggered by temperature changes, mechanical stresses and vapor fuming. The mechanisms and design strategies will be explained in the presentation.
Pendent-controlled fluorescent and phosphorescent conjugated solids

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Despite the importance of conjugated materials in organic optoelectronic devices, the rational design of their properties as solid state ensembles is currently not possible. This talk will summarize work in which discrete co-facial aromatic interactions, involving pendant groups of conjugated materials, dictate the conformation, aggregation, and resulting spectroscopy of conjugated materials as solids. The weak nature of this interaction results in surprising sensitivity to seemingly insignificant changes in chemical structure that impact interaction strengths and the resultant conformations and optical properties of these solids. This non-covalent control extends to a wide variety of alkyne-containing conjugated materials, including organometallic phosphors.
Pyrrole-based organic semiconducting small molecules for organic field-effect transistors

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Pyrrole is an excellent building block for the synthesis of organic semiconductors. The smallest S, N-heteroacene, thieno[3,2-b]pyrrole is a good building block for organic semiconductors due to its electron density and easily modifiable NH group. Recently we demonstrated that organic semiconductors from thieno[3,2-b]pyrrole (TP) display “nearly-ideal” OFET characteristics without compromising charge carrier mobilities or threshold voltages. We have varied the structure and topology to investigate the relatively under-explored banana shape thieno[3,2-b]pyrrole semiconductors. Banana shaped donor-acceptor molecules with benzothiadiazole (BT) acceptors and thieno[3,2-b]pyrrole (TP-BT2T-BT) have been reported by our group (Figure 1a), and the OFET parameters were evaluated in a bottom-gate/bottom-contact (BGBC) OFET architecture. Hole mobility of 0.08 cm² V⁻¹ s⁻¹ was measured for TP-BT2T-BT with benzothiadiazole as the acceptor.

Compared to TP, the selenopheno[3,2-b]pyrrole (SeP) donor is a relatively electron-rich block that is capable of providing more electron density into hole-transporting semiconducting materials. Therefore, replacing TP with SeP has a great potential to improve the hole-transporting properties of the BT based small molecules. In this study, SeP and BT based small molecules with selenophene (SeP-BT2Se-SeP; Figure 1c) and thiophene (SeP-BT2T-SeP; Figure 1b) spacers are investigated for OFET activity and properties. Selenopyrrole and thienopyrrole spacers are selected to systematically study the effect of the heteroatom’s size on the spacer and obtain well-conjugated coplanar backbone structures that facilitate better charge transfer and molecular packing. To understand the structure-property relationship, optoelectronic properties and OFET properties of the SeP-based small molecules are compared with each other and TP-BT2T-BT.
Designing simple conjugated polymers for scalable and efficient solar cells

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Conjugated polymers have a long history of exploration and use in organic solar cells, and over the last twenty plus years, marked increases in the solar cell efficiency have been achieved. However, the synthetic complexity of these materials has also drastically increased, which makes the scalability of the highest efficiency materials difficult. If we are able to design conjugated polymers which can exhibit both high efficiency and straightforward synthesis, the road to commercial reality would be more achievable. For that reason, we began to explore quinoxaline-based conjugated polymers and designed new synthetic approaches towards PTQ10 monomers. In this talk, we will show how to design conjugated polymers with consideration for high efficiency along with reducing the synthetic complexity and use of green chemistry processing. For example, shown in the image below, the complete synthetic route (16 steps) for our previously designed FTAZ-polymer is shown from the initial feedstocks, and while this material can achieve high efficiency, the potential for scalability is low. By contrast, some of our new chemistry can allow for a significant reduction in the synthesis (6 steps) while maintaining high efficiency. Finally, we will also discuss adding side chains on these polymer motifs which work towards green-solvent processing.
Efforts to stabilize organic photovoltaics

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Organic photovoltaics (OPVs) are promising because they can be flexible and lightweight, but they suffer from performance loss over time. This loss is often due to phase separation between the conjugated polymer and the fullerene derivative blended in the device’s active layer. Previous work showed that a copolymer comprised of a poly(3-hexylthiophene) (P3HT) backbone with a random distribution of fullerene-functionalized side-chains can stabilize the morphology and OPV performance when it is added to P3HT:fullerene blends. In this work, we use optical microscopy to show that the same copolymer prevents phase separation in multiple thin film blends of different conjugated polymers (PTB7, PTB7-Th, and PffBT4T-2OD) with fullerene. The ability to prevent phase separation in multiple blends is likely due to the fact that the copolymer is miscible with each of the different blend components and, in the PffBT4T-2OD case, can lower the Flory-Huggins interaction parameter of the blend. We fabricated devices with PffBT4T-2OD because the thin films showed the greatest reduction in phase separation with copolymer addition. When the copolymer is used in devices, however, unanticipated changes in the device conductivity limit device performance. Our results suggest that although the copolymer has potential as a general OPV stabilizer, device performance depends on multiple factors.
Water soluble poly(Phenylene Ethynylene)s for bio applications

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Water soluble conjugated polymers and conjugated polyelectrolytes have received considerable attention for bio-applications, including bio-sensing, diagnostics and therapy. Our group has focused on the development of water soluble poly(phenylene ethynylene)s (PPE), due to their bright fluorescence and other properties that render them useful in bio-applications. In this talk recent work will be described that has focused on next-generation water soluble PPE-type conjugated polymers. This includes the application of chain growth polymerization to prepare highly fluorescent, low dispersity polymers and methods for preparing well-defined PPE-type polymers that are functionalized with specific biofunctional moieties.
Well defined conjugated polymers

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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 one is 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 remarkable 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 well-defined polymer templates to prepare broader classes of well-defined conjugated polymers.
Investigation of (Hetero) bimetallic catalysts in the synthesis of π-conjugated polymers

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In the recent decade, several advances have been made in the controlled synthesis of π-conjugated polymers, which are attractive targets for organic electronics. The ability to access semiconducting polymers with precise molecular weights, low dispersities, high regioregularity, and end-group functionalization is important for tuning the performance of optoelectronic devices. Control over these parameters can be achieved through catalyst-transfer polymerization (CTP), a method that proceeds in a chain-growth manner. The presence of a metal-polymer π-complex influences chain-growth behavior by allowing the catalyst to stay adhered to the growing polymer chain. The discovery of this controlled polymerization has advanced the field of π-conjugated polymer synthesis. In this presentation, our work towards enabling the use of bimetallic catalysts to expand monomer scope will be discussed.
Transition-metal-free photopolymerization of pi-conjugated polymers

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π-Conjugated polymers (CPs) are commonly synthesized by Pd- or Ni-catalyzed polycondensation reactions, and require extensive purification to remove transition-metal impurities that can compromise device performance. We have discovered a mechanistically distinct approach to the synthesis of CPs based on the catalyst-free photopolymerization of Grignard monomers in saturated LiCl solution. This reaction displays high efficiency for n-type polymers, and enables the synthesis of all-conjugated n-type block copolymers. I will discuss experimental and computational mechanistic studies, which suggest an unusual photoinduced $S_{RN1}$-type mechanism.
Exploring the choice of boron coupling partner in Suzuki-Miyaura catalyst-transfer polymerization

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Conjugated polymer synthesis via a chain-growth mechanism enables precise control over molecular weight and molecular weight distribution, while also enabling access to backbone compositions that are typically difficult to obtain via a step-growth mechanism (e.g. block copolymers). A number of different cross-coupling chemistries can be used to bring about chain-growth polymerization of aromatic monomers including Kumada-Corriu and Suzuki-Miyaura reactions. Suzuki-Miyaura coupling is particularly useful when the arene monomer bears functional groups which are sensitive to strong nucleophiles. In this talk, we will highlight some of our recent work examining the choice of boron coupling partner in Suzuki-Miyaura cross-coupling polymerization (tunable B(OR)₂ group in Figure 1). We have noted that the choice of organoboron impacts both the rate of polymerization and the molecular weight of the final material. The boron group bound to the aromatic monomer can be considered as a tunable moiety to modulate polymerization behavior when using Suzuki-Miyaura coupling for the chain-growth polymerization of aromatics.

**Suzuki-Miyaura Catalyst-Transfer Polymerization (SM CTP)**

![Chemical Reaction Diagram]

**How Does Choice of Organoboron Impact Polymerization**

**Figure 1.** Method to prepare halogenated boronic esters, and exploration of these monomers in cross-coupling polymerization
Synthetic development and optical characterization of π-conjugated poly(purine)s

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Our research explores new methods to synthesize sequence-regulated conjugated polymers based upon the purine scaffold. Purines feature a fused bicyclic structure with a strong molecular dipole moment and several sites for reactivity – specifically, the C2, C8, C6 and N9 (or N7) positions. The synthetic addressability of these sites provides a compelling opportunity to study fundamental design-structure-property relationships and expand the scope of possible building blocks for organic electronics. In this vein, our research exploits this synthetic tailorability of the well-defined purine scaffold to access a set of monomers with varying connectivity patterns (conjugated-structural isomers) and investigate their impact on polymeric photophysical and material properties. We will describe the synthesis and characterization of the first fully π-conjugated poly(purine)s synthesized via either direct arylation polymerization (DArP) or microwave-assisted Suzuki cross-coupling. The ability to produce these conjugated poly(purine)s via multiple polymerization methodologies highlights the versatility of the purine monomer scaffold. Characterization of the resultant polymers reveals a clear relationship between molecular structure and photophysical properties, which trend systematically with the optical properties of the monomer. We will also describe differences between polymer properties that emerge due to changes in coupling pattern, which give rise to either linear-conjugation or cross-conjugation about the purine-based ring-system. Finally, we will describe the impact of regioselectivity, comonomer incorporation, and the nature of conjugation in the poly(purine) system on material properties and energy flow in these π-conjugated polymers.
Exploring isomeric effects on optical and electrochemical properties of red/orange electrochromic polymers

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Subtle structural changes in monomeric building blocks serve as a synthetic handle to manipulate the perceived color of conjugated polymers that find applicability in electrochromism. With this in mind, it is paramount to understand the influence of minimal structural alterations, such as isomeric effects, that manipulate optical and electrochemical characteristics. Herein, a family of dialkylthiophene-co-3,4-propylenedioxythiophene (ProDOT) copolymers are synthesized via direct arylation polymerizations, with a key design motif being minimal changes in the structural composition of the ProDOT comonomer. Variation in the substitution pattern on the propylene bridge provides insight into the role of stereo- and compositional isomers on the resulting polymer properties. Specifically, time-dependent density functional theory calculations reveal changes in the number and placement of comonomers with varying composition and stereocenters impacting the calculated absorbance spectra, which ultimately manifests in differences in the calculated color. Experimentally, UV-vis absorbance spectroscopy and colorimetry reveal a dependence on the stereo- and regiospecificity, while electrochromic properties, such as contrast and switching times, are not drastically affected by the substitution patterns. This work highlights how subtle structural changes can manipulate and be used to optimize optical features without sacrificing electrochromic properties. In addition to fundamental insights into monomeric design of ProDOT building blocks and their optical and redox characteristics, the results provide an additional structural handle for fine-tuning the observed color of electrochromic polymers.
π-Face taming vs. appending pendant solubilizing chains for soluble π-conjugated polymers

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Pendant solubilizing chains appended to π-conjugated polymers control polymer solubility and assembly, which further control optical, electronic, mechanical, and thermal properties of the polymer thinfilms. However, the pendant solubilizing chains do not overcome the strong van der Waals interactions between 2D-π-conjugated materials including ladder polymers, nanoribbons, 2D-grids, and 2D-π-conjugated polymers. Recently, we have designed and developed π-face tamed monomers known as bifacial monomers containing an aryl and a cycloalkyl face. Upon polymerization, the cycloalkyl group is randomly positioned either above or below the polymer backbone and helps tame interchain π-π stacking interactions. Soluble 1D-π-conjugated polymers without pendant solubilizing chains have been realized through this approach. The bifacial polymers also exhibit the bifacial cyclophane monomer height dependent fluorescence quenching with TCNQ (tetracyanoquinodimethane) acceptor. The Stern-Volmer constant (Ksv) decreased with an increase in the bifacial cyclophane monomer height indicating that the height of the bifacial cyclophane monomer determines the photoinduced charge transfer properties of the polymer backbone. In order to enhance the photoinduced charge transfer with acceptor molecules we have designed and synthesized copolymers and studied the impact of the co-monomer percentage on photoinduced charge transfer interaction with TCNQ. In this talk, I will discuss the (i) design and synthesis of the novel bifacial π-conjugated homo- and co-polymers and (ii) impact of the polymer architecture on polymer solubility, optical properties, and photoinduced charge transfer interactions with acceptor molecules.
Organoarsenic polymers by practical As-C bond formation techniques

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The development of practical carbon-heteroatom bond formation as well as new polymerization methods for heteroatom-containing polymers is not only of considerable scientific interest but also important for preparing useful materials with unusual properties. Safe and facile reactions for As-C bond formation protocols promote further advancement in organoarsenic chemistry. We have developed several practical methods for As-C bond formation based on the arsenic homocycles, cyclo-(AsMe)$_5$ and cyclo-(AsPh)$_6$ (Scheme 1). Organoarsenic electrophiles and nucleophiles are generated in situ from the arsenic homocycles by addition of iodine and organolithium reagents, respectively. The in situ generation methods do not require isolation and purification of the arsenic intermediates because neither salts nor by-products are formed. Without isolation, the obtained solution of the arsenic intermediates can be subsequently used for the next substitution reaction to produce various organoarsenic compounds such as 9-arsafluorenes, 2,5-diaryl-1-phenylarsoles, and dithienoarsoles. These compounds can be used as monomers for preparation of arsole-containing p-conjugated polymers.

The coordination direction of arsenic atom is more versatile than that of phosphorus, and various complex forms can be attained by organoarsenic ligands. In addition, trivalent arsenic compounds are stereochemically stable because of the higher inversion barrier relative to that of phosphorus compounds. Furthermore, organoarsenic compounds are much less reactive to oxygen compared with phosphorus analogues, which are generally prone to oxidation, and thus most phosphines are spontaneously oxidized even under the ambient atmosphere. Therefore, arsenic-containing polymers are a promising alternative to open a new door toward trivalent pnictogen-based materials.
Optical properties of silicon nanosheets modified with conjugated units
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Silicon nanosheets (SiNS) have attracted much attention as a class of silicon-based nanomaterials. Modification of layered polyhydrosilane \((\text{Si}_6\text{H}_6)_n\) with organic groups readily provides SiNS. The organic groups prevent the SiNS kinetically from hydrolysis by moisture and air-oxidation and improve the solubility and dispersibility of SiNS in organic solvents. Recently, we prepared SiNS with conjugated units by dehydrogenative coupling of arylmethylamine derivatives with \((\text{Si}_6\text{H}_6)_n\). Interestingly, optical properties of SiNS were remarkably affected by the aromatic units. The phenyl- and naphthyl-containing SiNS exhibited inter- and intramolecular \(\pi\)-stacking, respectively, leading to red-shifts of photoluminescence (PL) bands. In contrast, SiNS with carbazole units showed no \(\pi\)-stacking formation but exhibited intramolecular photo electron transfer.

In this study, optical properties of SiNS having electron rich triphenylamine and deficient quinoline units (NS-TP and NS-Qu) were investigated. Interestingly, intramolecular photo charge transfer (ICT) occurred for NS-TP. DFT calculations on a model indicated that the catenated silicon layer of NS-TP enhanced ICT as electron-acceptor. For the quinoline-containing NS-Qu, efficient photo energy transfer from the quinoline units to the silicon layer was observed. These clearly indicate that the SiNS electronic states are considerably influenced by the substituents. We also found that platinum-catalyzed reactions of \((\text{Si}_6\text{H}_6)_n\) with arylacetylenes gave arylethenyl-substituted branched polysilanes. The polysilanes exhibited photo energy transfer from the arylethenyl substituents to the polysilane backbone. Photo current generation and device applications of these SiNS and polysilanes were also studied.

Preparation of Silicon Nanosheets Modified with Conjugated Units
Cross-conjugated poly(thienylene vinylene)s (PTVs) and poly(selenylene vinylene)s (PSVs)

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We describe our methodologies, through combination of acyclic diene metathesis (ADMET) and post-polymerization modification (PPM) reactions, for the preparation of poly(thienylene vinylene)s (PTVs) and poly(selenylene vinylene)s (PSVs) with systematically varied structures. First, we prepared PTVs, PSVs and their random copolymers (PSV-co-PTV). By replacing sulfur atoms with selenium, PSVs were found to possess reduced crystallinity and a smaller bandgap of ca. 1.6 eV, while PSV-co-PTV shows physical/electronic properties between those of the corresponding homopolymers. Secondly, we successfully prepared a series of novel PTVs and PSVs functionalized with F, Cl, Br and I atoms at the 4-positions of thiophene rings. Such halogenation not only displays capabilities of fine-tuning polymer properties but also provides opportunities for further functionalization through PPM reactions, which enabled us to introduce several thiophene and benzene-based conjugated side chains on the polymer backbone. Interestingly, the obtained PTV and PSV derivatives with strongly electron-withdrawing side-chains displayed rarely observed fluorescence, suggesting changes in excited state structure and dynamics. Our methodologies provide a facile means to systematically study the structure-property relationships of poly(chalcogenylene vinylene)s, which can enhance our basic understanding in CPs and potentially lead to new materials for emerging electronic applications.

\[
\text{TV-Br} \xrightarrow{\text{Acyclic Diene Metathesis (ADMET)}} \text{PTV-X}
\]

\[
\bullet = \text{F; Cl; Br; I; } \quad \begin{array}{c}
\text{S} \\
\text{S-CHO} \\
\text{S-COOCH}_3
\end{array}
\]
**π-Conjugated polymers possessing unique element-blocks**

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As predicted in part from the theoretical calculations, the incorporation of heteroatoms into the π-electronic systems is effective to design π-conjugated polymers that exhibit excellent optoelectronic functions. In the course of our studies on the main chain-reactive organometallic polymers, we describe herein the synthesis and transformations of the regioregular organometallic polymers into element-block π-conjugated polymers.

Polymers containing organometallic units such as titanacycles are prepared by the polymerization of diynes with a low-valent titanium complex that accompanies the metallacyclization processes. Their reactions that involve the main chain-transformations produce π-conjugated polymers possessing heteroles of a variety of elements such as Sn, P, As, Sb, Bi, S, Se, and Te. In addition, the reaction of the tellurophene-containing polymers with butyllithium provides more reactive organolithium polymers whose transformations provide π-conjugated polymers possessing other elements such as Ge and Si that are not accessible by the direct transformation of the titanium-containing precursors. π-Conjugated polymers containing plural elements are also obtained by the use of appropriate reagents for the polymer reactions or by the further transformations of the element-block polymers. Depending on the elements incorporated into the π-conjugated systems, the polymers exhibit a wide variety of interesting optoelectronic functions. For example, the HOMO and LUMO energy levels are affected largely by the elements, resulting in a drastic change in their electronic properties. Some of the polymers are luminescent materials whose color is tunable by the elements. Some of the elements-containing polymers are also found to serve as fluorescent chemosensors. The macromolecular design of functional materials based on the present synthetic methods will also be described.
Hybrid materials containing cyclosilane fragments

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Conjugated polymers containing extended silicon segments appeal for the potential to combine the physical properties of soft matter with the electronic properties of semiconductors. This talk will focus on hybrid materials containing sigma-conjugated silanes as well as both organic and inorganic (e.g. B, N) substituents. A focus will be understanding the interplay of pi- and heteroatom-functionalization with sigma-conjugated silanes. Synthetic approaches and optoelectronic properties will be discussed.
Sulfenate anions as organocatalysts for benzylic chloromethyl coupling polymerization (BCCP)

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Organocatalytic polymerizations have a number of advantages over their transition metal-catalyzed counterparts, including ease of catalyst preparation and storage, environmental friendliness, and new modes of reactivity. We present an organocatalytic polymerization method called benzylic-chloromethyl-coupling polymerization (BCCP, Figure 1A). BCCP is catalyzed by sulfenate anion organocatalysts (ArSO₂⁻, Figure 1B) that have not been used in polymer chemistry before, but which are easily generated from bench-stable sulfoxides. The sulfenate anion organocatalyst promotes an umpolung polycondensation via step-growth propagation cycles involving sulfoxide intermediates. BCCP is a rare example of a polymerization that links monomers by C=C double bond formation and offers transition-metal-free access to a wide variety of conjugated and non-conjugated polymers that cannot be synthesized by traditional precursor routes.
Organoboranes as electron-deficient building blocks for new conjugated materials

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The optical and electronic properties of organic π-conjugated materials can be dramatically altered by incorporation of heteroatoms. A particularly effective method is to embed electron-deficient boron atoms into the molecular skeleton. The ability of boron to participate in π-delocalization can have a dramatic effect on the electronic structure of conjugated materials by selectively lowering the LUMO orbital levels. The electronic structure can also be modulated by B-N Lewis pair (LP) functionalization. Such an approach offers intriguing opportunities due to (i) the ensuing planarization of the molecular skeleton; (ii) the increased electron-deficient character as the LUMO energy is lowered; (iii) the potential for stimuli-responsive “smart” materials and molecular switches enabled by the reversibility of the LP formation.

In our recent work, we have explored the effects of tricoordinate boranes in conjugated oligomers and polymers on the luminescent and photovoltaic properties. We have also developed B-N Lewis pair functionalized polycyclic aromatic hydrocarbons as new building blocks of conjugated polymers.

Tricoordinate Borane Polymer

Boron-Nitrogen Lewis Pair Polymer
Putting “conductivity” back into conducting polymer research

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With the discovery of near metallic conductivity in films of polyacetylene in the late 1970s, the field of “Conducting Polymers” was initiated. After further development to polypyrroles, polyanilines, and the ultimate development of PEDOT/PSS as a commercial material, extension of work into semiconducting properties for light emission, photovoltaic light harvesting, transport for field effect transistors became dominant. All the while, redox doping remained important to many applications including charge storage (batteries and supercapacitors), chemical/bio sensing, and electrochromism. With the advent of more mature conjugated polymer structures, has come solubility for effective processing and printing, along with controlled oxidation and reduction potentials needed for stable, charged and conducting materials. In this presentation, we detail synthetic developments in the preparation of dioxythiophene-based polymers and copolymers using direct heteroarylation polymerization methods to yield low-oxidation potential polymers that are easily doped to highly electrically conducting states. Combining 3,4-propylenedioxythiophene (ProDOT) monomers disubstituted at the 2-position of the propylene bridge with nonpolar (e.g. alkyl) and polar (e.g. ester, oligoether, etc.) substituents, we control solubility to allow environmentally-benign solvent processing. Copolymerization of these functional ProDOTs with dimethyl ProDOT, EDOT, and biEDOT provide increasingly electron rich conjugated backbones which, upon careful oxidative doping, reach conductivities up to 250 – 400 S/cm. Potential-dependent conductivity profiles are monitored in situ to determine the breadth of the windows of high conductivity. Using chemically cleavable side chains, the electroactive fraction of the conjugated polymer is increased and has yielded doped compositions with conductivities in excess of 450 S/cm. These high and reversibly switchable conductivities provide opportunities for new thermoelectric materials, switches for flexible/printable circuits, and controlled modulation of infrared absorption.
Advances in all-polymer solar cells and non-fullerene electron acceptors

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Recent advances in molecular engineering of materials and morphology engineering of the blend active layer have narrowed the gap between the theoretical device efficiency and the state-of-the-art experimental values in organic photovoltaics (OPVs). In this talk I will discuss our recent efforts in addressing fundamental issues of: (i) blend morphology control to enhance photocurrent and fill factor in all-polymer solar cells (all-PSCs); (ii) bandgap engineering to concurrently maximize charge generation and minimize optical bandgap energy loss; and (iii) electrochemical and photochemical instability of small-molecule non-fullerene acceptors (NFAs). We have found that random copolymerization of the donor and acceptor moieties is a powerful and rational approach to control the blend morphology of new acceptor polymers. Highly efficient all-PSCs with near unity internal quantum efficiency and low energy loss are realized without using any solution processing additives. The results show that the blend morphology, photovoltaic properties, and energy utilization of all-PSCs can be optimized by varying the random copolymer composition. A new class of NFAs, bis(naphthalene-imide)arylenelidenes (BNIAs), has been developed and found to combine excellent charge transport and electrochemical redox properties with good photovoltaic properties. The underlying structure-property relationship further revealed that the blend photophysics and morphology led to distinguished device performance between fused-ring and non-fused-ring BNIAs.
Structure-property studies of non-planar azadipyrromethene-based macromolecules for organic photovoltaic applications

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Azadipyrromethene (ADP, see image) is an aromatic monoanionic bidentate ligand whose core resembles half of a phthalocyanine ligand. Complexes of ADP have strong visible to near-IR absorption, high electron affinity and easy synthesis, making them attractive for a variety of applications. We have demonstrated that homoleptic zinc(II) complexes of ADP with phenylethynyl pyrrolic substituents (Zn(WS3)2, see image), are promising candidates as non-fullerene acceptors for solution-processed organic photovoltaics (OPVs). The complex’s distorted tetrahedral structure (non-planar) facilitates favorable phase separation from the common conjugated polymer donor, poly(3-hexylthiophene) (P3HT), yielding good performance in OPVs. To further understand their structure-properties and increase OPV performance, we investigated replacing the phenyl in the phenylethynyl pyrrolic substituents with larger aromatic groups such as naphthyl and phenanthrenyl groups. Because these larger aromatic groups reduced solubility in organic solvents, we added hexyl solubilizing groups at the para position of the proximal phenyls. We found that the hexyl and the larger aromatic groups both contribute to improving crystallinity of the zinc(II) complexes, electron mobility and OPV performance. The best performance was obtained with 1-naphthyl substitution, called Zn(L2)2. OPVs using P3HT as the donor gave a high power conversion efficiency (PCE) of 5.5% and the PCE was not very sensitive to the P3HT:Zn(L2)2 weight ratio. Fluorination increased the PCE to 5.8%. Additionally, Zn(L2)2 can be synthesized on the gram scale using inexpensive starting materials without chromatography column purification, increasing its industrial accessibility. Due to its non-planar structure, Zn(L2)2 shows isotropic charge transport. Interestingly, it had high hole mobility, making it a good candidate as donor to be paired with a conjugated polymer acceptor. This combination of properties demonstrates the potential of these types of molecules for optoelectronic devices.
Tunable conjugation topologies for fluxional macromolecular pi-electronics

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The palate used to create high performance organic electronic materials is rich in aromatic building blocks, including numerous variations of benzene, thiophene and pyrrole rings. Although these materials can be photoexcited leading to subsequent exciton migration or subjected to redox processes to inject charge carriers, they all are formed from “static” ground electronic states. This presentation will highlight a new avenue of research whereby photoswitchable structural units undergo electrocyclizations leading to subtle but electronically dramatic alterations of pi-electron conjugation topology. This is achieved through the photochemical creation and disruption of local aromatic substructures along the polymer backbone as a way to externally attenuate electronic properties thus providing a way to toggle between two distinct electronic ground states. This presentation will also introduce new prospects for radial topologies and their impact on linear conjugated polymer electronics.
Going against the grain: A new design paradigm for low bandgap polymers
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The most commonly applied approach to the generation of low bandgap ($E_g < 1.5$ eV) and reduced bandgap ($E_g = 1.5$–$2.0$ eV) conjugated polymers is via the utilization of a donor-acceptor (D-A) framework. Such frameworks employ a backbone of alternating electron-rich and electron-deficient moieties in order to produce a hybrid material with HOMO levels characteristic of the donor and LUMO levels characteristic of the acceptor, thus resulting in a reduced HOMO-LUMO energy and lower bandgap. The widespread application of such frameworks has since led to a number of assumptions and misconceptions in the literature, the most basic of which is that monomeric units act exclusively as donors, acceptors, or neutral spacers. At odds with this assumption, however, is the recent knowledge that the commonly applied class of acceptors, thieno[3,4-b]pyrazines (TPs) also exhibit properties of very strong donors comparable to 3,4-ethylenedioxythiophene, leading to the use of the term ambipolar units to describe these building blocks. As TPs exhibit a high-lying HOMO, this should allow for a new design model in which ambipolar TP units are paired with an acceptor, rather than the traditional pairing with a donor. Several such ambipolar-acceptor frameworks have now been successfully produced via direct arylation polymerization to give materials with bandgaps of 0.97–1.12 eV. The synthesis of such ambipolar-acceptor frameworks will be presented along with their optical and electronic characterization. Furthermore, the potential broader applications of this new design paradigm will also be discussed.
Design, synthesis, and characterization of conducting plastics

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Conjugated polymers (CPs) play a leading role in the field of organic semiconducting materials. These polymers have great electronic, thermal, and optical properties. Besides, they have better solubility, low-temperature processability, and mechanical properties when compared to conventional semiconductors. These characteristics are very attractive for applications such as Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs), photovoltaic devices, power storing devices, and sensors. Polyaniline (PANI) stands out among the many different conducting polymers (CPs) such as polyacetylene (PA), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy), due to its outstanding air and moisture stability in the conductive state. It is also simple to prepare, can be made highly conductive, redox reversible, and cost-effective. PANI is one of the very few CPs that have gained some large scale commercial applications, mostly in printed circuit board manufacturing (final finishes), antistatic, and electrostatic dispersive (ESD) coatings, and corrosion protection. Diketopyrrolopyrrole (DPP)-based compounds have unique optoelectrical properties and good thermo- and photostability, which has resulted in their extensive utilization in organic semi-conductive materials. In this presentation, we will discuss our design strategy, synthesis, and characterization of two kinds of CPs; polyphenoxazine, which is a polyaniline mimic, and a new n-type DPP polymer developed from a new DPP scaffold.
Reimagining semiconducting polymers for alternative energy applications

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Conjugated polymers have been the cornerstone of organic electronics, with applications in areas such as photovoltaics, field effect transistors, and electrochromics. Specifically, polymer based solar cells have generated significant attention due to the promise of a lightweight, flexible, and inexpensive solar energy conversion platform. However, a number of challenges are still apparent, including, accessibility, scalability and efficiency. Our related efforts have focused on novel, simplified polymer and device architectures and synthetic methods. Specifically, we have spent significant effort focusing on scalability of polymer synthesis, which is best embodied in our work on Direct Arylation Polymerization (DArP), which is a C-H activation route to the synthesis of conjugated polymers. In this case, the identification of defects and their elimination via optimization of polymerization conditions has been the central focus of our work. Efforts toward oxidative direct arylation, or halogen-free polymerization, will also be discussed along with results focused toward the replacement of Palladium with inexpensive first row transition metals such as Copper. Our work on ternary blend solar cells will also be discussed, focusing on how proper selection of components in ternary blends can lead to a synergistic enhancement of properties without increasing the complexity of device fabrication. Here our development of the organic alloy model will be discussed in relation to the influence of polymer blending on the open circuit voltage in ternary blend solar cells. Finally, efforts toward the synthesis of non-conjugated electroactive polymers will be introduced.
General Topics: New Synthesis & Characterization of Polymers
Balaka Barkakaty, Organizer; Dana Garcia, Organizer,

April 5, 2021

Chromophore compatibility in electro optic polymers
Kaitlyn Crawford, Presenter; Gavin Pour

Optoelectronic properties of π-conjugated polymers derived from boron difluoride formazanate dyes
Jasveer Dhindsa, Presenter; Ryan Maar; Stephanie Barbon; Joe Gilroy

Tuning molecular fluorescence via controlled polymerization-mediated charge transfer
Dr Yinyin Bao, Presenter

Photoresponsive sponges from azobenzene/Q-type silsesquioxane networks
Joseph Furgal, Presenter; Naihsuan Hu

Characterizing organic solar cells in space
Lennart K. Reb, Presenter; Michael Böhmer; Benjamin Predeschly; Sebastian Grott; Christian Weinid; Goran Ivanedekic; Renjun Guo; Christoph Dreßigacker; Roman Gernhäuser; Andreas Meyer; Prof. Dr. Peter Mueller-Buschbaum

3D printing of unsaturated polyester networks
Tyler White, Presenter; Viswanath Meenakshisundaram; Keyton Feller; Christopher Williams; Timothy Long

Tailoring solid state properties of quadruple hydrogen bonding containing block copolymers
Boer Liu, Presenter; Xi Chen; Glenn Spiering; Jae Sang Lee; Matthew Green; Robert Moore; Timothy Long

Morphology-dependent mechanical properties of shape memory poly(isocyanurate-urethane) (PIR-PUR) aerogels
A B M Shaheen ud Doulah, Presenter; Hojat Majedi Far; Chandana Mandal; Nicholas Leventis; Chariklia Sotiriou-Leventis

Development of aqueous size exclusion chromatography conditions to characterize polyzwitterion-block-N-isopropyl acrylamide copolymers
Phillip Pickett, Presenter; Sara Orski; Vivek Prabhu

Carbon aerogels derived from poly(tetrahydroquinazoline) for high capacity and selective adsorption of carbon dioxide
Vaibhav Edlabadkar, Presenter; Saidulu Gorla; Rushi Soni; Nicholas Leventis; Chariklia Sotiriou-Leventis

Highly proton conducting, chemically stable sulfonated polytriazoles based on trifluoromethyl and phosphine oxide moieties for proton exchange membranes
ARIJIT GHORAI, Presenter; Hartmut Komber; Brigitte Voit; Susanta Banerjee

Balancing processing ease with combustion performance in aluminum/PVDF energetic filaments
Ashton Craig, Presenter; Matthew Knott; Jena McCollum
Multi-tiered conjugated oligomers as models to examine π-π interactions in semiconducting conjugated materials
Ashley E Johns, Presenter; David Collard

Direct visualization of diblock copolymer conformation in the subdomain through heavy z-labelling
Christian Steinmetz, Presenter; Wenpeng Shan; Xueyan Feng; Michael Dimitriyev; Abhiram Reddy; Rohit Gupta; E. Bryan Coughlin; Edwin Thomas; Gregory Grason

Development of structure-property-processing relationships and thermotropic liquid crystallinity of a series of poly(3-alkylthiophene)s with branched side chains
Bronson Cox, Presenter

Unique Thickness Relaxation Behavior Characterized in ultra-thin polystyrene films using X-Ray reflectivity: Effect of temperature on physical aging
Tulika Sharma, Presenter; Yuichiro Tamano; Yoshiaki Nishio; Harumi Sato; Isao Takahashi

Charge density and hydrophobicity-dominated regimes in the phase behavior of complex coacervates
Jun Huang, Presenter; Jennifer Laaser

General Topics: New Synthesis & Characterization of Polymers
April 6, 2021

Modular synthesis of therapeutic peptide brush polymer nanoparticles via polymerization-induced self-assembly
Hao Sun, Presenter

Metallopolymer based double-network hydrogel as promising antimicrobial materials with antibiotics
Jihyeon Hwang, Presenter; Yujin Cha; Tianyu Zhu; Chuanbing Tang

Development of robust hydrogels for biomedical devices with exceptional thermal and chemical stability
Buddhabhushan Salunkhe, Presenter; Thomas Schuman; Baojun Bai

Combination therapy using brain accumulating polymeric nanoparticles for tackling HIV-infected brain reservoirs in drug abuse population
Dr. Nagesh Kolishetti, Presenter; Bapurao Surnar; Anuj Shah; Mohammad Kamran; Royden Jamie-Ramirez; Venkata Atluri; Adriana Yandart Arias; Madhavan Nair; Shanta Dhar

Designing functional conjugated materials for biological integration
Dr. Joshua Tropp, Presenter; Rebecca Keate; Jonathan Rivnay

Synthesis and evaluation of polyisobutylene-grafted graphene oxide nanocomposite films with improved oxygen barrier properties
Ms. Dana Michelle Pinson, Presenter; Moustafa Zhago; Beibei Chen; Benjamin M Alameda; Luke Galuska; Taylor Hood; Sergei Nazarenko; Xuyang He; Robson Storey; Derek Patton

Adhesion and tie layer resin technology for multilayer packaging
Mou Paul, Presenter; Barry Morris; Jeffrey Weinhold; Karlheinz Hausmann

A new class of bio-based triblock copolymer prepared via RAFT polymerization: A potential thermoplastic elastomer
Mr. Uddhab Kalita, Senior Research Fellow, Presenter; Sarthik Samanta; Nikhil Singha

Novel biobased cyclic diacids for polyamides with tailored functional properties
Prerana Carter, Presenter; James Trettin; Brent Shanks; Prof. Eric W Cochran; Jean Philippe Tessonnier

Expanded versatility of hydroesterificative Polymerization via bioderived monomers
Janaya Sachs, Presenter; Ian Tonks

Comparative studies of the sorption behavior of agricultural chemical with engineered soil surrogates (ESSs) and real soils
Md Ragib Hasan, Presenter; Arjun Pandey; Ghada Abdalla; Robert Cook; David Spivak

New and atom economic synthetic route towards a bio-based angelica lactone-norborenone polymer
Andrea Dell’Acqua, Presenter; Bernhard Stadler; Sarah Kirchhecker; Sergey Tin; Johannes De Vries

From α to δ: converting pine tree sap into monomers for ROMP
Mr. Mark Yarolimek, Presenter; Heather Bookbinder; Brianna Coia; Justin Kennemur

Non-isocyanate polyurethanes for thermoplastics and foams: opportunities for green chemistry and sustainability
Jose Sintas, Presenter; Josh Wolfgang; Timothy Long

Dynamics of blended versus grafted thermo-responsive polymers in cellulose nanocrystal nanocomposites
Dr. Huyen Vu, Presenter; Jeremiah Woodcock; Jan Obrzut; Jeffrey Gilman; E Coughlin

The vibrant interplay of elemental sulfur and polymer chemistry to address global challenges
Dr. rer. nat. hatice mutlu, Presenter; Timo Sehn; Daniel Döpping; Patrick Theato

General Topics: New Synthesis & Characterization of Polymers
April 8, 2021

Precise synthesis of high performance polyolefin materials from only ethylene feedstock
Prof. Shengyu Dai, Presenter

A facile synthesis of derivatives of tetraphenylcyclopentadienone and dendritic polymer via symmetrical functionalization of 2,5-diaryl-3,4-diphenylcyclopentadienone
Dr. Syeda Shaista Gillani, Assistant professor, Presenter

Chain-straightening polymerization of olefins to form polar functionalized semi-crystalline polyethylene
James Eagan, Presenter; Omar Padilla-Velez; Kyle O’Connor; Samantha Macmillan; Anne Lapointe; Geoffrey Coates

RAFT dispersion polymerisation of lauryl methacrylate in ethanol-water binary mixtures: synthesis of diblock copolymer vesicles with deformable membranes
Rebecca Gibson, Presenter; Alan Fernyhough; Osama Musa; Steven Armes
Synthesis and aqueous solution properties of shape-shifting stimulus-responsive diblock copolymer nano-objects
Oliver Deane, Presenter; Steven Armes; Osama Musa; Alan Fernyhough

The synthesis of polycycloolefins through vinyl-addition polymerization
Justin Burroughs, Presenter

Design, synthesis, and characterization of melt-processible vinyl-addition polynorbornenes
Xinyi Wang, Presenter; Yewon Jeong; Christopher Love; Holly Stretz; Gila Stein; Prof. Brian Long

Incorporation of siloxane linkages into commodity polymers as a path towards backbone cleavage and exchange
Anne Radzanowski, Presenter; Roshni John Chethalen; E Coughlin

Insight mechanism of anionic ring-opening polymerization in ionic liquids
chandan giri, Presenter; Paul A Rupar

Synthesis of cleavable polymers by the introduction of dynamic covalent bonds within the backbone
Roshni John Chethalen, Presenter; Anne Radzanowski; E Coughlin

Reactive MT copolymers based on phenylsilsesquioxane
Yan Cong, Presenter; Pei Bian; Thomas McCarthy

One step forward in emulsion thiol-ene photopolymerization
Mr Cuong Minh Quoc Le, Presenter; Marc SCHMUTZ; Abraham Chemtob

Aluminum-based initiators from thiols for epoxide polymerizations

Ms. Niloofar Safaie, Presenter; Bandana Rewal; Kohji Ohno; Robert Ferrier

Aqueous ring-opening metathesis polymerization-induced self-assembly (ROMPISA)
Dr. Spyridon Varlas, Presenter; Jeffrey Foster; Robert Keogh; Lucy Arkinstall; Robert Mathers; Rachel OReilly

Ice recrystallization inhibiting polymer nano-objects via polymerization-induced self-assembly (PISA)
Panagiotis Georgiou, Presenter; Ioanna Kontopoulou; Thomas Congdon; Thomas Whale; Matthew Ian Gibson

Oxazoline-methacrylate graft-copolymers with UCST behaviour in oil
Matilde Concilio, Presenter; Nga Nguyen; Remzi Becer

Improving the mechanical properties of aliphatic polyester thermoplastic elastomers through star architectures
Stephanie Liffland, Presenter; Marc Hillmyer

General Topics: New Synthesis & Characterization of Polymers
April 9, 2021

Regioselectivity of organocatalytic ring-opening polymerization in 5-membered cyclic sugar-based carbonates
Yidan Shen, Presenter; Yue Song; Hai Wang; David Tran; Mei Dong; Karen Wooley

Development of hydrolytically labile poly(thioether ketal) thermoplastics
Sarah Lauren Landrum; Reese Sloan, Presenter; Matthew Fisher; William Walker; Benjamin M Alameda; Derek Patton
Functionalized δ-hexalactone (FDHL) monomers to synthesize higher Tg aliphatic polyesters
Atik Faysal, Presenter; Prof. Thomas Schwartz; William Gramlich

Co-continuous polymer networks with tailorable morphologies via ROMP-induced macrophase separation
Jessica Ann Weaver, Presenter; Chukwuemeka Chikelu; Caroline Schauer; Andrew Magenau

Thiol-containing copolymers and polydisulfide networks: synthesis and characterization
Yongneng Wu, Presenter; Devon Shipp

Multifunctional triblock copolymer based on fluoroacylate via polymerization-induced self-assembly (PISA): Synthesis and application as a thin film dielectric material
SIVA PONNUPANDIAN, Presenter; Sarthik Samanta; Andrew Lowe; Nikhil Singha

Imparting new functionality to poly(arylene ether sulfone)s using thiolene chemistry
Brady Hall, Presenter; Andrew Brenner; Michael Schulz

Poly(L-Lactide) chain-end macromonomer synthesis and graft-through ring-opening transesterification copolymerization with γ-methyl-ε-caprolactone
Lucie Fournier, Presenter; Daniela Rivera Mirabal; Marc Hillmyer

Dienes and diamondoids: poly(2-(1-adamantyl)-1,3-butadiene) and random copolymers with isoprene via redox-emulsion polymerization and their hydrogenation
Connor Hill, Presenter; Armando McDonald; Mark Roll

Continuous dimethylidioxirane generation for polymer epoxidation
Grace Putka Ahlqvist, Presenter; Eileen Burke; Jeremiah Johnson; Timothy Jamison

Polymer backbone metamorphosis of polyesters to polyolefins via the Ireland-Claisen rearrangement
Rachael Ditzler, Presenter; Aleksandr Zhukhovitskiy

Exploring polymerization techniques for the polymerization of silyl ketenes as monomers
Sarah Mitchell, Presenter; Emily Pentzer

Versatile homotelechellic bottlebrush polymers via chain-transfer ring-opening metathesis polymerization
Cheyenne Liu, Presenter; Logan Dugas; Robson Storey; Yoan Simon

Dynamic covalent exchange in poly(thioether anhydrides)
Kelly Tillman, Presenter; Rebecca Meacham; Anne Rolsma; Patrick Mather; Devon Shipp

Fully oxygen-tolerant photoinduced ATRP
Dr. Grzegorz Szczepaniak, Presenter; Matylda Lagodzinska; Sajjad Dadashi-Silab; Adam Gorczynski; Krzysztof Matyjaszewski

Application of the Passerini three-component reaction for the chain end modification of end-functionalized polymers with aldehyde groups
Mr. Li Chieh Chou, Presenter; Arisa Hirama; Ryohei Kakuchi

Thiol-ene click engineered late-stage modification: Synthesis of long chain polyurethane dendrimers
Dhruba Poudel, Presider/Presenter, Presenter; Richard Taylor
Multimechanistic polymerization: Iron guanidine complex combines ATRP with ROP
Ruth D. Rittinghaus, Presenter; Sonja Herres-Pawlis

General Topics: New Synthesis & Characterization of Polymers
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Two-dimensional polymerization in a homogenous reaction system: theory and application
Dr. Yuwen Zeng, Presenter; Ge Zhang; Michael Strano

Modeling short-chain branched polyethylenes in dilute solution under variable solvent quality: Basic configurational properties
Wengang Zhang, Presenter; Fernando Vargas-Lara; Sara Orski; Kathryn Beers; Jack Douglas

Cyclic olefin copolymer based anion exchange membranes
Jamie Gaitor, Presenter; Megan Treichel; Tomasz Kowalewski; Kevin Noonan

Using a bottom-up approach to investigate the molecular structure of aqueous poly(N-Isopropylacrylamide) at room temperature via IR spectroscopies
Daniel Kuroda, Presenter

Effect of chemical identity and morphology on water- and salt- transport in amphiphilic-zwitterionic copolymer membranes
Ria Ghosh, Presenter; E Coughlin

Study of dynamic covalent exchange in methacrylic anhydride copolymers
Arielle Santefort, Presenter; Devon Shipp

A 2D Perchlorinated Carbon Framework
Cheng-Hao Liu, Presenter; Yoko Sakai-Otsuka; Thaksen Jadhav; Muhammad Rizwan Niazi; Ehsan Hamzehpoor; Akeala Michels-Gualteri; Dmitrii Perepichka

Covalent adaptable networks: Exploring silanolate networks for self-healing materials
Jordan Kaiser, Presenter; Luke Baldwin

Self-healing tailor-made polymers based on furan derivative and 1,2,4 triazole-3,5-dione (TAD) ‘click’ chemistry
Nikhil Singha, Presenter

Exploring the properties of bottlebrush polypentenamers
Taylor Isais, Presenter; William Neary; Justin Kennemur

Application of an autonomous continuous-flow platform for multi-objective optimisation of polymer synthesis
Dr Stephen T Knox, Presenter; Sam Parkinson; Richard Bourne; Nicholas Warren

Investigation of the Detailed Mechanisms of DBU-Catalyzed PLGA Copolymerization via a Full-Scale Population Balance Analysis
Samruddhi M Patil, Presenter; Jin Yoo; You-Yeon Won

Semi-fluorinated poly(ether imide)s with benzyl ether moiety: Synthesis, characterization, gas permeation study and molecular dynamics simulations
Rimpa Chatterjee, Presenter

Effect of methyl group distribution in sustainable polyglycolide copolymers on material properties
Dynamic in-situ variation of backbone structure during ring-opening copolymerization of carbonyl sulfide with an oxetane derived from D-xylose
David Tran, Presenter; Donald Daresbourg; Karen Wooley

Effect of poly(cyclosilane) microstructure on thermal properties
Qifeng Jiang, Presenter; Syndee Wong; Rebekka Klausen

Degradable polyphosphoramidate via ring-opening metathesis polymerization
Yifei Liang, Presenter; Nathan Gianneschi

Stimuli-responsive properties of pH- and temperature-responsive block copolymers synthesized via ARGET ATRP
Sorfina Suzali; Yunyi Huang; Hunter Koltunski; Henry Liautaud; Colton Carney; Benjamin Hamill; Elizabeth Glogowski, Presenter

General Topics: New Synthesis & Characterization of Polymers
April 13, 2021

Mechanochemistry of metallocene-containing polymers
Yujin Cha, Presenter; Ye Sha; Tianyu Zhu; Chuanbing Tang

Solid-state mechanochemical ring-opening metathesis polymerization
Gue Seon Lee; Jeung Gon Kim, Presenter

Tailorable design and methodical synthesis of structurally and functionally tunable ionenes + ionic liquid composites for high-performance engineering applications

Incorporation of halogen bonding in poly(vinyl ethers) towards the formation of supramolecular materials
Dr. Kira B. Landenberger, Ph.D., Presenter; Yudai Morota; Takanaga Suzuki

Molecular control over dynamic properties in imine-based covalent adaptable networks
Sybren Schoustra, Presenter; Joshua Dijksman; Han Zuilhof; Maarten Smulders

Non-isocyanate polyurethane foams derived from 1,1′-carbonyldiimidazole functionalized precursors
Josh Wolfgang, Presenter; Jose Sintas; Tyler White; Timothy Long

Borane catalyzed ring-opening polymerization, copolymerization and depolymerization reactions controlled by Lewis acid strength
Dr. Francesca M. Kerton, Presenter; Kori Andrea

1,2,3-triazole based poly(ionic liquids) as polymeric dielectrics
Jukka Niskanen, Presenter; Mathieu Tousignant; Alexander Peltekoff; Prof. Benoit H. Lessard

Accessing chemically recyclable polymers through ring-opening copolymerization/depolymerization of strained monomers with unstrained monomers
Connor Gallin, Presenter; Jeffery Byers

Vanillin and soy derived vinyl monomers copolymerization targeting synthesis of latexes with high bio-based content
Yehor Polunin, Presenter; Timothy Burns; Eric Serum; Mukund Sibi; Andriy Voronov

**Design, synthesis and application of precision synthetic biopolymers with defined sequences**
Dr. Ruijiao Dong, Presenter; Rongjun Chen; Andrew Livingston

**Highly selective cationic co-polymerization of 2-MeTHF to bio-based polyether polyols**
Bernhard Stadler; Wietse Smit, Presenter; Sergey Tin; Alexander Kux; Reni Grauke; Cornelia Koy; Michael Glocker; Horst Beck;

Sandra Hinze; Adrian Brandt; Johannes De Vries

**Regioregularity effects on the thermotropic liquid crystalline phase transitions of poly(3-dodecylthiophene)**
Hyeonjung Park, Presenter; Moon Jong Han; Youngkwon Kim; Eun Ji Kim; Hyeong Jun Kim; Dong Ki Yoon; Bumjoon Kim

**Synthesis and characterization of Azulene incorporated polymers as dielectric materials**
K A Niradha Sachinthani, Presenter; Emily Pentzer
Chromophore compatibility in electro optic polymers

Kaitlyn Crawford, kcrawford@ucf.edu, Gavin Pour. Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States

Copper wire is the traditional material to transmit telecommunication information, but the theoretical speed and volume limits, at which electrons can travel through copper wire, are near capacity and cannot accommodate the projected global demands. Compelling solutions using fiber optic cables are on the horizon as, compared to Cu, they can handle 6000x the bandwidth, are of lower cost, lighter weight, and maintain lower temps. In parallel, the global market for optical modulators (necessary fiber optic component) is set to exceed $22B by 2025. This increase coincides with exponentially increasing telecom demands from healthcare, military, and industries. A bottleneck for replacing Cu wire with fiber optic cables is the limited availability of nonlinear optic (NLO) materials that are necessary for optical modulation. Electro optic polymers (EOPs) often include asymmetric chromophores combined with a glassy, amorphous polymer. EOPs can have exceptionally high initial EO responses, but can be short-lived because the anisotropic chromophore orientation becomes lost over time, the chromophores are often unstable, and EO responses can be thwarted by limited poling efficiency. We are addressing limitations of temporal stability, chromophore availability, and poling efficiency of EOPs. In our approach we are expanding the library of our newly discovered family of stable chromophores. We are evaluating the intermolecular compatibility between the chromophore, the selected polymer, and the solvating medium in correlation to EO temporal stability and poling efficiency achieved by our custom-built poling station. Preliminary results suggest a significant influence on chromophore aggregation, observed optical properties, and film quality with respect to solvent choice. During this meeting we will focus on detailed dissemination of these findings, the synthetic methods of our newly developed class of asymmetric chromophores, and their compatibility with glassy, amorphous polymers.
Optoelectronic properties of π-conjugated polymers derived from boron difluoride formazanate dyes

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Organic π-conjugated molecular and polymeric materials exhibit sought after optical and electronic properties due to the delocalization of π-electrons within their frameworks and are often semiconducting. This leads to their use in a variety of organic electronics such as light emitting diodes, lasers, photovoltaic devices, memory devices, etc. One such class of materials include boron difluoride adducts of chelating N-donor ligands that have many interesting properties, including high molar absorptivities and unusual redox chemistry that can be readily tuned through structural variation. Our group works with boron difluoride formazanates, a class of nitrogen rich materials that have found applications as fluorescent cell imaging agents, near-infrared emitters, electrochemiluminescent emitters, multifunctional polymers, and as precursors to a variety of unusual boron-nitrogen heterocycles.

Incorporating platinum(II) into the main chain of organic π-conjugated polymers through acetylenic units is known to significantly improve optoelectronic and redox properties of the resulting materials. In this work, π-conjugated molecular compounds and polymers derived from boron difluoride formazanates will be introduced. One such example is a readily accessible conjugated polymer (2) that couples electron-poor boron difluoride formazanate spacers (1) and electron-rich platinum(II)-acetylide subunits to afford a promising polymer candidate (2) for use in organic electronics that exhibits a narrow band gap and switchable optoelectronic properties. This and other π-conjugated polymers prepared in our lab will be presented.
Tuning molecular fluorescence via controlled polymerization-mediated charge transfer

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It is essential to tune emission color of molecular fluorophores for both scientific research and practical applications. However, owing to the complex interplay between the charge-transfer and singlet excitons, it is highly challenging to obtain multicolor emission from a single fluorophore in solid state. In current study, we report a general strategy for tuning emission color from a single fluorophore by controlled radical polymerization-mediated through-space charge transfer. Using a library of well-defined donor polymers grown from an acceptor fluorophore by atom transfer radical polymerization, we reveal their solid-state emission color can be efficiently tuned by precision macromolecular engineering, including: (i) varying monomer substituent, (ii) transforming end groups, and (iii) tailoring polymer chain length. Both experiments and multiscale modelling confirm that the color tunability originates from the structurally dependent charge transfer process. Thanks to the simple chemical composition, we further demonstrate that such polymer systems can be processed into thin films enabling versatile photolithography.

The single fluorophore-based polymers with increasing molecular weight from left to right
Photoresponsive sponges from azobenzene/Q-type silsesquioxane networks

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High surface area materials are of considerable interest for gas storage/capture, molecular sieving/capture, catalyst supports, slow release drug delivery systems and as scaffolds for photo rearrangeable/healable materials. We have developed a set of facile routes to mechanically robust, hydrophobic polymer networks using fluoride catalyzed hydrolysis and/or hydrosilylation chemistries. These materials offer specific surface areas up to 1300 m$^2$/g, tunable pore sizes, and thermal stabilities above 200 °C. The polymerization times and surface areas can be controlled by adjusting the solvent (type and volume), catalyst and the various cross-linking components. We have also synthesized and characterized a series of photo-responsive materials with photoactive cross-linkers such as dynamic covalent groups, metal ion coordination, and photo-chromic structures. With these cross-linkable groups we are able to change pore geometries to expel fluids or other analytes, and/or decompose the material on-demand to reform it later. Up to 17% reversible volume reductions are possible in photo-isomerizable systems. These materials can find use in healable polymers, capture and release systems and for molecular separations.
Characterizing organic solar cells in space

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Organic solar cells based on polymers can reach an exceptional specific power, i.e. electric power per mass, exceeding their inorganic counterparts by magnitudes. This makes them particularly interesting for space applications. However, research towards extra-terrestrial applications of organic solar cells was mainly restricted to terrestrial conditions so far. We report the characterization of two types of polymer solar cells in space. During a sub-orbital rocket flight, we collected current-voltage characteristics under stable irradiance conditions. In low Earth orbit altitudes, we identify phases of direct solar irradiation and weak diffuse-light irradiation arising from the Earth’s surface by tracking the evolution of short-circuit currents. During phases of strong solar irradiance, both polymer solar cell types (bulk heterojunction absorber PBDB-T:ITIC and PTB7-Th:PC71BM in inverted architecture) achieved a power per area of more than 4 and 7 mW cm⁻², respectively. Thus, the different solar cells reached their performance expectations exposed to space conditions. Even during a phase of being turned away from the sun, the solar cells generated power by collecting faint scattered light from the Earth. These results highlight the suitability of polymer solar cells for near-Earth applications and beyond.

Schematic Overview of the Solar Cell Characterization Experiment on the Rocket Flight.
3D printing of unsaturated polyester networks

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Unsaturated polyester (UPE) resins enjoy numerous uses as structural adhesives in glass fiber laminates, concrete flooring, and masonry repair. Typical UPE resins consist of a UPE oligomer with up to 50 wt\% of a reactive diluent such as styrene, which ultimately provides the cured resin with its thermal and mechanical properties. The ability of these resins to cure rapidly under UV light in conjunction with a photoinitiator makes them amenable to vat photopolymerization (VP) 3D printing. However, the volatility and toxicity of styrene limits the use of traditional UPE resins for VP. This study utilizes a nonvolatile, styrenic-based ionic liquid as a crosslinker to produce UPE resins suitable for VP 3D printing. UPE oligomers containing 0, 25, and 40 mol\% of phthalic anhydride (PA) in the backbone were synthesized to study the effect of saturation content on photocuring kinetics. Utilizing diglyme as a nonreactive, low-volatility diluent provided homogeneous solutions of the UPEs and ionic liquid crosslinker. Photorheological experiments revealed an increasing cure time with increased PA content in the backbone. Likewise, the cure time rose drastically with increasing diglyme content from 20 to 50 wt\%. Photorheology also revealed that the cure time remained largely unchanged upon varying the crosslinker content from 0 to 40 wt\% when all other variables were kept the same. Thermogravimetric analysis further showed an increase in the 5 wt\% decomposition temperature of the cured resins from 215 to 280 °C as the ionic liquid content increased from 0 to 40 wt\%. VP of a selected UPE resin afforded geometrically complex 3D printed structures demonstrating the ability of this method to utilize a common industrial feedstock as part of a novel VP resin. Finally, 3D printed test specimens exhibit ionic conductivities spanning from $10^{-8}$ to $10^{-5}$ S cm$^{-1}$ between 60 and 150 °C indicating a potential additional functionality for 3D printed UPE parts.
Tailoring solid state properties of quadruple hydrogen bonding containing block copolymers

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Nucleobase functionalized supramolecular polymer enables the longevity and recyclability of thermoplastic elastomers due to the formation of physical crosslinks through hydrogen bonding (H-bonding). This work described the influence of H-bonding distribution on the thermoplastic properties and self-assembly of nucleobase functionalized triblock copolymers. RAFT polymerization afforded the synthesis of A-(AB)-A type acrylic triblock copolymers containing cytosine and ureido-cytosine (UCy) functionality. ¹H NMR confirmed the random incorporation of CyA and nBA through the monomer reactivity ratio estimation. DSC revealed the microphase-separated structure of cytosine and UCy-functionalized copolymers, where the glass transition temperature of the central block is similar to that of its random copolymer macro-CTA. Thermomechanical and morphological analysis addressed the effect of the central block H-bonding on self-assembly and microphase-separated morphology. Dynamic mechanical analysis (DMA) revealed multiple tan delta transitions correlating to the glass transition and H-bonding dissociation in the central and external blocks. The UCy-functionalized triblock copolymer possessed an extended plateau window on DMA compared to the cytosine analog. Cytosine-functionalized triblock copolymers exhibited a cylindrical microphase-separated morphology on small-angle X-ray scattering, while UCy-functionalized copolymers showed less ordered structure due to the enhanced H-bonding interaction. Incorporating UCy functionality into the soft block features improved tensile strength, extensibility, and toughness compared to the random analog. Thus, these A-(AB)-A nucleobase-functionalized block copolymers demonstrated the improved mechanical properties for application as thermoplastic elastomers.
Morphology-dependent mechanical properties of shape memory poly(isocyanurate-urethane) (PIR-PUR) aerogels

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This work compares the catalytic activity of several metal ions with a well-known catalyst, dibutyltin dilaurate (DBTDL), in the formation of poly(isocyanurate-urethane) (PIR-PUR) aerogels, and in turn, correlates the variable catalytic activity with the nanomorphology (SEM) and mechanical properties (Dynamic Mechanical Analysis – DMA) of the resulting aerogels. Fourth-period anhydrous salts from FeCl\textsubscript{3} to GaCl\textsubscript{3} as well as InCl\textsubscript{3} and SnCl\textsubscript{4} catalyze formation of PIR-PUR from 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (Desmodur N3300A) and triethylene glycol (TEG) at 20% w/w monomer concentration in acetonitrile. \textsuperscript{119}Sn NMR, indicates that the metal ion first complexes with TEG followed by reaction with the isocyanate. The gelation rate was followed with rheometry, and was found for fourth-period metal ions to increase from Fe to Cu, and decline from Cu to Ga. It was higher with Cu(II) or Cu(I). For equal catalyst concentrations, the fastest gelation (9 min) was observed with CuCl\textsubscript{2} and the slowest with FeCl\textsubscript{3} (5.75 h).

As the catalyst concentration decreased, gelation time increased, and the morphology of PIR-PUR aerogels changed from bicontinuous to spheroidal. For equal gelation times, the morphology was about the same, irrespective of catalyst. A definitive trend was then observed between the elastic modulus (E) and the gelation time – thereby the morphology. The shape memory effect was also analyzed, and the fill factor varied from 0.49 – 0.62. The energy absorption capability was found inversely proportional to the gelation time and varied from 0.019 – 0.089 MJ/m\textsuperscript{3}.

![Graph showing the trend between the elastic modulus (E) and the gelation time.](image)

The trend between the elastic modulus (E) and the gelation time – thereby the morphology.
Development of aqueous size exclusion chromatography conditions to characterize polyzwitterion-block-N-isopropyl acrylamide copolymers

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Block copolymers that exhibit both an upper critical solution temperature and a lower critical solution temperature are difficult to characterize due to inherent solubility difference between the two blocks. For example, accurate determination of both the molar mass and molar mass distribution is challenging for polyzwitterion-block-N-isopropyl acrylamide (NIPAM) copolymers in aqueous solutions due to self-assembly. However, there are a few examples of using size exclusion chromatography (SEC) for characterization, in which hexafluoro isopropanol (HFIP) is used in all cases. Yet, researchers are hesitant to use this solvent due to how expensive and hazardous HFIP is. Therefore, alternatives to HFIP for SEC analysis would be desirable. Here, a systematic methodology featuring aqueous SEC is demonstrated using several solvent conditions to enable the elution of polyzwitterion-block-NIPAM copolymers on Agilent PolarGel and Tosoh TSKgel column sets. These SEC conditions include 0.2 M KI in water on the PolarGel columns and 0.2 M KI/30 % DMF in water on the PolarGel and TSKgel columns. These aqueous systems can be utilized for the characterization of similar water-soluble block copolymers that are relevant for drug delivery and other biomedical applications.
Carbon aerogels derived from poly(tetrahydroquinazoline) for high capacity and selective adsorption of carbon dioxide

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DMF solutions of a tetrahydroquinazoline (THQ) monomer (1) were gelled via HCl-catalyzed ring opening polymerization at 100 °C. Poly(tetrahydroquinazolines) (PTHQ) wet gels (2) were dried with supercritical fluid CO₂ in an autoclave to aerogels, which undergo complete ring-fusion aromatization at 240 °C/O₂. Based on selectively ¹⁵N-enriched materials in combination with solid-state CPMAS ¹³C and ¹⁵N NMR, it was found that the skeletal framework of fully-oxidized PTHQ aerogels includes amide, imide and urea groups. Structure 3 shows a simplified version of the fully oxidized PTHQ backbone. Fully oxidized PTHQ aerogels were subjected to pyrolytic carbonization at 800 °C/Ar yielding carbon aerogels with some microporosity. Etching at 1000 °C under flowing CO₂ increased the micropore volume dramatically. PTHQ-derived carbons were evaluated for their CO₂ adsorption capacity and selectivity towards other gases. CO₂-etched carbon aerogels showed very high CO₂ uptake (11.2 ± 0.9 mmol g⁻¹ at 273 K, 1 bar), which was attributed to pore filling beyond monolayer coverage starting with preferential interaction of CO₂ with surface pyridinic and pyridonic N on carbon (identified by XPS) in a near energy-neutral reaction. The high selectivity of CO₂ versus H₂ in the range of (407 ± 104) is attractive for pre-combustion capture of CO₂ and the high selectivity of CO₂ versus N₂ in the range of (52 ± 18) is attractive for post-combustion CO₂ capture from flue gases.
Highly proton conducting, chemically stable sulfonated polytriazoles based on trifluoromethyl and phosphine oxide moieties for proton exchange membranes

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Proton exchange membrane (PEM) is the main component of fuel cell where it works as a solid electrolyte barrier to proton transfer and prevents fuel crossover between cathode and anode. Sulfonated aromatic ionomer membranes are considered as a promising alternative due to their outstanding PEM properties and variation in molecular design.

In the current investigation, a series of trifluoromethyl and phosphine oxide moieties containing sulfonated polytriazoles (PTPFBSH-XX, XX=60, 70, 80 and 90) is synthesized from a newly prepared diazide monomer, sulfonated diazide and dialkyne via azide-alkyne click polymerization. A well-networked ionic channel for proton transportation has been generated due to the presence of the trifluoromethyl groups, phosphine oxide moieties, basic triazole rings and sulfonic acid groups in the sulfonated polytriazoles. Accordingly, the synergistic effects of such moieties in the polymeric backbone can lead to a promising development to improve the thermal, mechanical, water management and peroxide resistance properties of PEM materials, and help in accomplishing better proton conductivity.

The sulfonated aromatic fluorocopolymers have exhibited excellent stress-strain (tensile strength: 49–72 MPa, elongation at break: 27–48 %) and thermal (10% decomposition temperature: 284–290 °C) properties. The proton conductivities of copolytriazoles are found to be as high as 16–142 mS/cm at 90 °C under fully hydrated state and the activation energies are ranged from 10.6 to 13.9 kJ/mol. The exceptional oxidative stability of polymers (18–39 h) supports its effectiveness even in PEM conditions. The morphological analysis (AFM, SAXS, TEM and SEM) demonstrated nanophase segregated, inter-connected ionic networks of the membranes.

Therefore, this system of new phosphorus containing sulfonated fluorinated polytriazoles can be developed as a feasible prospect of PEM materials.

SAXS pattern of PTPFBSH-XX (XX = 60, 70, 80, and 90) polymer membranes and 3D AFM images (tapping mode) of PTPFBSH-90 polymer membranes.
Balancing processing ease with combustion performance in aluminum/PVDF energetic filaments

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Molecular weight (Mw) effects in poly(vinylidene fluoride) (PVDF) influence both processability and combustion behavior in energetic Al–PVDF filaments. Results show decreased viscosity in unloaded and fuel-lean (i.e., 15 wt% Al) filaments. In highly loaded filaments (i.e., 30 wt% Al), reduced viscosity is minimal due to higher electrostatic interaction between Al particles and low Mw chains as confirmed by Fourier-transform infrared spectroscopy. Thermal and combustion analysis further corroborates this story as exothermic activity decreases in PVDF with smaller Mw chains. Differential scanning calorimetry and Thermogravimetric analysis show reduced reaction enthalpy and lower char yield in low Mw PVDF. Enthalpy reduction trends continued in nonequilibrium burn rate studies, which confirm that burn rate decreases in the presence of low Mw PVDF. Furthermore, powder X-ray patterns of post-burn products suggest that low Mw PVDF decomposition creates a diffusion barrier near the Al particle surface resulting in negligible AlF3 formation in fuel-rich filaments.
Multi-tiered conjugated oligomers as models to examine \( \pi-\pi \) interactions in semiconducting conjugated materials

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The electronic structure of semiconducting \( \pi \)-conjugated materials continues to attract interest through both experimental and theoretical approaches. To explore the effects of intermolecular interactions between conjugated systems, we have embarked on an examination of the electronic structure of a series of molecules in which conjugated segments are held in a stacked arrangement. This arrangement mimics the packing of conjugated molecules in the solid state. Previous work made use of pseudo-geminal disubstituted \([2.2]\)paracyclophane to hold pairs of oligo(phenylene vinylene) segments in a stacked arrangement. The compounds consisting of a stacked pair of conjugated segments emit at longer wavelengths than the corresponding isolated, unstacked oligomers. This emission indicates the presence of a low-energy excimer-like state that arises from the interaction of the \( \pi \)-systems of the two segments. An extension of this work is underway to study compounds which have two, three, and four oligo(phenylene ethynylene) segments held in a multitiered architecture. The oligomers are characterized using UV-Vis and fluorescence spectrometry, and by voltammetry techniques, to determine the evolution of optoelectronic properties as conjugated oligomers are assembled into multisegment architectures.
Direct visualization of diblock copolymer conformation in the subdomain through heavy z-labelling

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Structural features within the subdomain morphology are investigated through direct imaging of labelled linear diblock copolymers. High electron density labels were used to mark the block junctions and α-chain ends. A series of linear poly(methyl methacrylate)-b-polystyrene (PMMA-b-PS) diblock copolymers with varying volume fractions of polystyrene (φPS) were synthesized in a sequential multistep RAFT polymerization. A pentafluoro phenyl ester functionalized chain transfer agent (CTA) was employed to polymerize methyl methacrylate yielding an α-functionalized PMMA macro-CTA. Exploiting the inability of maleimidederivatives to undergo homopolymerization, one single molecule of pentafluoro phenyl maleimide ester was precisely inserted into the chain upon re-initiation. Through the favored cross propagation of maleimide based radicals with styrene, the PS block was formed with high control over the molecular weight and low dispersity. The resulting PMMA-b-PS diblock copolymers undergo a post-polymerization modification step in which electron dense (high Z) monoamino-functionalized T₈ polysilsesquioxane (POSS) cages were grafted onto the preselected sites along the backbone i.e. the free chain-end and the block junction. Successful grafting is evidenced through the absence of pentafluoro phenyl moieties in the ¹⁹F-NMR and appearance of POSS signals in the ¹H-NMR. Films were cast from toluene and characterized through SAXS and Atom Probe Tomography gaining access to 3D imaging and composition measurements on the atomic scale elucidating the chain conformation in melt.
Development of structure-property-processing relationships and thermotropic liquid crystallinity of a series of poly(3-alkylthiophene)s with branched side chains

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Semiconducting conjugated polymers bearing branched side chains have attracted significant attention by virtue of their greater solubility and melt processability compared to analogous materials that have n-alkyl side chains. However, a systematic exploration of the effect of the structure of such side chains on the properties of the materials has not been conducted. In this study we sought to gain an understanding of the relationship between the length of the side chain, location of the branch, and the identity of the alkyl branch on the properties of regioregular poly(3-alkylthiophene)s. Through this strategy we aimed to lower the melting point of the polymers to explore the possibility of thermal processing and the potential to access thermotropic liquid crystalline phases. Increase in solubility of the branched-chain polymers relative to the straight chain analogues, which hinders the formation of aggregates in solution, also provides expanded opportunities to vary processing conditions for the deposition of thin films. Methyl-branched poly(3-hexylthiophene)s and poly(3-decylthiophene)s were prepared and characterized by differential scanning calorimetry and x-ray diffraction, and determination of field effect mobility.
Unique Thickness Relaxation Behavior Characterized in ultra-thin polystyrene films using X-Ray reflectivity: Effect of temperature on physical aging

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With the miniaturization of technology, ultra-thin polymer films have received close scientific attention from the point of view of both physics and technology. It is important to study the ultra-thin films in presence of substrates to understand fundamental phenomena. However, these ultra-thin polymer films exhibit kinetically nonuniform layered structure in which chain mobility at the surface region is high whereas molecular chains at the interface region are strongly bound. As a result, the glassy state of polymer thin films exhibits a strong deviation from the bulk. Therefore, clarification of the mechanism of polymer thin films is necessary scientifically and industrially.

In this study, the time-dependent relaxation process of annealed polystyrene (PS) (M_w=955,000 g mol⁻¹, M_w/M_n=1.09, R_g=30 nm) ultra-thin films (~6nm) supported on SiO₂ were investigated in the temperature range of 30°C (T_g bulk -80°C) to 140°C (T_g bulk +30°C) to understand the relaxation mechanism below, near and above T_g bulk. X-ray reflectivity (XRR) was used to measure the precise change in film thickness, and the data obtained were fitted by the Kohlrausch-Williams-Watts function. Differential scanning calorimetry and XRR were utilized to measure T_g bulk (~110°C) and T_g apparent (~80°C) of 6 nm PS film respectively. An interesting and unusual thickness relaxation behavior in PS ultra-thin films was observed (Fig 1). The ultra-thin films showed positive thickness relaxation (expansion in thickness with time) at temperatures ≤60°C and suddenly reversed its behavior by depicting negative thickness relaxation (contraction in thickness with time) at temperatures ≥70°C up until 110°C and again reversed the behavior for temperatures >110°C. We are currently investigating the thickness relaxation in the temperature range of 60°C to 70°C and 110°C to 120°C to find the temperature where the nature of relaxation is reversed.

**Figure 1.** Normalized time-dependent thickness measurement of the PS obtained at different temperatures.
Charge density and hydrophobicity-dominated regimes in the phase behavior of complex coacervates

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Post-polymerization modification of poly (N-acryloxy succinimide) was used to prepare polycation and polyanion libraries with different charge densities and hydrophobicities. The 54 acrylamide-based copolymers had charge densities ranging from 40-100% and nonionic aliphatic sidechain lengths ranging from 0-12. These polymers were employed to explore the phase behavior of polyelectrolyte complex coacervates prepared using polycation/polyanion pairs with similar charge density and nonionic sidechain lengths. The salt responses were investigated using optical turbidity, revealing that there exist three different regimes in the coacervate phase behavior. For polymers with hydrophilic nonionic sidechains, the salt resistance increases with increasing charge density. For polymers with large hydrophobic sidechains, the salt resistance increases with increasing hydrophobicity. For polymers with intermediate length hydrophobic sidechains, a switch from charge density-dominated to hydrophobicity-dominated behavior is observed at intermediate charge densities. The solubilities of the polyelectrolytes were not directly correlated to their phase behavior, indicating the difficulty of explaining the coacervate phase behavior in terms of changes in the polymer-water interaction parameter, and motivating an urgent need for models of coacervate phase behavior that accurately reflect the molecular-scale interactions at play.
Modular nanoparticle platform for drug delivery application in pancreatic cancer

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In this study we proposed the design principle of a modularly fabricated, nanoparticle-based drug delivery platform composed of Amphiphilic Invertible Polymers (AIPs) layered with alternating layers of hyaluronic acid (HA, 200 kDa) and poly (l-lysine), PLL. This platform is used for encapsulation and targeted transport of a combination chemotherapy against pancreatic cancer (PC). The combination therapy consists of gemcitabine (GEM) and an extra-cellular receptor kinase inhibitor (ERKi), which we have shown earlier to be effective against pancreatic cancer cells. While GEM is a relatively hydrophilic and frontline chemotherapy for PC, poor ligand efficiency and water solubility as well as off-target toxicity are major challenges for clinical translation of ERKi in PC. AIPs are a class of environment-responsive polymers, which shows conformational switch in response to polarity-shift of the environment. This is because, chemical structure of AIPs macromolecules is composed of alternating hydrophilic (PEG) and hydrophobic (PTHF) blocks, conformation of which is controlled by polarity of the surrounding media. We prepared the micellar assemblies of AIPs (AIP nanoparticles) loaded with either GEM or ERKi, first, which were then layered with HA and PLL following established layer-by-layer methodology. Our central hypothesis is based on the fact that when both GEM and ERKi will be encapsulated and transported via polyelectrolyte-layered AIP nanoparticles, synergistic suppression of cancer cells will be achieved due to: (a) chemosensitization of GEM by ERKi (b) increased drug loading achievable for highly hydrophobic chemotherapy, such as ERKi via layered AIP nanoparticles, and (c) targeted transport of the drug combination that will be achieved via active targeting mechanism. In this work, we first present the formation and physico-chemical characterization of HA/PLL layered, drug-loaded AIP nanoparticles, and then present how drug loading, release and in vitro activity can be affected by nanoparticle design.
One-pot, PhotoATRP Induced self-assembly (PhotoATR-PISA) enables simplified synthesis of responsive polymer nanoparticles

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Herein, we demonstrate, for the first time, the use of photo-controlled atom transfer radical polymerization (PhotoATRP) for polymerization induced self-assembly (PISA) using UV light ($\lambda = 365$ nm) and ppm levels (ca. < 20 ppm) of copper catalyst at ambient temperature. Utilizing Cu$^{II}$Br$_2$/tris(pyridin-2-ylmethyl)amine (TPMA) catalyst systems, PISA was accomplished all in one-pot starting from synthesis of solvophilic poly(oligo(ethylene oxide) methyl ether methacrylate) (POEGMA) blocks to core-crosslinked nanoparticles (NPs) utilizing poly(glycidyl methacrylate) (PGMA) and N,N-cystamine bismethacrylamide (CBMA) as the solvophobic copolymer and core-crosslinking agent, respectively. Sequential chain-extensions were performed for PGMA demonstrating potential capabilities for accessing multi-block copolymers with temporal control via switching the UV light on and off and accessing higher order morphologies all in one-pot without any work up. Thermal treatment of the NPs was implemented, revealing low to high order morphology transition occurred with the variety dependent on the original solid content (%) and treatment time. Further, core-crosslinking of PISA nanoparticles all in one-pot was achieved via the slow incorporation of the CBMA during the PISA process and without any interference with NPs' morphology evolution. Finally, the disulfide installed in the CBMA core-crosslinks allowed for the stimuli-triggered dissociation of nanoparticles using DL-dithiothreitol at acidic pH.
Modular synthesis of therapeutic peptide brush polymer nanoparticles via polymerization-induced self-assembly

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Synthetic oligopeptides represent a class of powerful therapeutics because of their biocompatibility, straightforward synthesis, predictable metabolism, and high degree of modularity in molecular design. However, these advantages are typically compromised by natural processes prevalent in cells and tissues that have evolved to degrade them. Moreover, cell internalization of peptides is typically inefficient, often requiring selective cell surface interactions through the use of cell penetrating sequences. To tackle these challenges, we employed one-pot photoinitiated polymerization-induced self-assembly (PISA) to access spheric nanoparticles which are characterized by a high-density display of proapoptotic peptides (amino acid sequence: KLAKLAKKLAKLAK) in the hydrophilic shell. The modularity of peptide brush polymer nanoparticles was evaluated by tuning variables including compositions of the hydrophilic macroCTA and hydrophobic polymer core, giving rise to peptide brush polymer nanoparticles with tunable size (36-105 nm in diameter) and loadings of peptides ranging from 20 to 48 wt.%. Moreover, high concentrations of peptide brush polymer nanoparticles of up to 150 mg/mL were achieved in the photo-PISA process. Emergent properties include both proteolytical resistance and bioactivity, including cell penetration and apoptotic efficiency. All of these features were significantly higher for the peptide brush polymer nanoparticles compared to their linear peptide analogues. These results highlight the potential of photoinitiated PISA in the large scale and modular synthesis of functional, proteolytically resistant peptide–polymer conjugates for intracellular delivery.
Metallopolymers based double-network hydrogel as promising antimicrobial materials with antibiotics

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Double network (DN) hydrogels are composed of two contrasting polymer networks: highly crosslinked electrolyte polymers as the first network and poorly crosslinked neutral polymers as the second network. In order to overcome the low mechanical strength of traditional single hydrogels, DN hydrogels have been extensively exploited in various fields because they could provide high mechanical strength and toughness, and high water content. Metallopolymers based DN hydrogels have been fabricated via a two-step network formation. Because metallopolymers combine a versatile organic polymer framework with functional metals, metallopolymers based DN networks can provide inherent functionalities from organometallic molecules. Taking advantage of the metallopolymers, metallocenium-containing DN hydrogels can embed antibiotics via ion-complexation with metal cations, which have exhibited robust antibacterial activities with synergistic effects of antibiotics and metal-building blocks.
Development of robust hydrogels for biomedical devices with exceptional thermal and chemical stability

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Hydrogels are unique for their high-water content, softness, flexibility, etc. in various fields like tissue engineering, drug delivery, electrophoresis media, ophthalmic lenses, sensors, coatings, etc. Despite beneficial properties, the polymers can be sensitive towards their environment, e.g., to thermal sterilization, which may limit their use in a biomedical application. Many hydrogels are sensitive and readily degrade under application of heat and/or radiation. In this talk, we demonstrate a range of thermally and chemically stable hydrogels which can be a good candidate for hydrogel applications that require thermal and salinity stability. Primary screening of several polymers for hydrolytic and thermal stability in aqueous, elevated temperature up to 150 °C, and neutral, high salinity, or acidic or basic conditions was performed. Homopolymers of sodium styrene sulfonate and N, N’-dimethylacrylamide found to be thermally stable for longer than three months of exposure. We also report the reactivity ratios for the comonomers obtained using Kelen-Tudos and Fineman – Ross methods. Covalently crosslinked, robust hydrogel compositions were developed, that exhibit elastic moduli >3000 Pa at 90 wt.-% water content. We systematically evaluated the effect of temperature, pH, and brine solutions of different ionic strengths on swelling behavior and rate of the hydrogels. The hydrogels exhibited superior resistance towards heat, steam, strong acids and supercritical CO₂. The hydrogels can be synthesized to obtain self – healing capability.
Combination therapy using brain accumulating polymeric nanoparticles for tackling HIV-infected brain reservoirs in drug abuse population

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Human immunodeficiency virus (HIV) infection in the brain and HIV-associated neurocognitive disorders (HAND) are major issues to patients with HIV. Most of the therapeutic options cannot be used to tackle the virus in the brain and treat HAND, due to the inability of antiretroviral drugs and neuroprotectants to cross the blood-brain barrier (BBB). Nano-formulations have shown significant promise in medicine for therapy and diagnosis of various diseases. Recently polymeric nano-formulations made using FDA approved poly(lactic-co-glycolic) acid (PLGA), and polyethylene glycol (PEG) functionalized with a terminal triphenylphosphonium (TPP) cation were shown to accumulate in brain using various animal models. In this work, we examined a combined antiretroviral therapy along with antioxidant- and anti-inflammatory-based neuroprotectants using biodegradable PLGA-PEG-TPP, based polymeric nanoparticle to reduce the burden caused by viral reservoirs in the brain and tackle the oxidative stress and inflammation in astrocytes and microglia. A major achievement in this work is to optimize and deliver antiretroviral drug-loaded nanoparticles which can reduce the viral reservoirs. Data from Elvitegravir and Efavirenz loaded nanoparticles in reducing the viral load will be discussed. HIV-induced neurodegeneration further become worse in the presence of recreational drugs; such as methamphetamine and cocaine. We will discuss our data on therapeutic and protective effects of our antiviral and neuroprotectant-loaded nanoparticle.

Schematic of different drug loaded polymeric nanoparticles for tackling HIV viral load in brain and providing neuroprotection
Designing functional conjugated materials for biological integration

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Organic bioelectronics has recently offered various healthcare technologies such as neural interfacing electrodes, biochemical sensors, and drug delivery devices, with exciting developments on the horizon. Applications in tissue regeneration, for example, allow for the electroactive nature of organic bioelectronic materials to affect cell adhesion, signaling, and fate. Such applications require increased biocompatibility and biofunctionalization, which are limited by the organic semiconductors currently in use. Recently, collagen has been investigated as a biomimetic regenerative medium due to its prevalence in the extracellular matrix and its chemical and mechanical properties, which closely mimic physiological tissue. However, collagen alone fails to facilitate the necessary electroactive processes that could play a vital role in directing and accelerating tissue regeneration. We demonstrate a novel derivative of an organic semiconductor poly(3,4-ethylenedioxythiophene) (PEDOT) that can covalently link to collagenous materials and augment otherwise non-conductive materials with enhanced electroactivity. This is accomplished by synthetically modifying PEDOT with N-hydroxysuccinimide (NHS) activated acid groups that target the amine-rich structure of collagen and thus covalently bind to collagenous materials. The results of this study demonstrate a novel conducting polymer that can augment collagen-rich materials with enhanced electroactivity that may both improve regenerative outcomes and serve as a tool to investigate the mechanistic benefits associated with electrical stimulation of tissue. The outlined approach has potential beyond the functionalization of synthetic biomaterials, to natural decellularized tissue for applications in nerve regeneration and bone growth.
Synthesis and evaluation of polyisobutylene-grafted graphene oxide nanocomposite films with improved oxygen barrier properties

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Oxidative degradation of asphalt mixtures is one of the major causes of roadway deterioration resulting in major expenses for roadway repair. Three molecular weights of amine-functionalized polyisobutylene (PIB-NH₂) were each synthesized and grafted onto a graphene oxide aerogel (aGO) to yield PIB-modified graphene oxide (PIB-g-GO). Nanocomposite films were fabricated using a styrene-butadiene-styrene (SBS) copolymer as a model matrix and PIB-g-GO as a functional additive to explore the influence of PIB-g-GO on oxygen barrier properties of the nanocomposite films. Grafting of PIB-NH₂ onto the aGO was confirmed by thermogravimetric analysis (TGA) and Fourier transformed infrared spectroscopy (FT-IR). Wide angle x-ray scattering (WAXS) was used to determine the d-spacing of the aGO before and after grafting of the PIB-NH₂. Atomic force microscopy was used to determine the platelet size of the aGO and PIB-g-GO. Solution casting was used to create films for oxygen barrier measurements. SBS films were prepared with varying content of PIB-g-GO (0.25 – 1.00 wt.% relative to polymer matrix); films containing unmodified GO and neat polyisobutylene were also prepared for direct comparison. All films were tested in a MOCON instrument for oxygen barrier properties. Films containing unmodified GO exhibited a modest decrease of 22.9% in oxygen permeation while films containing PIB-g-GO resulted in a 41.4 – 62.9% decrease in oxygen permeation.
Adhesion and tie layer resin technology for multilayer packaging

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Tie layer resins are a family of functional polymers which can help bond together or compatibilize dissimilar polymers such as polyethylene (PE) and polyamide or PE and ethylene vinyl alcohol (EVOH). Tie resins are used in a wide range of coextrusion processes such as blown and cast film, extrusion coating/lamination and injection-molding for packaging and non-packaging uses in food, medical, consumer and industrial applications. Typical examples of tie resins include maleic anhydride grafted polymers, ethylene-acid copolymers, ethylene-ester copolymers. The adhesive property of a tie resin is very critical for delivering the total functionality of a multilayer package. It becomes even challenging when the packaging fabrication involves orientation and shrink as stretching and orientation can significantly reduce interlayer adhesion. Orientation of multilayer films is important for various commercial packaging forms, especially when they are related to shrink such as barrier shrink bags, retail skin packaging, shrink films etc. Orientation enhances barrier properties and improves mechanical properties and can support packaging weight reduction. This is of a significant interest in light of sustainable packaging as oriented films can help to reach the goal of packaging waste reduction.

This paper will focus on a review of tie resins and how it impacts adhesion in multilayer packaging. A major emphasis will be on factors such as tie resin formulation (polymer matrix, functional polymer, additives, modifiers), processing conditions and how they impact adhesion in multilayer packaging, specifically in highly oriented structures. The paper will concentrate on journal and patent literature including brief summary of impactful data and will aim to establish fundamental understanding on adhesion in highly oriented structures.

\[
\text{Anhydride} + \text{PA 6} \rightarrow \text{Imide Linkage}
\]

CH₂-C-O \quad \text{H₂N-(CH₂)$_5$-CONH-}

CH₂-C-O \quad \text{N-(CH₂)$_5$-CONH-}
A new class of bio-based triblock copolymer prepared via RAFT polymerization: A potential thermoplastic elastomer

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Thermoplastic elastomers (TPEs) are a class of exceptional polymers. They can show thermoplastic as well as elastomeric properties at the same time and thus can easily be processed, recycled, and reused. In recent times, polymers prepared from bio-resources have been able to attract a great deal of attention because of their green and sustainable background. Terpenes are recognized to be the largest group of natural products and some of them can be used as monomers for polymerization. They are found in several essential oils of many types of plants and flowers, insects, and marine organisms. β-Myrcene (MY), a terpene vinylic monomer, carries the same backbone as that of an isoprene unit, the building unit of natural rubber, and many other synthetic polymers. Because of this very reason, several efforts have been made and reported to synthesize elastomers and elastomeric materials based on MY. In this work, reversible addition-fragmentation chain-transfer (RAFT) polymerization was used to prepare an ABA type triblock copolymer polystyrene-b-poly(β-myrcene)-b-polystyrene (SMS). The poly(β-myrcene) block acted as the soft domain and the polystyrene blocks as the hard domain of the potential TPE. NMR, FTIR & GPC analyses confirmed the successful preparation of the block copolymers (BCPs). Phase-separated morphology of the hard and soft domains for the BCPs was observed via DSC & AFM analyses. The SMS BCPs exhibited a maximum tensile strength of 3.4 MPa and elongation at break of 625% with a remarkably low tension set of 4.12%. Scrapes of the SMS BCPs were also recycled and reused successfully. All of these indicate the potential applicability of the synthesized BCPs as a TPE.

**Synthesis of a bio-based Thermoplastic elastomer via RAFT polymerization**
Novel biobased cyclic diacids for polyamides with tailored functional properties

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Current efforts for developing biobased monomers focus primarily on retrosynthetic pathways to provide direct replacements to petrochemicals. An alternate strategy includes utilizing “bioprivileged” platform intermediates to access novel monomers with properties that are not readily accessible from petroleum. Muconic acid, obtained through fermentation of sugar or lignin, has been identified as a bioprivileged compound key to the production of unsaturated diacids that can substitute for adipic acid and terephthalic acid to manufacture polyamides and polyesters with tailored functional properties.

In this study, trans,trans-muconic acid (ttMA) was reacted with ethylene using Diels-Alder chemistry to produce an unsaturated cyclic dicarboxylic acid. This molecule was further co-polymerized with hexamethylenediamine and adipic acid, at 10 and 25 mol\% diacid replacement. The properties of the resulting cyclo-aliphatic polyamides were analyzed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The insertion of the cyclic diacid into Nylon’s aliphatic backbone altered its crystallinity thereby reducing its melting temperature. Additionally, the polymers exhibited an increased glass transition temperature and higher storage modulus than conventional Nylon-6,6. Next, ttMA was reacted with various vinyl-bearing groups for targeted property enhancements such as improved hydrophobicity and flame retardance. These functionalized cyclic diacids were incorporated back into the polyamide backbone to test their end-use performance. Overall, this study demonstrates the potential of bioprivileged molecules in producing novel monomers with tuneable properties.

Copolymerization of biobased cyclic monomer with adipic acid and hexamethylene diamine
Expanded versatility of hydroesterificative Polymerization via bioderived monomers

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The hydroesterificative copolymerization of bioderived α,ω-enols such as 10-undecenol (derived from castor oil) and CO has been demonstrated to give polyester. Novel monomers for hydroesterificative polymerization have been made through the combination of 10-undecenol and diol building blocks: isosorbide, p-xylene glycol, and ethylene glycol. A screen of various pressures, acids, and phosphine ligands has enabled polymerizations at lower pressures and with a commercially available catalyst system. Moderate molar masses (Mₙ = 6-10 kg/mol) were achieved using a simple catalyst system of Pd(OAc)₂, PPh₃ and TsOH·H₂O. The resulting polymers were found to give a range of glass transition temperatures (-19 to 15 °C), dependent on the monomer functional groups. Additionally, this polymerization technique has been shown to work with bioderived monomers made from 10-undecenol and feedstocks such as vanillin and 5-hydroxy-2-methyl-furfuraldehyde. This demonstrates the effectiveness of hydroesterification to access bioderived polyesters with attractive cyclic and aromatic features.
Comparative studies of the sorption behavior of agricultural chemical with engineered soil surrogates (ESSs) and real soils

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The population of the world is increasing day by day and expected to reach 9.7 billion by the year 2050. The rapid human population growth coupled with increasing consumption of foods creates unprecedented pressure on soils. The overuse of the agricultural land, and also the use of various agricultural chemicals such as fertilizers, pesticides, etc., will lead to unsustainable degradation of soils that is not well understood. Furthermore, the molecular-level interactions of compounds added to soils, such as agricultural chemicals, are not very well known. The complex and heterogeneous nature of the soils, which varies from location to location, environment, and human activities, makes the study of the soils very challenging. Therefore, synthesizing a natural mimics of soil, referred to as Engineered Soil Surrogates (ESSs), to relate their bulk properties with structural compositions is anticipated to overcome these limitations. ESSs that are polymeric in nature are envisioned to be synthesized by atom transfer radical polymerization (ATRP). These polymeric ESSs should consist of the following components: silica particles as mineral, linear hydrocarbons of varying chain length to represent lipids, oligo(O-aryl) groups consisting of hydroxy, methoxy, and acetyl substituted aromatic groups to mimic lignin, and cyclic glucose oligomers (O-alkyl) to represent polysaccharide residues of soil organic matter (SOM) present in the soils. Therefore, the primary goal of this study is to synthesize a series of ESSs and compare the sorption behavior with that of the real soils such as Pahokee peat.

Model of the ESSs
New and atom economic synthetic route towards a bio-based angelica lactone-norbornene polymer

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In the last decades, our society is facing the unprecedented challenge of moving away from a fossil-based economy due to environmental and socioeconomic constrains. Switching to a renewable-based chemical economy can be achieved in many ways. Platform chemicals are compounds promptly obtained in high yields from renewable resources either chemically or by fermentation. They can be further converted to a number of useful compounds (e.g. fine chemicals, monomers for polymers etc.). Levulinic acid (LA) represents a prominent example of this class, being produced by acidic degradation of lignocellulose. LA itself has been employed in the synthesis of a wide range of chemicals, e.g. herbicides, solvents, fuels. One example of a useful compound which can be obtained from LA via dehydration under acidic conditions is alpha-angelica lactone (α-AL). The latter has been studied as monomer in photo- and cationic-vinyl polymerizations, where however it affords only sticky colourful oligomers, and in ring-opening polymerization, showing problems in controlling the selectivity. Our group focused on the preparation of monomers by modifications of the carbon-carbon double bond. The beta-isomer of AL (α,β-unsaturated lactone) can be obtained under solvent-free conditions in the presence of catalytic amounts of base. β-AL reacts with cyclopentadiene in a Diels-Alder reaction, affording the norbornene-derivatized lactone. Functionalized norbornenes have already been reported as useful monomers for adhesives, shape-memory materials, and polymer-based electrolytes. We employed ring-opening metathesis polymerization (ROMP) of the adduct to obtain a new bio-based material. A variety of solvents were effective, ethyl acetate being the most promising due to its safety, low toxicity, and the living behaviour of the polymerization. The polymer can be cast into films with good transparency, making them suitable for optical wave guides or transparent coating applications. Due to the lactone moiety, the material shows reduced hydrophobicity compared to pure polynorbornene.
From α to δ: converting pine tree sap into monomers for ROMP

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Pinenes present an excellent class of biomass chemicals, as these xylochemicals can be harvested in large quantities, non-destructively, from some of the most abundant tree species on Earth. A facile synthesis will be discussed that converts the most abundant terpene into a 100% biomass-based monomer that is well suited for chain-growth polymerization. The polymerization itself is shown to be robust and high yielding as a result of the unique structure of the monomer. Polymers resulting from this pathway contain highly precise microstructures containing high regioregularity as well as a retention of stereochemical information. The advantages of the monomer, an overview of the polymer and its’ properties, as well as an overall discussion of the robustness of the polymerization will all be discussed.
Non-isocyanate polyurethanes for thermoplastics and foams: opportunities for green chemistry and sustainability

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The interest for monomers with reduced toxicity and broader applications is driven in part by the green chemistry revolution. As synthetic chemistries continue to develop, the desire to infuse sustainability into research catalyzes the development of new pathways for polymer synthesis. One such example is the utilization of carbonyldiimidazole (CDI) to drive the isocyanate-free synthesis of polyurethane foams and thermoplastics in a solvent-free, catalyst-free process. The versatile reactivity of CDI enables new families of bis-carbonylimidazole (BCI) monomers, which readily react with amines to form linear and crosslinked polyurethanes. Aliphatic and aromatic diols react with CDI to form these BCI monomers at high yields. Reacting these BCI monomers with triamines in the melt results in foaming caused by the thermal degradation of the BCI monomer to produce CO₂. This new CDI chemistry presents the potential for new structure-property relationships for high performance applications and safer engineering platforms for manufacturing while simultaneously implementing green chemistry. The elimination of petroleum-derived solvent, while simultaneously increasing the versatility of the final polyurethane harmonizes BCI monomers with green chemistry. Current research focuses on understanding the fundamental structure-property relationships in the isocyanate-free CDI system with the goal of creating a more circular use for polyurethanes globally.
Dynamics of blended versus grafted thermo-responsive polymers in cellulose nanocrystal nanocomposites

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Cellulose nanocrystals (CNCs) have been exploited due to their natural assembly to helicoidal structures that have potential applications in advanced materials. However, the persistent layer of water surrounding CNC rods hinder effective interfacial adhesion between CNCs and polymer systems, compromising efficient stress transfer between the two components. Understanding the interplay between water and local polymer dynamics at the CNC-polymer interface is paramount to optimizing macroscopic mechanical performance. Therefore, we designed a series of CNC composites with poly(diethylene glycol methyl methacrylate) (PMEO₂MA), a thermoresponsive polymer with lower critical solution temperature of 26 °C in water. By incorporating a water sensitive dye (RhB) into the thermoresponsive polymer, we were able to use fluorescence lifetime imaging microscopy (FLIM) to probe the local dynamics in response to water. Nanocomposite films containing 5% to 100% weight percent of blended and grafted PMEO₂MARhB were prepared via controlled evaporation-induced self-assembly. In blended PMEO₂MARhB-CNC system, the fraction of confined polymers at the CNCs interface decreases with increasing polymer loading, resulting in shorter fluorescence lifetimes. On the contrary, longer fluorescence lifetimes were observed for grafted PMEO₂MARhB-CNC due to polymer chains being restricted to the CNC rods’ surface. Observation of transient polymer dynamics was performed by exposing the nanocomposite films to variation of relative humidity.
The vibrant interplay of elemental sulfur and polymer chemistry to address global challenges

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Given that polymers are among the most important man-made materials, one dominant challenge in polymer chemistry is to identify novel resources which can substitute the finite supply of petrochemicals. Concurrently, the development of new polymers that address this concern is imperative to improve the standpoint for environmental benefit. On the one hand, converting elemental sulfur, the by-product of the petroleum industry, into useful polymers and related materials is ever-evolving way to address the challenges raised by waste valorisation. On the other hand, multicomponent reactions that benefit from inherent modular character, easy reaction setup, and high tolerance towards diverse functional groups ensure sustainable synthesis patterns. Accordingly with the idea to overcome global challenges and minimize sulfur resources, herein, we introduce innovative polymerization methods to deliver new class of polymers. To achieve this, we explore the applicability of cost-effective multicomponent redox condensation of elemental sulfur as a novel polymerization approach to deliver two previously unknown polymer classes, namely poly(thiomalonamide)s and poly(imidazothione)s. The developed synthesis protocols proceed with the merits of mild conditions, broad substrate scope, operation simplicity and metal-free conditions. Last but not at least, to enrich the product structures of the multicomponent redox condensation of elemental sulfur, the synthesis of so far unprecedented alternating copolymers based on 2,4-thiophene/arene repeating units was also studied. It is anticipated that the cost-effective multicomponent redox condensation of elemental sulfur would enable the creation of novel polymers which could be used in real-life nanotechnological applications.

(poly(2,4-thiophene)s)

(poly(thiomalonamide)s)

(poly(imidazothione)s)
Precise synthesis of high performance polyolefin materials from only ethylene feedstock

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High performance polyolefin materials are widely used in military, aerospace, medical and other high-end industries. In this report, a variety of high-end polyolefin materials are prepared with various late-transition-metal catalytic systems by only using ethylene as the feedstock. Late-transition-metal catalysts possess many unique and practical features, such as the ability to synthesize branched polyethylene using only ethylene as the feedstock and the ability to directly copolymerize ethylene with polar comonomers for the synthesis of polar functionalized polyolefins. Moreover, the molecular structure of catalyst has a decisive influence on polymerization activity and polymer microstructure. By modulating the structures of the late-transition-metal catalysts and the polymerization conditions, controlling the chain transfer and chain walking process in the ethylene polymerization, various high-performance polyolefin materials such as polyolefin thermoplastic elastomer, polyolefin synthetic lubricating oil and ultra-high molecular weight polyethylene (UHMWPE) can be precisely synthesized by only using ethylene as the feedstock. Polar functionalized polyolefins can also be prepared directly with the aid of a small amount of polar monomers.
A facile synthesis of derivatives of tetraphenylcyclopentadienone and dendritic polymer via symmetrical functionalization of 2,5-diaryl-3,4-diphenylcyclopentadienone

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A proficient and quick approach is used for the synthesis of tetraphenylcyclopentadienone and their derivatives (3, 3a-k) with the use of sodium ethoxide as a catalyst. Using the developed protocol, a series of 2,5-diaryl-3,4-diphenyl and 2,3,4,5-tetrarylcyclopentadienones have been prepared in high yields (up to 95%). Further the symmetrical functionalization of 2,5-diaryl-3,4-diphenylcyclopentadienone is carried out in four steps. The reduction (step I: formation of amine) of the nitro groups present in the 2,5-bis-(4-nitropheny1)-3,4-diphenylcyclopenta-2,4-dienone 3a to get the 4 which further reacted with 2-Bromo-2-methylpropionyl bromide to produce 5 (step 2: formation of amide). The resultant 5 was served as initiator to proceed with the atom transfer radical polymerization (ATRP) of tert-butyl acrylate (t-BA) to yield 6 (step 3: formation of ester), in which the ester side groups were loaded to acid-catalyzed hydrolysis (step 4: formation of acid) to get the dendritic polymer 7. All the derivatives were characterized by spectroscopic techniques. The important features of the present protocol are very short reaction times, performance simplicity, high yields and synthesis of dendritic polymer, would show high luminous efficiency, good thermal stability and can be fabricated into organic light-emitting diodes (OLEDs).
Chain-straightening polymerization of olefins to form polar functionalized semi-crystalline polyethylene

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We report the synthesis and study of a sandwich α-diimine Pd(II) catalyst capable of copolymerizing functionalized and long-chain α-olefins into semi-crystalline polyethylene-like materials. The combination of a Pd center to promote rapid chain-walking and a sterically demanding DBB sandwich ligand to promote [2,1]-insertion resulted in a highly selective chain-straightening polymerization of α-olefins, yielding polymers with melting temperatures up to 120 °C. ¹³C NMR and isotope labelling studies revealed that at 1.0 M 1-decene, the catalysts exhibits just 4% regio-insertion errors and 6% propagation errors, resulting in 90% chain-straightened material. This high level of net [ω,1]-enchainment is much higher than related (α-diimine)M (M = Ni or Pd) catalysts. In addition, the Pd catalyst has good functional group tolerance and copolymerizes 1-decene and methyl decenoate into semi-crystalline ester-functionalized polymers with incorporation percentages proportional to the comonomer ratio (up to 13 mol%).
RAFT dispersion polymerisation of lauryl methacrylate in ethanol-water binary mixtures: synthesis of diblock copolymer vesicles with deformable membranes

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Polymerisation-induced self-assembly (PISA) is widely recognised to be a powerful platform technology for the rational synthesis of diblock copolymer nano-objects. RAFT alcoholic dispersion polymerisation is an important PISA formulation that has been used to prepare block copolymer spheres, worms and vesicles. In this study, we have utilised the RAFT dispersion polymerisation of lauryl methacrylate (LMA) using a poly(N-(2-methacryloyloxy)ethyl pyrrolidone) (PNMEP) stabiliser in order to prepare vesicles with highly deformable membranes. More specifically, a PNMEP₂₈ macro-CTA was chain-extended with LMA in an 80:20 w/w ethanol-water mixture to produce a series of PNMEP₂₈-PLMAₓ diblock copolymer nano-objects (Mₘ/Mₙ ≤ 1.40; LMA conversions ≥ 99% in all cases, as indicated by ¹H NMR spectroscopy). Differential scanning calorimetry studies confirmed that the membrane-forming PLMA block had a relatively low glass transition temperature. Transmission electron microscopy and small angle X-ray scattering were used to identify copolymer morphologies for these highly asymmetric diblock copolymers. A mixed sphere and vesicle morphology was observed when targeting x = 43, while polydisperse vesicles were obtained for x = 65-151. Slightly smaller vesicles with lower mean aggregation numbers and thicker membranes were obtained when targeting higher PLMA DPs. A minor population of sheet-like lamellae was observed for each target copolymer composition, with lamellar stacking leading to a structure peak in the scattering patterns recorded for PNMEP₂₈-PLMA₁₂₉ and PNMEP₂₈-PLMA₁₅₁. Bearing in mind potential industrial applications, RAFT chain-end removal strategies were briefly explored for such PNMEP₂₈-PLMAₓ vesicles. Thus, 96% of dithiobenzoate chain-ends could be removed within 3 h at 50 °C via LED irradiation of a 7.5% aqueous dispersion of PNMEP₂₈-PLMA₈₇ vesicles at a wavelength of 405 nm. This appears to be an attractive method for RAFT chain-end removal from diblock copolymer nano-objects, particularly those comprising highly hydrophobic cores.
Synthesis and aqueous solution properties of shape-shifting stimulus-responsive diblock copolymer nano-objects

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We report the synthesis of poly(2-(N-(acryloyloxy)ethyl pyrrolidone)-poly(4-hydroxybutyl acrylate) (PNAEP₈₅-PHBAₓ) diblock copolymer nano-objects via reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization of 4-hydroxybutyl acrylate (HBA) at 30 °C using a highly efficient one-pot protocol. Given the relatively low glass transition temperature of the PHBA block, these nano-objects required covalent stabilization prior to transmission electron microscopy (TEM) studies. This was achieved by core crosslinking using glutaraldehyde, which reacts with the pendent hydroxyl groups between neighboring PHBA chains to form acetal linkages. TEM analysis of the glutaraldehyde-fixed nano-objects confirmed that pure spheres, worms or vesicles could be obtained at 20 °C in acidic aqueous solution (pH 3) simply by varying the mean degree of polymerization (x) of the PHBA block. Aqueous electrophoresis, dynamic light scattering and TEM studies confirmed that raising the dispersion pH above the pKa of the terminal carboxylic acid group located on the PNAEP chains was sufficient to induce a vesicle-to-sphere transition. ¹H NMR studies of linear PNAEP₈₅-PHBAₓ diblock copolymer nano-objects indicated that this change in morphology was accompanied by an increase in the degree of hydration of the PHBA chains. A series of PNAEP₈₅-PHBA₃₄₀-₃₇₅ worms formed free-standing gels in acidic aqueous solution owing to multiple inter-worm contacts. Rheological studies indicated that the critical temperature corresponding to the maximum worm gel viscosity, |η*|, could be tuned from 2 °C to 50 °C by adjusting the PHBA DP, with significantly stiffer worm gels being obtained for longer PHBA blocks at lower temperatures. This ability to tune the worm gel viscosity is likely to be important for their use as a wholly synthetic biocompatible matrix for either long-term 3D cell culture or stasis induction studies. However, this would require worm gels to be generated at neutral pH, rather than acidic pH.

![Synthesis of shape-shifting PNAEP₈₅-PHBAₓ diblock nano-objects](image)
The synthesis of polycycloolefins through vinyl-addition polymerization

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The polymerization of cycloolefin monomers remains an area of interest due to the unique physical properties of the resulting polymers. While cycloolefin monomers can be homopolymerized through a variety of methods, radical and ionic polymerizations are prone to rearrangement and chain transfer reactions that yield undesired oligomeric products. Conversely, ring-opening metathesis polymerization often requires a highly strained cyclic olefin (e.g., norbornene derivatives), limiting the scope of applicable monomers. Vinyl addition polymerization has also been shown to polymerize cyclic olefin monomers, however, homopolymerizations are limited to norbornene and cyclopentene derivatives. To overcome these limitations in the polymerization of cyclic olefins, we sought to study the polymerization process and their thermomechanical properties. Herein, homo- and copolymers of cyclononadiene and 1,2-nonadiene were synthesized using the catalyst, [{(π-allyl)NiOCOCF₃}₂]. All polymers were obtained in high yield (up to 97%), and it was found that the cyclononadiene polymerization proceeded six times faster than that of 1,2-nonadiene. The homopolymerization of both monomers exhibited living character, suggesting that block copolymers may be accessed via this method. We also demonstrated that the thermomechanical properties of the resultant polymers could be tailored by varying the feed ratio of cyclic (cyclononadiene) to acyclic (1,2-nonadiene) monomers. Lastly, we found that cycloallenes with multiple ring sizes could be polymerized through this method. We anticipate that this study will serve as the foundation for further studies into poly(cycloallene) development.

Synthesis of cycloolefin polymers and the kinetic plot of the polymerization of cyclononadiene (red) and 1,2-nonadiene (blue).
Design, synthesis, and characterization of melt-processible vinyl-addition polynorbornenes

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Unsubstituted vinyl-addition polynorbornene (VAPNB) possesses many outstanding properties, such as high thermal, chemical, and oxidative stabilities, which makes it a promising candidate for engineering and high-performance applications. However, VAPNB’s limited solubility in common organic solvents, brittleness, and narrow service window between its glass-transition temperature ($T_g$) and decomposition temperature ($T_d$) limit its processability and overall utility. While studies have shown that the solubility of VAPNB may be dramatically enhanced by the introduction of side-chain moieties, thereby facilitating solvent processing to yield robust films, their overall industrial appeal would be enhanced if they could be melt-processed into various form factors.

Herein, we describe our efforts to develop melt-processable VAPNBs (service window $>$ 100 °C) via monomer design. In this work, a systematic series of VAPNBs with various functional groups were synthesized using a Pd-based vinyl-addition catalyst. This library of materials is used to examine the relationship between molecular structure and thermal properties. The $T_g$ and $T_d$ of homopolymers and copolymers were characterized by multiple techniques, including modulated DSC, DMA, ellipsometry, and TGA. Furthermore, $T_g$ prediction curves were also constructed and compared to experimentally determined values. We found that the resulting (co)polymers possessed sufficiently suppressed $T_g$'s and consistently high $T_d$ values to yield a tailored service window of $>$ 100 °C while maintaining a $T_g$ $>$ 150 °C. Finally, we demonstrated the melt processibility of select VAPNBs by melt extrusion and characterized their mechanical properties via tensile testing.
Incorporation of siloxane linkages into commodity polymers as a path towards backbone cleavage and exchange

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Plastics have fundamentally shaped modern life, however a significant challenge arises when examining end-of-life options. Most plastic materials are not or cannot be recycled and end up either in a landfill or leaching into the environment. The strictly carbon backbones of most commodity polymers pose a challenge in terms of breakdown and recycling due to a lack of reactivity. Siloxane linkages provide a promising route to address this lack of reactivity as they are known to be dynamic in nature and cleavable with acids or bases. Synthesis of a new class of difunctional atom transfer radical polymerization (ATRP) initiators containing MM-disiloxane linkers allowed for incorporation of the linkage into the backbone of commodity polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). The synthesized polymers were susceptible to cleavage and exchange in solution with the presence of an acid catalyst, as evidenced by gel permeation chromatography results. Ability to cleave traditionally unreactive polymers provides a mild method of decreasing molecular weight, leading to lower viscosity and allowing for easier reprocessing. Additionally, cross-exchange between vinyl polymers of different identities may allow for in situ compatibilizer formation through the creation of AB diblock copolymers with potential applications in multilayer packaging as an adhesive or tie layer.
Insight mechanism of anionic ring-opening polymerization in ionic liquids

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Ionic liquids (ILs) are widely used as a green solvent both in academics and industry for a wide range of chemical reactions. In the field of polymer chemistry, many cationic and radical polymerizations in ILs have been reported(1). In contrast, anionic polymerizations in ILs have been largely unexplored due to the incompatibility of strong bases with many ILs(2). We have recently discovered that activated aziridine anionic polymerizations(3) are compatible with many ILs. This is due to the relatively low basicity of the propagating anions. Our efforts to understand the impact of ILs on the polymerizations of aziridines will be discussed.
Synthesis of cleavable polymers by the introduction of dynamic covalent bonds within the backbone

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One of the major barriers for degradation/depolymerization of commodity plastics is the chemical and thermal resistance of the strong C-C bonds in polymer backbones. Introduction of dynamic covalent bonds such as siloxane linkages would allow for the cleavage of the polymer backbone with possible avenues for reprocessing/recycling. In our study, siloxane linkages were introduced at a specific location in the polymer backbone which allows for scission and exchange of the polymer strands using a catalyst, fluoride source is commonly used. Performing atom transfer radical polymerization (ATRP) using initiators containing siloxane linkages on styrene or methyl methacrylate as model systems, we synthesized polymers with cleavable and exchangeable linkers. Exchange of siloxane linkage between the above-mentioned polymers and 1,3-divinyl tetramethyldisiloxane (DVTMS) using Tetra-n-butylammonium Fluoride (TBAF) as the catalyst was performed. Characterization by gel permeation chromatography (GPC) shows reduction of molecular weight by a factor of two, consistent with cleavage at the mid-point. NMR spectroscopy ($^1$H, $^{13}$C) demonstrates the incorporation of a vinyl end-group from exchange with DVTMS. Further elaboration of the reactive end-group is possible by using known vinyl chemistries. The findings from the cleavage experiments reveal the potential of utilizing dynamic covalent bonds in the field of chemical upcycling of plastics. Incorporation of siloxane linkages can be a strategy for developing a much-needed closed loop of chemical/polymer circularity.
Reactive MT copolymers based on phenylsilsesquioxane

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Polysilsesquioxanes with an empirical structure of (RSiO\textsubscript{3/2}) are a sub-class of silicones that has been studied in detail and significant literatures are available on both cage-like polyhedral oligomeric silsesquioxanes (POSS) and higher molecular weight linear polymers that are often described as having ladder or ladder-like structures. Materials of this composition are also used and described as T-resins (using the MDTQ silicone nomenclature) in numerous applications. Our interest is in new isomeric silicones and we have begun a program to study MT resins that have been neglected in the literature for reasons that are not apparent. Phenylsilsesquioxane was chosen as the T component (T\textsuperscript{T}) for reasons which include that the homopolymer is the most studied polysilsesquioxane. Initial studies used trimethysiloxy (M), hydridodimethysiloxy (M\textsuperscript{H}) and vinylidimethysiloxy (M\textsuperscript{V}) as M components. M\textsuperscript{H} and M\textsuperscript{V} were chosen to take advantage of the well-developed and important platinum-catalyzed hydrosilylation curing chemistry. Figure 1 shows examples of a hard objects that were prepared from low viscosity precursors.
One step forward in emulsion thiol-ene photopolymerization

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Emulsion polymerization processes, also referred to as polymerizations in dispersed systems, offer a range of synthetic routes to polymer particles of variable size from nanometer to micrometer range. This technology, in particular emulsion and suspension polymerization, has resulted in high tonnage industrial applications, including coatings or inks, as well as niche applications in drug delivery and immunoassay. However, the conventional approach for conducting an emulsion polymerization process relies exclusively on chain-growth radical polymerization using thermal or redox radical initiators. Therefore, finding new means to expand this process industrially beyond chain radical polymerization is highly desirable. Herein, we report the successful photoinitiated thiol-ene radical polyaddition of an emulsion based on two bifunctional thiol-ene monomers. This novel process offers a range of advantages: flash kinetics, tunable molecular weight, high solid contents, low monomer residues, facile process up-scaling. Moreover, it has been successfully shifted toward visible light irradiation, therefore increasing the safety aspect and greener in terms of energy consumption. This new step photopolymerization in emulsion thus opens an avenue for the synthesis of linear polysulfide latex for diverse applications.
Aluminum-based initiators from thiols for epoxide polymerizations

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We developed a novel aluminum-based initiator that facilitated polymerization of various epoxides (epichlorohydrin, propylene oxide, etc.) up to molecular weights of 100 kg/mol while maintaining relatively narrow polydispersity. The initiator was synthesized through a thiol ligand and trialkyl aluminum reaction, with the thiol ligand choice enabling polymer end group control. Copolymerization of epichlorohydrin and propylene oxide demonstrated the ability of this method to control polymer architecture. We further investigated catalyst concentration and initiator structure on the kinetics of epoxide polymerizations through \textsuperscript{1}H NMR spectroscopy. Finally, we combined our polymerization method with another facile method, reversible addition-fragmentation with chain transfer (RAFT) polymerization, to synthesize block-co-polymers made from vinyl and epoxide monomers. To do this, we made a macroinitiator from polystyrene (PS) and poly(methyl methacrylate) (PMMA), synthesized by RAFT polymerization, and further polymerized epoxide from it. Therefore, this new synthetic tool allows for the facile and controlled polymerization of epoxides into well-defined, functional polyether materials.

General scheme for polymerization and copolymerization of different epoxides using BnSAI\textsubscript{2}Me.
Aqueous ring-opening metathesis polymerization-induced self-assembly (ROMPISA)

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Metathesis chemistry has emerged as versatile technology, facilitating polymerization under a broad range of reaction conditions. To date, numerous catalysts have been developed which mediate metathesis in aqueous media. However, most reports involve the laborious preparation of water-soluble Ru-based catalysts, which often exhibit poor performance in water due to slow dissociation of the solubilizing ligands. We recently reported an alternative strategy for conducting controlled ring-opening metathesis polymerization (ROMP) in aqueous media. Our strategy involved polymerization of a water-soluble monomer in a water-miscible solvent to produce an active catalytic species. Chain-extension of the resulting macroinitiator in water proceeded with unprecedented control for all of the monomers tested. This strategy was further extended to prepare nano-objects of various morphologies via ROMP-mediated polymerization-induced self-assembly (ROMPISA).

To date, a limited number of compounds have been identified that are suitable as core-forming ROMPISA monomers. Recently, we developed a methodology to predict monomers for RAFT-mediated PISA that evaluates changes in polymer hydrophobicity with increasing chain length. We have since adapted this method to predict monomers for aqueous ROMPISA. This computational strategy also provides information about the dependence of nanoparticle morphology on polymer hydrophobicity, which has facilitated the discovery of relationships between monomer structure and the nature of the resulting nanostructures.

Our ROMPISA approach has also been successfully applied for the development of tubular polymersomes via 1D fusion of spherical counterparts. This out-of-equilibrium morphology was found to arise spontaneously during ROMPISA, and the composition of each formulation could be manipulated simply by targeting different core-block degrees of polymerization. We termed this unique phenomenon “polymerization-induced polymersome fusion”, which operates via the build-up of membrane tension exerted by the growing polymer chains. Based on our findings, we envision that our methodology will be generally useful for a broad variety of biotechnological applications.
Ice recrystallization inhibiting polymer nano-objects via polymerization-induced self-assembly (PISA)

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Ice growth is a major problem in cell storage, infrastructure maintenance and in food industry. Chemical tools to modulate ice formation/growth have great (bio)technological value. Existing solutions to control ice growth have focussed on using antifreeze/ice-binding proteins from extremophile organisms, while recently polymeric inhibitors have emerged. Previous reports of nanomaterial architectures containing ice recrystallisation-active macromolecules did not show enhancements in activity. In contrast, native antifreeze proteins show size and aggregation state-dependent activity, which we have successfully mimicked here. In this work, the concept of using polymerization-induced self-assembly (PISA) to generate unique nanomaterials that are capable of inhibiting ice growth is shown for the first time.

We introduce polymer nanomaterials that are potent inhibitors of ice recrystallisation using PISA, employing steric stabilizing polymers known to inhibit ice growth such as poly(vinyl alcohol) and others, with not any known activity such as PEG, and poly(vinyl pyrrolidone) (PVP). Crucially, engineering the core-forming block with poly(diacetone acrylamide) enabled PISA to be conducted in saline media, whereas poly(2-hydroxypropyl methacrylate) cores led to nanoparticle coagulation.

In the first case, a PVA graft macromolecular chain transfer agent was developed to perform PISA and the most active particles inhibited ice growth as low as 0.5 mg.mL⁻¹, and were more active than the PVA stabiliser block alone, showing that the dense packing of this nanoparticle format enhanced activity. PEG and PVP coronas were also active when assembled into nanoparticle formulations, whereas the core-block composition had no impact. This challenges the hypothesis that specific ice-binding domains are essential for activity. Larger nanoparticles demonstrated higher activity than smaller ones, but ice-nucleation activity was not observed in this case. This approach offers a platform towards ice-controlling soft materials using a broad range of polymers which are synthetically accessible and tuneable.
Oxazoline-methacrylate graft-copolymers with UCST behaviour in oil

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The ability of combining hydrophilic and hydrophobic monomers into well-defined polymers with specific architectures, and the possibility of triggering their self-assembly behaviour via external stimuli open a variety of potential applications. Among all, thermoresponsive polymers are gaining special attention due to their potential applications in the biomedical field, as well as in water-recovery strategies, and in architecture. However, the temperature-responsive behaviour of linear (co)polymers and (co)polymers with more complex architectures has been studied especially in water or in alcohol/water mixtures. Indeed, only a limited amount of studies reports polymers with thermoresponsiveness in non-aqueous media. Here, the synthesis of linear oxazoline (co)polymers, as well as graft-copolymers consisting of a methacrylates backbone and oxazoline side chains is reported, and their solubility behaviour in oil is evaluated via turbidity measurements and thermal analyses.

Schematic depiction of the UCST behaviour of oxazoline-methacrylate graft-copolymers in oil.
Improving the mechanical properties of aliphatic polyester thermoplastic elastomers through star architectures

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A series of sustainable aliphatic polyester thermoplastic elastomers (APTPEs), consisting of multi-arm star polymers with arms of poly(L-lactide)-block-poly(γ-methylcaprolactone), were investigated and compared to analogous linear poly(L-lactide)-block-poly(γ-methylcaprolactone)-block-poly(L-lactide) triblock polymers. Linear analogues with comparable arm molar mass and comparable overall molar mass were synthesized to distinguish the impact of architecture from molar mass effects. The star block polymers significantly outperformed their linear analogues with respect to ultimate tensile strength and toughness, exhibiting more pronounced strain hardening than corresponding linear APTPEs. The stars exhibited high ultimate tensile strengths (~33 MPa) and large elongations at break (~1400 %), outperforming commercial, petroleum-derived styrenic TPEs. The star polymers also exhibited superior recovery compared to the linear APTPEs when subjected to cyclic strain cycles, suggestive of the impact of architecture towards improved polymer mechanical properties. Upon exploration of the polymer stress relaxation behavior, the star APTPEs demonstrated slower relaxation than their linear analogues, indicating the improved performance at a broader range of operating conditions provided by the star architecture. Dynamic mechanical thermal analysis indicates that the star architecture does not negatively impact processability, an important feature for potential industrial applications. Overall, this work illustrates that simple changes in the macromolecular architecture in sustainable APTPEs results in materials with greatly enhanced mechanical properties. A comprehensive understanding of the relationship between polymer architecture and mechanical properties can be capitalized on to develop property-specific and industrially relevant sustainable materials.
Regioselectivity of organocatalytic ring-opening polymerization in 5-membered cyclic sugar-based carbonates

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The regiochemistries of glucose-based cyclic carbonates during ring-opening polymerizations (ROPs) are of essential importance, providing molecular insight and guidance into design and synthesis of polymer materials. In this work, investigations on regioselectivity were conducted for organobase catalyzed ROPs of three 5-membered cyclic carbonates with carbonate linkages formed through the 2- and 3- positions, and bearing different pendent acetal groups through the 4- and 6- positions of methyl-α-d-glucopyranoside using naturally sourced aldehydes. Regioirregularity was observed in all 4,6-acetal-protected poly(d-glucose carbonate)s (PGCs), as indicated by $^1$H and $^{13}$C NMR spectroscopies. Explicit ratios between isomers of unimers and dimers were obtained to study the steric hindrance and/or electronic effects provided by the various protecting groups on regioselective preference during the ring-opening process. Correspondingly, the detailed proton-carbon connectivities of the unimer isomers were determined by a combination of 2D-NMR studies, including homonuclear correlation spectroscopy (COSY), $^1$H-$^{13}$C heteronuclear single quantum correlation (HSQC), and $^1$H-$^{13}$C heteronuclear multiple-bond correlation (HMBC), and further confirmed by single crystal structure analyses, which revealed a preference of O3-to-O2 polymerization direction. Moreover, comparison between the dimers revealed a significant transcarboxylation reaction coincident with the ring-opening reaction that also resulted in a regioirregular backbone connectivity. Overall, this work provides a fundamental understanding of the regiochemistry of organocatalytic ROP of 5-membered glucose carbonates with varying acetal protecting groups.
Development of hydrolytically labile poly(thioether ketal) thermoplastics

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Considerable attention has been focused on developing materials that readily degrade in the natural environment. While many reports have focused on incorporating esters and anhydrides into polymer backbones, ketals have been underutilized in applications outside biomedical applications. Herein, we report a route to synthesize hydrolytically labile poly(thioether ketal) thermoplastics via thiol-ene photopolymerizations. We found that the incorporation of ketal moieties along the polymer backbone enabled rapid degradation under acidic aqueous environments. In each case, polymer hydrolytic stability was predicated on two variables – 1) hydrolytic stability derived from the stability of the ketal moiety and 2) polymer backbone hydrophobic/hydrophilic characteristics. The thermal properties of the resulting materials were found to be characteristic of general thiol-ene materials, i.e. $T_\text{g}$ well below room temperature.
Functionalized δ-hexalactone (FDHL) monomers to synthesize higher T₉ aliphatic polyesters

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Achieving a glass transition temperature (T₉) above room temperature (except PLA) is one of the main obstacles for the current bio-based thermoplastics. Even polylactic acid (PLA) has mostly been used in the disposable packaging market among bio-based thermoplastics but it cannot compete with petroleum-based polystyrene and polyethylene terephthalate thermoplastics because of its lower T₉, toughness, and moisture resistance. Functionalized δ-hexalactone (FDHL) monomers are hypothesized to be synthesizable from hydroxymethyl furfural (HMF) and lignin-derived pendant groups (Figure 1a, route A), generating a variety of aliphatic polyesters and potentially overcome current polymer challenges. Different bulky, lignin derivatives were incorporated as pendant groups in the monomer to increase the glass transition temperature (T₉) beyond that possible from poly(δ-valerolactone). A successful FDHL monomer synthesis used commercially available methyl cyclopentanone-2-carboxylate as a starting material (Figure 1a, route B). Different alkyl (methoxy and cyclohexanol) and aromatic (phenol, 1-naphthol, and 2-phenyl phenol) groups were attached as pendant groups. ROP of these six-membered monomers resulted in new polymers ranging from 5 to 30 kg mol⁻¹ with narrow dispersity (Figure 1b). The polymerizations were carried out at room temperature using acidic to super-basic organocatalysts. Typical equilibrium polymerization behavior was observed at room temperature, and the reaction was observed to be pseudo-first-order to monomer concentration in solution. The T₉ for poly(MDHL) was found -44 °C, while T₉ observed for poly(PDHL) was 6 °C due to the presence of the bulky phenolic group pendant to the main polymer chain. Other recently synthesized polymers bearing bulkier groups (cyclohexanol, naphthols, and phenyl phenols) further increased the T₉ due to the presence of bulkier pendant groups.

(a) Schematic diagram for the synthesis of FDHL monomers and polymerization path to get different polyesters. b) Structures of the synthesized new polyester polymers bearing different bulky pendant groups.
Co-continuous polymer networks with tailorable morphologies via ROMP-induced macrophase separation

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A multi-step synthesis strategy combining reversible addition-fragmentation chain transfer (RAFT) and ring-opening metathesis polymerization (ROMP) yielded a new route to co-continuous materials with phase-separated poly(norbornene) and poly(acrylate) domains. Rapid ring-opening of macromonomers with highly functionalized (>95%) end-groups was observed, on the time scale of less than five minutes. Systematic changes to the norbornene: crosslinker ratio (4:1 to 0.25:1), macromonomer weight percent (20-50%), and degree of polymerization (25-300) led to tunable glass-transition behavior and morphologies (1 or 2 phases). The synthesis parameters were shown to produce interconnected spherical-like domains on the scale of ~2-10 microns, as shown by scanning electron microscopy. Room-temperature acidic conditions were found to dually etch the poly(acrylate) domain, at sites of ester bonds as well as polymer side-chain groups, while largely preserving the poly(norbornene) domain, as evidenced by spectroscopy, calorimetry, microscopy, and thermogravimetric analysis. Finally, we determined which phase-separated materials can be etched to produce macroporous networks. This work expands upon the current available chemistries for making polymerization-induced, phase-separated networks with macroscale features.
Thiol-containing copolymers and polydisulfide networks: synthesis and characterization

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Thiols are a versatile functional group that exhibit reactivity towards a large variety of substrates. However, directly polymerizing monomers which contain free thiol functional groups using radical intermediates is typically not possible due to the chain transfer activity of the thiol group. To obtain thiol-containing polymers, one strategy is to polymerize monomers that contain protected thiols. One example of this approach is the use of thiolactone derivatives; these can undergo ring opening when reacted with primary amine and result in the release of free thiols. Thus, incorporating thiolactone functional groups into polymer and treating with primary amine can yield thiol-containing polymer. In this work, two thiolactone monomers were synthesized and were copolymerized with either N,N-dimethylacrylamide (DMA) or tert-butyl acrylate (tBA) by using RAFT polymerization. The hydrophobicity of copolymers can be tuned by adjusting monomer type and initial monomer feeding ratio. Benzylamine and propylamine were used to ring-open the thiolactone to yield thiol-containing polymers. Thiol-containing polymers were then used in polydisulfide networks synthesis by oxidizing thiol. Such networks have potential application on reversible cross-linking gel and shape-memory material.
Multifunctional triblock copolymer based on fluoroacrylate via polymerization-induced self-assembly (PISA): Synthesis and application as a thin film dielectric material

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Developing a fluoropolymer, especially fluoroacrylate based triblock copolymers, via surfactant-free emulsion polymerization is a challenging goal. This investigation reports the preparation of a triblock copolymer of sodium 4-vinylbenzene sulfonate (SS), butyl acrylate (BA), and 2,2,2-trifluoroethyl acrylate (TFEA) via PISA process using RAFT polymerization technique. Initially, poly(sodium 4-vinylbenzene sulfonate) [PSS] was prepared via RAFT polymerization in DMSO and was used as a macro-RAFT agent to prepare diblock copolymer of SS and BA. During this block copolymerization, the PSS macro-RAFT with grown poly(butyl acrylate) moiety acted as surfactant leading to PISA process. This diblock copolymer, poly(sodium 4-vinylbenzene sulfonate-block-butyl acrylate) (PSS-b-PBA), was used as a macro-RAFT to polymerize the fluoro monomer TFEA. Thus, the triblock copolymer, poly(sodium 4-vinylbenzene sulfonate)-block-poly(butyl acrylate)-block-poly(2,2,2-trifluoroethyl acrylate) [PSS-b-PBA-b-PTFEA (TBCP)] was prepared via PISA process. The chemical composition was interpreted from the \textsuperscript{1}H NMR and FTIR spectroscopic analyses. The morphology of the diblock and the triblock copolymer was studied by transmission electron microscopy (TEM) analysis.

Interestingly, the TBCP film was highly transparent and showed interesting mechanical properties with a remarkably high elongation of 1500%. Moreover, the TBCP exhibited excellent hydrophobicity having a water contact angle (WCA) of ~122°. The TBCP films showed dielectric properties, which was analyzed using the AC-impedance analyzer. The prepared TBCP can be used as potential piezoelectric materials and in actuators.
Imparting new functionality to poly(arylene ether sulfone)s using thiol-ene chemistry

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A series of poly(arylene ether sulfone)s (PAEs) with pendant alkenes were synthesized and the substitution pattern of leaving groups on the monomer (e.g. ortho/ortho, ortho/para, and meta/meta) varied in order to investigate their effect on the properties of the resulting polymer. The polymers were subsequently modified using thiol-ene chemistry to further probe the effect of side-chain structure.
Poly(L-Lactide) chain-end macromonomer synthesis and graft-through ring-opening transesterification copolymerization with γ-methyl-ε-caprolactone

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As the need for petroleum-based plastic alternatives is growing, efforts have been made to develop a wide variety of biobased polymer architectures. In this regard, we have investigated the synthesis of a novel, biobased, and degradable graft copolymer. A one-pot strategy was developed for the synthesis of the macromonomer, a telechelic poly(L-Lactide). Using simple and mild conditions, the lactone chain end polymer was obtained after three steps. Conditions were optimized and complete conversion was reached in each case. The polyester was characterized by $^1$H and $^{13}$C NMR spectroscopy, SEC and MALDI-TOF mass spectrometry. This new macromonomer was then copolymerized with γ-methyl-ε-caprolactone to synthesize a fully biobased graft copolymer. The kinetics of the graft-through copolymerizations were investigated. Conditions were optimized and a series of graft copolymers, with diverse structures (graft length, backbone length and graft density variations), were analyzed by NMR spectroscopy, SEC, TGA and DSC. Mechanical properties were also evaluated, and the structure-property relationships were studied.
Dienes and diamondoids: poly(2-(1-adamantyl)-1,3-butadiene) and random copolymers with isoprene via redox-emulsion polymerization and their hydrogenation

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A novel route to adamantane substituted diene copolymers is demonstrated using emulsion polymerization, with an improved monomer synthesis. Heterogenous dehydration of 2-(1-adamantyl)-3-buten-2-ol using Amberlyst\textregistered-15 cationic exchange resin at ambient temperature gave 2-(1-adamantyl)-1,3-butadiene (1) in excellent yield and presents an attractive alternative monomer synthesis route. Emulsion polymerization of 1 and mixtures of 1 and isoprene was carried out at room temperature using redox pair-type hydroperoxide initiator. All poly1 and poly(1-ran-isoprene) samples were soluble in common organic solvents and exhibited high 1,4-microstructure. A continuous increase in glass transition temperature from -63 to 172 °C was observed by increasing the ratio of 1 in the comonomer feed of poly(1-ran-isoprene), and T\textsubscript{g} values were in good agreement with the Fox equation. After complete hydrogenation to poly(1-vinyladamantane-alt-ethylene-ran-propylene-alt-ethylene), a continuous increase in T\textsubscript{g} was observed from -55 to 152 °C. The high solubility and improved access to 2-(1-adamantyl)-1,3-butadiene opens the door to exploration of diene polymers with enhanced high temperature properties.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Relationship between T\textsubscript{g} and the weight composition of adamantyl containing monomer with Fox prediction lines. \textbullet and solid line: poly(1-ran-isoprene). \textcircled{o} and dashed line: poly(1-vinyladamantane-alt-ethylene-ran-propylene-alt-ethylene)}
\end{figure}
Continuous dimethyldioxirane generation for polymer epoxidation

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Post-polymerization modification of commodity polymers yields new applications for materials already produced industrially. Incorporation of small amounts of epoxides into unsaturated polymers such as polybutadiene expands their use for grafting and compatibilization applications, but controlled epoxidation of these polymers in a safe, scalable manner presents a challenge. We describe the development of a reactor for the continuous flow generation and use of dimethyldioxirane (DMDO) and its application to the low-level epoxidation of unsaturated polymers. A continuous stirred tank reactor (CSTR) prevents reactor clogging by allowing solid precipitates to settle, enabling the pumping of a homogeneous solution of oxidant. Modification of relative concentrations, flow rates, and temperatures achieves variable epoxidation levels. This method has been demonstrated on gram scale.
Polymer backbone metamorphosis of polyesters to polyolefins via the Ireland-Claisen rearrangement

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Post-polymerization modification (PPM) is a powerful strategy to access a wide breadth of material properties from a single polymer backbone. This approach has been largely limited to side-chain and end-group modification, which constrains accessible material properties. Little attention has been directed towards the modification of polymer backbone composition—referred to as polymer backbone metamorphosis—to produce dramatic property changes on demand. Through the utilization of sigmatropic rearrangements, polymer backbone metamorphosis of polyesters to polyolefins was achieved. The polyesters were synthesized by ring opening transesterification polymerization of ω-vinylactones, providing the backbone structure to facilitate Ireland-Claisen rearrangement (ICR). We have shown the application of ICR conditions induce total rearrangement of polyesters into polyolefins with no observed degradation. Material properties and changes imparted through ICR will be discussed.
Exploring polymerization techniques for the polymerization of silyl ketenes as monomers

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The properties and applications of polymers are directly related to the backbone of the polymer and therefore the respective monomer. It is of interest to access new properties for materials, and in turn the need for new polymeric backbones. Our group is interested in silyl-substituted ketenes as attractive new monomers mainly due to these compounds containing a cumulated double bond allowing for three unique polymeric backbones to be produced. These compounds are more stable and easy to store relative to aryl and alkyl ketenes. Recently we found that through anionic polymerization silyl ketenes can polymerize, however with little control over propagation and secondary reactions. Further studies showed that oligomers could be formed with a thiolate initiator that avoided backbiting issues, however higher molar mass polymers were not obtained. This work focuses on exploring alternative polymerization techniques to polymerize silyl ketenes, such as group transfer polymerization (GTP) and cationic polymerization. These techniques offer potential of controlled polymerization of silyl ketene monomers under easily accessible reaction conditions. In this work, we examine polymerization reaction parameters (reaction time, temperature, concentration, and catalyst identity) of various ketenes to obtain polyester, polyketone, and polyketene acetal backbones.
Versatile homotelechelic bottlebrush polymers via chain-transfer ring-opening metathesis polymerization

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Novel polymer synthetic pathways enable topologically complex architectures and hinge upon the continued improvement of functionalization strategies, including the facile fabrication of telechelic polymers. In ring-opening metathesis polymerization (ROMP), chain-end functionalized polymers have been achieved through a variety of techniques, including sacrificial synthesis, tandem ring-opening/ring-closing ene-yne ROMP, pulsed monomer addition, and chain-transfer agent (CTA) addition. While these existing methods are versatile and promising, none to our knowledge have been implemented in systems with complex architectures. Herein, we describe the preparation of homotelechelic bottlebrush polymers via grafting-through ROMP with various functional CTAs and macromonomers. In general, the degree of polymerization was found to be independent of catalyst concentration and dependent on the ratio of CTA to macromonomer. A library of polystyrene, poly(methyl methacrylate), and polyisobutylene-based bottlebrushes were generated with useful CTAs, including end-functionalized atom-transfer radical polymerization (ATRP) initiators, reversible addition-fragmentation chain-transfer (RAFT) CTAs, and UV-active chromophores. Bisfunctional bottlebrush macroninitiators were subsequently chain-extended with either activators regenerated by electron transfer (ARGET) ATRP or RAFT polymerization to afford novel ABA triblock copolymers. Importantly, this technique is a powerful, modular platform in which unique brush architectures and functionalization can be accessed in a few steps without arduous post-polymerization modification, thereby opening the way for increasingly versatile polymer topologies.
Dynamic covalent exchange in poly(thioether anhydrides)

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The integration of dynamic functionality into polymer networks to produce new polymer-based materials with recycling, reconfiguring, and self-healing capabilities has been of much interest recently. Our research focuses on the dynamic covalent exchange (DCE) of anhydride moieties, conducting experiments on model compounds and network polymers. Analysis of the exchange process in symmetric model compounds methacrylic anhydride and 4-pentenoic anhydride, which produce an asymmetric anhydride upon exchange, was undertaken using 13C NMR spectroscopy. The equilibrium constant (Keq) was determined to be approximately 2-3, and the activation energy (Ea) for the production of the asymmetric anhydride was 178 kJ mol⁻¹. Carboxylic acid proved to have a catalytic effect on the exchange rate. Poly(thioether anhydrides) were made using 4-pentenoic anhydride and mixtures of dithiol (1,6-hexanedithiol) and tetra thiol (pentaerythritol tetrakis(3-mercaptopropionate)) via radical-mediated thiol-ene polymerizations. Compositional effects were compared through network relaxation rates using dynamic mechanical analysis. The activation energy and stress relaxation times for various polymer compositions were correlated to crosslink density. It was determined that cross-link density of the polymer system does not significantly impact Ea; however, relaxation time (t) nearly quadrupled from the least cross-linked system to the most cross-linked system. The network polymers exhibited self-healing and facile recycling behavior, which we attributed to the anhydride DCE process that occurs readily in these materials at elevated temperatures. Using the composition with the fastest relaxation, complete visible recovery of damage (notch) within a 4 hour duration at 90 °C. Recycling under compression molding for 15 minutes using 76 MPa hydrostatic pressure at 90 °C was successful. Both healed and recycled samples were successful in recovering or surpassing their original mechanical properties.
Fully oxygen-tolerant photoinduced ATRP

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Atom transfer radical polymerization (ATRP) has become a powerful tool for the synthesis of polymers and advanced materials. However, like any radical polymerization, ATRP is inhibited by oxygen. This hampers its practical use under aerobic conditions and specialized equipment is often needed to achieve good results. Conventional ATRP methods thus tend to be time-consuming and challenging for non-experts.

In recent years, more attention is focused on tackling the problem of oxygen intolerance in ATRP. Possible approaches can be divided into two broad groups: activator regeneration and oxygen scavenging. However, the vast majority of reported methods suffer from at least one critical flaw, such as complexity, use of high loadings of copper catalysts, limited oxygen tolerance, or incompatibility with a wide spectrum of solvents.

Herein, we demonstrate the oxygen–tolerant photoinduced ATRP occurring in both water and organic solvent in an open reaction vessel. Sodium pyruvate is the essential component in this novel method, acting as a hydrogen peroxide scavenger and enabling the continuous regeneration of the copper activator under UV irradiation (Scheme 1). This protocol proved to be highly efficient in the polymerization of N-isopropylacrylamide with ppm level of Cu catalyst in aqueous media. The polymers were synthesized to nearly quantitative monomer conversions, high molecular weights, and low dispersities in less than 30 min. Moreover, the well-controlled polymerization of methyl acrylate was achieved in dimethyl sulfoxide in open-air conditions without compromising the control over the molecular weight distribution.

Scheme 1. Fully oxygen-tolerant photoinduced ATRP triggered by sodium pyruvate.
Application of the Passerini three-component reaction for the chain end modification of end-functionalized polymers with aldehyde groups

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In this research, we designed a novel pyrazole–carbodithioate-based chain transfer agent bearing an aldehyde group (CTA-CHO) to expend the synthetic utility of the end-functionalized polymers and the potential modification based on the aldehyde reactivity. The CTA-CHO was subjected to the reversible addition-fragmentation chain-transfer (RAFT) radical polymerization of vinyl monomers to furnish a well-defined polymers end-functionalized with aldehyde moiety. In order to showcase the reactivity and thus utility of polymers end-functionalized with aldehyde units, postpolymerization modification were performed by employing multicomponent reactions (MCRs). As a result, a wide range of analysis results including size-exclusion chromatography (SEC), $^1$H NMR, and FT-IR measurements revealed the high reactivity of aldehyde moiety under the catalyst-free Passerini three-components reaction. All in all, we succeeded in designing and using CTA-CHO for the synthesis of well-defined polymers end-functionalized polymers with aldehyde moiety. In addition, the chain end Passerini-three component reaction was revealed to proceed without the aid of additional activators nor catalysts, highlighting the synthetic benefits of the newly designed CTA-CHO.

Scheme. A chain-end modification via the Passerini three-component reaction of polymers bearing an aldehyde chain-end group.
Thiol-ene click engineered late-stage modification: Synthesis of long chain polyurethane dendrimers

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Compared to the synthesis of polyurethane (PU) polymers, construction of well-defined polyurethane dendrimers (PUDs) is challenging owing to high reactivity of externally added or in-situ formed isocyanates leading to formation of side products. For this reason, synthesis of dendritic PUs is limited to very few reports. With a major focus of dendrimer research on the interaction of the periphery and the core, herein, we report the synthesis of a common PU dendron, which allows for late-stage variation of both the periphery and the core. The periphery can be varied simply by installing a clickable unit in the dendron and then attaching to the core and vice-versa. Thus, a common dendron allows for varying periphery and core in the final two steps. To accomplish this, protecting group free one-pot multicomponent Curtius reaction was employed to afford a robust and versatile AB₂ type polyurethane dendron using commercially available simple molecules, 5-hydroxyisophthalic acid, 11-bromoundecan-1-ol, and 4-penten-1-ol. Subsequent late-stage modification of either dendrons or dendrimers via thiol-ene click reaction gave surface functionalized alternating aromatic-aliphatic PU homodendrimers to generation-three (G3). The versatility of this approach was demonstrated by bifunctional AB₂ type dendritic monomer that can either undergo a thiol-ene click or attachment to the trifunctional core. Furthermore, we demonstrated the utility of this synthetic strategy by allowing two different AB₂ type wedges to attach to a difunctional core, which gave three different dendrimers including a heterodendrimer or Janus dendrimer. This approach enables incorporation of functionalities at the periphery and the core that may not withstand the dendrimer growth and is applicable not only for the synthesis of PUDs but also for other dendritic macromolecules.

Figure. General strategy of dendrimer synthesis
Multimechanistic polymerization: Iron guanidine complex combines ATRP with ROP

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Bioplastics like polylactide gain more and more significance as replacement for conventional polymers. However, not all properties can be mimicked by bio-based or biodegradable homopolymers. Therefore, copolymerization becomes an important pathway for the development of new materials. We recently presented an iron guanidine catalyst that is biocompatible, robust and shows a higher polymerization activity for lactide than the industrially used tin octoate. Taking the predicted production growth rate of polylactide into account, the replacement of the toxic tin compound by a benign catalyst becomes a necessary step. The catalyst is, furthermore, capable of copolymerizing lactide, ε-caprolactone and glycolide to defined copolymers. It becomes even more significant being additionally an active catalyst for the atom transfer radical polymerization (ATRP).

Copolymerization is typically limited to a certain monomer class being polymerized via the same mechanism. Preparation of a block copolymer consisting of monomers with distinctive chemical structures typically includes different catalysts and purification steps in between to avoid deactivation of the second catalytic system leading to an uncontrolled polymerization with ambiguous copolymers. The iron guanidine complex is one of the rare catalyst examples, which can combine monomers of different classes in a copolymer by polymerizing them via different mechanisms. Block copolymers of lactide polymerized via lactone ring-opening polymerization and styrene via ATRP are obtained in a one-pot synthesis either by sequential addition or by simultaneous polymerization. Since both polymerization mechanisms proceed in a controlled manner, an adjustable polymer is synthesized. The presented catalytic system opens new pathways towards multimechanistic polymerizations and underlines that smart catalyst design improves conventional intensive polymerization procedures.
Two-dimensional polymerization in a homogenous reaction system: theory and application

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Generally, two-dimensional concatenation happens on 2D surfaces such as metal surfaces in CVD process or liquid-liquid interfaces in interfacial polymerization. However, such approaches suffer from minuscule synthetic and transfer efficiencies. Another strategy is to introduce microscopic reversibility, to achieve 2D crystals after extensive error correction. As a consequence, resulting materials are associated with low chemical stabilities, which further lead to problematic processabilities. Herein we demonstrate an irreversible 2D polymerization without any external 2D input can be achieved, resulting in covalently bonded 2D polymer platelets that are chemically stable and highly processable. Further fabrication of the product offers highly oriented, free-standing films which exhibit exceptional 2D elastic modulus and yield strength at 50.9±15.0 GPa and 0.976±0.113 GPa, respectively. Individual 2D molecules were found highly asymmetric by chemical AFM and their alignment is evidenced by polarized photoluminescence from different dipole transitions. This new synthetic route provides opportunities for 2D polymers in applications ranging from composite structures to barrier coatings.
Modeling short-chain branched polyethylenes in dilute solution under variable solvent quality: Basic configurational properties

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We perform molecular dynamics (MD) simulations of a coarse-grained model of linear low-density polyethylenes (LLDPEs) having short-chain branching in an implicit solvent and calculate basic configurational properties (radius of gyration $R_g$, hydrodynamic radius $R_h$, and intrinsic viscosity $[\eta]$) using the path-integration program ZENO. Solvent quality effects in our model are accounted for through the introduction of an attractive polymer-polymer interaction potential with solvent quality "strength" $\lambda$ that is tuned from a "good" solvent limit, where the inter-polymer interactions are purely repulsive, to a "very poor" solvent regime, where the polymers collapse due to their self-attractive intermolecular interactions. We also identify a compensation condition or "$\theta$ point" in our model between these limits, where the polymers are "ideal" in the sense in which attractive interactions effectively nullify inter-polymer repulsions so that the chains behave akin to Gaussian polymer chains in their average conformational properties. In order to compare with experiments performed in variable solvent qualities, we define a dimensionless measure of excluded volume interaction parameter $\delta$ in terms of the mass scaling exponent $\nu$ for $R_g$ or $\nu_h$ for $R_h$, which can be determined from both experiment and simulation. We illustrate our variable solvent approach to estimate polymer solution properties in the case of polyethylenes (PEs) and evaluate the $\delta$ value that corresponds to the experimental solvent conditions. Our combined use of MD and ZENO allows for the numerical estimation of polymer solution properties for polymers having general monomer structures and solvent qualities in a computationally tractable fashion and should be useful as a general computational tool for polymer structural characterization.
Cyclic olefin copolymer based anion exchange membranes

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Ion-transport materials are essential components for a variety of applications including ion exchange membranes, fuel cells, and redox-flow batteries. Polymers bearing pendant ionic groups are viable options for these applications, as the polymer backbone provides mechanical integrity and the ionic groups provide paths for charge conduction. Both the backbone and ionic groups can be tuned toward optimized material properties, performance, and stability. These features have significantly impacted the development of alkaline anion exchanges membranes (AEMs). In alkaline fuel cells, AEMs serve as a solid cationic support for hydroxide transport from cathode to anode. Various polymer backbone and cation pairings have been investigated toward highly robust and conductive thin film membranes, but no benchmark AEM has yet been developed. Concerns to be addressed with these materials center around long-term mechanical integrity, stability, and hydroxide conductivity. Further understanding of how these aspects are influenced by backbone stiffness, cation identity, and polymer architecture would aid toward the fabrication of AEMs with improved mechanical and performance properties. Herein, we utilize ring opening metathesis polymerization (ROMP) to develop a series of AEMs derived from cyclic olefin copolymers (COCs). Rigid cyclic substituents are incorporated statistically along the polymer backbone, leading to high T\(_g\) (>100 °C) ROMP polymers with good mechanical integrity and film forming properties. We employ the ubiquitous trimethylammonium cation as well as charge delocalized tetra(dialkylamino)phosphonium cation derivatives and compare the resulting polymer physical properties, performance properties, and alkaline stability.
Using a bottom-up approach to investigate the molecular structure of aqueous poly(N-isopropylacrylamide) at room temperature via IR spectroscopies

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Poly(N-isopropylacrylamide) (PNIPAM) is a thermo-responsive polymer with numerous applications in the different areas science and engineering. While the mechanism behind the phase transition behavior of aqueous PNIPAM has been extensively studied, the structure of PNIPAM in solution is still remains a matter of debate. Here, we present our effort on elucidating the structure of PNIPAM in water using a bottom-up approach. involving the monomer, dimer, and trimer units as models and a combination of IR spectroscopies (including FTIR and 2DIR spectroscopies) along with some computational studies (molecular dynamics simulations, MD). Our IR studies reveal the presence of two peaks in the amide I region of the spectrum of the oligomers and the polymer, which are assigned to different backbone conformations. These conformers present distinct IR signatures because of the strong vibrational coupling between neighboring units. MD simulations and vibrational theory confirm that the oligomers have distinct backbone conformation in solution, each with specific vibrational signatures. The bottom-up approach allowed us to infer that such backbone conformations also exist in PNIPAM as it reveals the same IR signatures. Finally, the proposed molecular model is successfully used to describe the PNIPAM amide I band changes with temperature in terms of its molecular structure. Overall, our studies strongly suggest that PNIPAM does not have a completely random backbone structure, but have distinct backbone arrangements between neighboring amides.
Effect of chemical identity and morphology on water- and salt- transport in amphiphilic-zwitterionic copolymer membranes

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Amphiphilic copolymers have gained a broad platform of research interest attributed to their superior self-assembly properties (globular or extended) over a broad range of pH, temperature, and ionic strength. Polyzwitterions have attracted special attention due to their hydrophilicity, charge sensitivity (net charge can be negative or positive) and coulombic attraction of the opposite charges over a range of different environments. These properties made them a widely popular material in the field of tailoring “smart” stimuli responsive systems, self-healing hydrogels, and water transport membranes. The primary focus of this work is to tailor amphiphilic-zwitterionic (A-Z) block copolymers that are mechanically robust membranes and to then correlate the effect of molecular weight, morphology and zwitterionic identity on water, and salt transport. A set of synthesized neutral Polyisoprene-b-Poly [2(Dimethylamino)ethyl Methacrylate] (PI-b-PDMAEMA) with different volume fractions of hydrophilic PDMAEMA block have been successfully synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerizations. The precursor polymers were treated with 1,3-propane sulfone or β-propiolactone for post-polymerization nucleophilic ring-opening reactions to give Polyisoprene-b-Poly (sulfobetaine methacrylate) (PI-b-PSBMA) or Polyisoprene-b-Poly (carboxybetaine methacrylate) (PI-b-PCBMA) copolymers with different compositions, morphology and zwitterionic moieties. These polymers combine both stimuli responsiveness and higher hydrophilicity of zwitterionic polymers and physical conformations of amphiphilic copolymers in their water and salt transport.
Study of dynamic covalent exchange in methacyrlic anhydride copolymers

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Covalent adaptable networks (CANS) have risen in popularity due to their thermoplastic like processability while retaining thermoset characteristics such as chemical resistance and thermomechanical stability. Polyanhydrides are an example of an intrinsic CAN capable of undergoing dynamic covalent exchange with the added benefit of surface eroding hydrolysis for biomedical applications. Additionally, radical polymerization of anhydride-containing monomers allows for the formation of highly crosslinked materials without the often harsh conditions used in polycondensation reactions, which can be plagued by disproportionation, oligomerization or cyclization of the anhydride. In this study, methacrylic anhydride is copolymerized with various acrylic monomers. The crosslinked products were analyzed in order to probe the anhydride dynamic covalent exchange. In addition to spectroscopic studies, the dynamic covalent exchange was assessed through the recyclability of the polymers. Finally, the erosion behavior of the polyanhydride copolymers was determined, and showed that copolymer with high anhydride content undergo surface erosion.
A 2D Perchlorinated Carbon Framework

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We report a π-conjugated, perchlorinated two-dimensional organic framework connected via direct C-C linkage through thermolysis polymerization. The resulting black polymer displays two-dimensional order and can be exfoliated. The bulk polymer demonstrates a low bandgap, in-plane electrical conductivity and field-effect charge transport. Ab-initio calculations show the observations are in good agreement to that of the spin-recombined framework.

- Top left: model of the polymer
- Bottom left: TEM image of the polymer demonstrating its 2D order
- Bottom left inset (left): Photograph of the polymer
- Bottom left inset (right): Selected area electron diffraction of the polymer
- Top right: Transfer curve of the polymer, showing the field-effect response
- Bottom right: IV curve of the polymer, showing its conductivity
Covalent adaptable networks: Exploring silanolate networks for self-healing materials

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The production of commodity and specialty plastics continue to rise alongside the awareness of their negative environmental impact. Today’s scientists are challenged to address this complex issue by focusing their research efforts on novel recycling methods or new reusable/eco-friendly polymers. These rigorous efforts gave birth to covalent adaptable networks (CANs) and their potential to market as a primary class of reusable materials. CANs contain a combination of the best characteristics of their predecessor materials, thermoplastics and thermosets, by containing reversible covalent crosslinks that allow them to be reprocessable and have a large service window. The scientific community has populated the CAN library with a plethora of reversible reactive functional groups that can exist throughout polymer networks providing capabilities such as self-healing, shape memory, and reprocessability. Of these CAN materials, reversible silanolate covalent bonds have received little attention and we believe they could be a valuable subset due to their structural similarity to silicon-based polymers. Herein, we explore the impact of silanolate content on the self-healing and reprocessability of soft and hard epoxy-based networks. By regulating the amount of dynamic exchange group present throughout the epoxy network, we can better understand how it impacts the materials recyclability and physical properties. DMA, DSC, and tensile analysis were used to study the self-healing efficiency, reprocessability, and thermal/physical properties of our epoxy networks.
Self-healing tailor-made polymers based on furan derivative and 1,2,4 triazoline-3,5-dione (TAD) ‘click’ chemistry

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Exploring new innovative self-healing polymers has been the contemporary theme in materials science and engineering. Among several intrinsic self-healing approaches, Diels-Alder “Click” chemistry based furan-maleimide reaction has been widely used. However, this system is relatively slow and requires elevated temperature. In this present study, “click” chemistry based on furan derivative and 1,2,4-triazoline-3,5-diene (TAD) has been used to prepare self-healing polymers. For this, furfuryl modified polymethacrylate was prepared via reversible addition fragmentation chain transfer (RAFT) polymerization. In this case, furfuryl group was attached to the polymer chain through its C2 position. This tailor-made furfuryl functionalized polymer was modified using TAD which was very fast (in ~1-2 min) even at ambient conditions. The furan-TAD reaction followed a reversible electrophilic substitution (ES) ‘click’ pathway, as evidenced by NMR spectra as well as via density functional theory (DFT) calculation. Interestingly, when we used 2,5 substituted furan (instead of the substitution only at the C2 position), the modification reaction followed Diels-Alder pathway. Importantly, in both the cases, the thermo-reversibility of this reaction was studied via DSC analysis as well as via trans-click reaction using fufuryl amine. The self-healing characteristics was studied by monitoring a knife-notched scar on the polymer surface via SEM as well as AFM analysis. These new self-healing polymers will have a variety of potential applications, like in specialty paints, coatings and different thermosets.

Modification of polymer using furan-TAD “click” chemistry
Exploring the properties of bottlebrush polypentenamers

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Experimental research on the structure-property relationships of bottlebrush (BB) polymers is limited by the number of backbone chemistries suitable to produce these materials. Polypentenamers possess a unique five-carbon graft topology with a flexible backbone between grafts and allow for the exploration of backbone rigidity and grafting density on the physical properties of BBs. By creating a series of polypentenamers with varying backbone and side chain lengths, the material properties of these BBs can be compared with those of vinyl- and norbornene-derived bottlebrushes, and the effects of the different polymer microstructures on the properties of the macrostructures can be elucidated. This presentation will highlight our recent investigations into the unique properties and behaviors of these BB systems.
Application of an autonomous continuous-flow platform for multi-objective optimisation of polymer synthesis

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The application of machine learning to polymer chemistry offers the opportunity for a step change in speed of innovation. High impact examples have been demonstrated in small molecule chemistry, such as those with pharmaceutical applications. In partnership with online analysis and automated reactor technology, machine learning provides the potential for rapid adjustments in response to observed changes, or the collection of high-resolution data with a much-reduced workload. Online analysis integrates particularly well with flow chemistry; and has been used to great success with polymer chemistry.

Herein, we present an automated polymer synthesis platform, with integrated online NMR spectroscopy and GPC capable of autonomous exploration of polymerisation reaction space.

The online analyses provide real-time molecular weight and conversion information for a range of RAFT polymerisations. High throughput experiments screen reaction conditions in an ordered fashion with little user input. Further complexity is achieved with integration of a multi-objective optimisation algorithm (TS-EMO), which reduces wasted experiments and explores the achievable reaction space for a range of RAFT polymerisations with varied RAFT agents, monomers and initiators. using a multi-objective optimisation algorithm (TS-EMO). The algorithm takes an initial near-random screen of conditions to generate a model for the system and uses this to identify further experiments to achieve the given objectives (in this case increased conversion and reduced dispersity). These results are then assimilated into the model and further optimisation performed. The incorporation of our pressurised flow reactor means that conventionally forbidden conditions (i.e. temperatures above the boiling point of solvents) are accessed and explored.
Investigation of the Detailed Mechanisms of DBU-Catalyzed PLGA Copolymerization via a Full-Scale Population Balance Analysis

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The homogeneous, cyclic organic amidine catalyst, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), has gained popularity for its use in the synthesis of biodegradable aliphatic polyesters such as poly(lactic-co-glycolic acid) (PLGA). PLGA is one of the most successful polymeric drug delivery materials in pharmaceutical industry. However, not much is known yet about the details of the DBU-catalyzed PLGA polymerization reactions. The present study is intended to address this gap.

For this investigation, a full-scale kinetic population balance model was developed that takes into account all possible reactions of the copolymerization, including initiation via activated alcohol and nucleophilic attack pathways, self- and cross-propagation, combination via inter- and intra-chain acylation, and DBU deactivation. Predictions of this model in terms of copolymerization rates, monomer sequence length distributions in PLGA products, etc. were compared with experimental data from our own work and also with those available in the literature. This analysis led to the determination of the values of all (16 different) reaction rate constants that were previously unknown.

As illustrated in the Mayo-Lewis plot shown below, the most striking finding of this study is the four-orders-of-magnitude difference in reactivity ratio between the two monomers, lactide (L) vs. glycolide (G), that is, $r_L \equiv k_{LL}/k_{LG} \approx 3.6 \times 10^{-3}$ and $r_G \equiv k_{GG}/k_{GL} \approx 12.4$ in this DBU-catalyzed process; this result is in contrast to what has previously been reported for tin-catalyzed PLGA polymerization reactions ($r_L \approx 0.20$ and $r_G \approx 2.8$). An important implication of this result is that it is practically impossible to produce DBU-catalyzed PLGA copolymers with uniform monomer sequence distributions using an ordinary batch reaction process. In this presentation, we will also discuss how the kinetic model can be used to design non-conventional copolymerization reactors for producing monomer sequence-controlled, uniform PLGA products.
Semi-fluorinated poly(ether imide)s with benzyl ether moiety: Synthesis, characterization, gas permeation study and molecular dynamics simulations

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Polymeric membrane based-gas separation has drawn great attention for a range of molecular separations over competing technologies. For any gas separation membrane it is desirable to have good selectivity for one gas over another, combined with high permeability. Aromatic polyimides can be used as membrane materials because of their outstanding set of physical properties. In this context, a series of poly(ether imide)s (PEI)s has been synthesized from the reaction of benzyl ether substituted, fluorinated diamine monomer, 4,4'-(2',5'-bis(benzyloxy)-3,3''-bis(trifluoromethyl)-[1,1':4,4''-terphenyl]-4,4''-diyl)bis(oxy))dianiline (TADBE) with different fluorinated and non-fluorinated aromatic dianhydrides. The membranes were prepared directly by the thermal imidization of the poly(amic acid)s following a programmed heating up to 250 °C. The polymers were well characterized by different analytical techniques. Synthesized polymers have drawn much attention because of their superior mechanical strength, thermal properties, organosolubility. The membranes were transparent and flexible and the PEIs were readily dissolved in numerous organic solvents and cast into freestanding flexible films with tensile strength up to 159 MPa and elongation at break up to 106 %. The films showed dielectric constant as low as 2.47 at 1MHz and 30 °C. The polymers showed 10% weight loss temperature above 440 °C in air with high T_g values (as high as 252 °C) under nitrogen. The structure-property correlations on gas transport properties and chemical structure and different physical properties of these PIEs were established. The best combination of selectivity and gas permeability value is seen for the polymer with 6FDA fragment (PEI-b). The group contribution method predicts the permeability coefficients exceptionally well in all three PEIs and for different gases. Whereas, molecular dynamics simulations provide a better insight on free volume: size, shape, connectivity and morphology of the PEIs.
Effect of methyl group distribution in sustainable polyglycolide copolymers on material properties

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Polyglycolide is a sustainable alternative to petroleum-based gas barrier materials and features promising gas barrier properties. However, polyglycolide is challenging to process because of its high crystallinity and narrow thermal processing windows. In this presentation, we show that the introduction of methyl groups to the polyglycolide backbone can lower the melting temperature, thereby widening the processing windows while maintaining gas barrier properties. In particular, poly(glycolide-stat-lactide) and poly(glycolide-stat-methylglycolide), two copolymers with similar methyl contents but different spatial distributions of methyl groups along the backbone were synthesized. The polymers were thoroughly compared with respect to molecular structure, semi-crystalline morphology, thermal properties, and gas permeability. Interestingly, the melting temperature and gas permeability of poly(glycolide-stat-methylglycolide) were lower than that of corresponding poly(glycolide-stat-lactide). These data suggested that the distribution of methyl groups on the backbone was crucial for the thermal and gas barrier properties in this sustainable material.
Dynamic in-situ variation of backbone structure during ring-opening copolymerization of carbonyl sulfide with an oxetane derived from D-xylose

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Poly(monothiocarbonate)s are a class of materials that are biodegradable and exhibit excellent thermal, mechanical, optical, and electrical properties compared to polycarbonates, their non-sulfur containing analogue. However, copolymerization involving carbonyl sulfide (COS) and epoxide/oxetane face the unavoidable oxygen/sulfur exchange reaction (O/S ER), which affects polymer backbone structure and composition. Factors, such as high temperature, contribute to this exchange reaction, producing polymers with lower sequence regularity, along with unwanted linkages, such as dithiocarbonate or carbonate linkages. In this work, by varying temperature and cocatalyst loading, the backbone regioselectivities and linkages were controlled during the direct incorporation of COS, a sulfur containing C1 building block derived from burning of fossil fuels, with a biomass derived oxetane. At low temperatures, poly(monothiocarbonate)s were formed. In contrast, promotion of the O/S ER was used to access polymeric materials composed of variation of backbone structure. As the temperature was increased, the monothiocarbonate linkages were replaced with carbonate linkages, until at a temperature of 140 °C, a polymer containing only carbonate and thioether linkages with head-to-head and tail-to-tail regiochemistries was obtained. Overall, this work represents a dynamic in-situ method for synthesizing sulfur-containing polymers that exhibit different compositions and structures. The ability to tune the physiochemical and thermomechanical properties by this relatively green chemistry route, further, provides an alternative to simple or traditional poly(monothiocarbonate) or polycarbonate production.
Effect of poly(cyclosilane) microstructure on thermal properties

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In contrast to hydrocarbon polymers, structure-based understanding of polysilane thermal property relationships is more limited and has focused on the influence of organic side chains. Two possible reasons for this issue are (1) the synthetic challenge of creating a structurally well-defined homologous series of polysilanes and (2) the propensity of some polysilanes to undergo skeletal rearrangement to polycarbosilanes at elevated temperatures. We recently described the synthesis and Cp₂ZrCl₂/n-BuLi-mediated dehydrocoupling polymerization of the bifunctional cyclosilane monomers 1,4Si₆ and 1,3Si₆. These directional building blocks template distinct linear(P1) or cyclic(P2) polymeric architectures. Herein, we report that replacement of our standard Cp₂ZrCl₂/nBuLi catalyst with Cp₂ZrMe₂ provided the desired linear poly(cyclosilane) P3, a structural assignment supported by ¹H and ²⁹Si NMR spectroscopy. We investigate the influence of poly(cyclosilane) microstructure on thermal behavior and decomposition using a combined theoretical and experimental study. The thermal stability of these poly(cyclosilane)s was investigated by differential scanning calorimetry and thermogravimetric analysis complemented by density functional theory (DFT) calculations.
Degradable polyphosphoramidate via ring-opening metathesis polymerization

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Backbone degradable polymers are attractive in a host of applications, including drug delivery, tissue engineering and fabricating semiconductors and recyclable materials. Historically, ring-opening polymerizations through radical, anionic, cationic, or organocatalyzed mechanisms have been adopted to fabricate polymers with degradable linkages. Recently, ring-opening metathesis polymerization (ROMP) has gained increasing attention for the production of such materials due to the excellent functional group tolerance and mild reaction conditions. Herein, we have demonstrated that at low reaction temperatures, we were able to achieve controlled polymerization of an otherwise non-polymerizable, low-ring-strain diazaphosphine-based cyclic olefin (PTDO). The resulting polymer readily underwent degradation in acidic conditions via the cleavage of the acid-labile phosphoramidate linkages. PTDO was compatible in random and block copolymerizations with various norbornenes, introducing partial or complete degradability into the polymeric backbones. When oligo(ethylene glycol) bearing norbornene was used as comonomer, we generated amphiphilic copolymers that could self-assemble into micellar nanoparticles that showed no discernable cell cytotoxicity. Current research efforts have been focused on ROMP of PTDO with different functional groups and its application in drug delivery.
Stimuli-responsive properties of pH- and temperature-responsive block copolymers synthesized via ARGET ATRP

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Applications ranging from enhanced oil recovery to architectural coatings, including paints, primers, and stains, require the optimization of properties of the materials used for each application. Stimuli-responsive polymers dramatically change properties, such as viscosity and solubility, in response to a small change in an external trigger, including pH or temperature. Understanding how changing the structure of the polymer affects the stimuli-responsive properties allows for the tailoring of the polymer structure to achieve the needed properties for each application. Copolymers of polyethylene glycol (PEG) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) were synthesized using Activator ReGenerated Electron Transfer Atom Transfer Radical Polymerization to study the stimuli-responsive properties when changing the block architecture of the copolymers. UV-Visible Spectroscopy and Dynamic Light Scattering were used to determine the change in water-solubility as a function of pH, temperature, polymer concentration, and polymer composition. Viscosity was measured as a function of time, shear rate, and temperature of polymer solutions with controlled pH, polymer concentration, and polymer composition. Additional properties, including interfacial tension and shear modulus, are being tested as a function of polymer concentration and polymer composition. Understanding the effect of block copolymer structure on stimuli-responsive polymer properties in solution enables tailoring these properties for applications including architectural coatings and enhanced oil recovery.
Mechanochemistry of metallocene-containing polymers

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Mechanophores are stimuli-responsive molecules that can show chemical transformations by external mechanical force. A force-induced cleavage of weak bonds can take place at these mechanophores. As an attractive mechanophore moiety, ferrocene has shown a new opportunity in mechanochemistry. The bond dissociation energy (BDE) of Fe-Cp is reported up to 91 kcal/mol, close to the covalent C–C bond. Even though ferrocene is highly stable, it shows selective chain scission under ultrasonication. We show that metallocene is an effective mechanophore in the polymer system. DFT calculation performed with constrained geometry simulates external force (COGEF) is well correlated with experimental results. We further expand the metallocene mechanochemistry to ruthenocene. Computational and experimental mechanistic studies show similarities and significant differences in the mechanochemistry of the two mechanophores. In this presentation, we will present mechanistic insights on the metallocene mechanochemistry.

Figure 1. Schematic illustration of metallocene-containing polymers under ultrasonication.
Solid-state mechanochemical ring-opening metathesis polymerization

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Ring-Opening Metathesis Polymerization is now possible without any solvent. A mechanochemical tool, ball-milling, provides sufficient mixing and energy delivery to the mixture of solid catalyst and monomers. A group of norbornene monomers of various functional groups including ionomer was polymerized quickly by the simple ball-milling. Details of reaction parameters such as the liquid-assisted grinding selective prohibition of chain degradation will be disclosed.

**Solid-State Ru-ROMP - Green & Unique Reactivity**

- Enhanced Green Metrics
- Not limited to monomer solubility
- Broad Monomer Scope
- High Molecular Weight by Liquid Assisted Grinding
- Mechanistic Investigation

No Solvent
Tailorable design and methodical synthesis of structurally and functionally tunable ionenes + ionic liquid composites for high-performance engineering applications

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We have designed and developed a diverse series of high-performance (HP) ionenes, or polymers which contain ionic groups along the main chain rather than as pendants. These materials merge the 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 fluorinated anions (i.e. Tf₂N), which are produced from established synthetic methods that impart great control over repeat unit complexity, functional group sequence, charge density, and regiochemistry. Varied connectivity and sophisticated structural segments known for imparting free volume, such as spirobisindane and Tröger’s base moieties, have also been incorporated along the backbone to improve gas transport performance. These ionenes are robust, exhibiting good thermal and mechanical stability, but extremely tailorable based on the versatile synthetic approaches which allow for innumerable potential derivatives based on deliberate combination of assorted monomers and linkages. These polymeric materials exhibit self-assembly when filled with “free” imidazolium-based ionic liquids (IL), which contributes additional tunability as the IL serves as a non-covalent cross-link between the polymer chains. We are investigating the effects of adding functional, ionic small molecules into the polymeric matrix which alter intramolecular interactions and promote further structuring within the ionic framework. These HP-ionenes and IL composites are thoroughly characterized in order to develop structure-property relationships between the polymer properties and the structural and functional features, and in order to understand the coordination between polymer chains and dispersed ionic additives. The performance of these novel ionenes and composites is tested in diverse applications including gas separation membranes, fibers, coatings, and 3D printing materials.
Incorporation of halogen bonding in poly(vinyl ethers) towards the formation of supramolecular materials

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Halogen bonding is rapidly gaining popularity as a reliable intermolecular interaction for the formation of supramolecular materials. While various examples of polymers, often polyacrylates and polymethacrylates, containing halogen bonding moieties have been reported, herein the novel incorporation of halogen bonding units into vinyl ether monomers to readily allow the use of this intermolecular interaction in polymers synthesized using cationic polymerization is presented. Three halogen bonding vinyl ether monomers with varying chain lengths between the halogen bonding unit and the vinyl ether moiety were developed and could successfully be polymerized in a controlled manner. Using these vinyl ether monomers, a variety of copolymer structures incorporating isobutyl vinyl ether (IBVE), which should not participate in halogen bonding, were developed. Halogen bonding interactions were tested with various halogen bond donors, such as triethylamine. Analysis of the resulting structures was started.

Vinyl ether monomers containing a halogen bonding unit (iodo-perfluorobenzene) were polymerized into a variety of polymer structures. Copolymers combined the halogen bonding vinyl ether (light purple) with a monomer exhibiting limited ability to participate in halogen bonding, isobutyl vinyl ether (dark green).
Molecular control over dynamic properties in imine-based covalent adaptable networks

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Covalent adaptable networks (CANs) are a promising type of polymers that combine the strength of thermosets, as a result of their crosslinked structure, with recyclability as a result of molecular bond-exchange reactions. The molecular dynamics of these bond-exchange reactions are very dependent on the composition of the polymer network. In this contribution, we demonstrate that the well-known physical-organic concept defined by the Hammett equation, which operates on the molecular level, can also be exploited to achieve quantitatively predictable and delicate chemical control over mechanical properties of vitrimer(-like) materials on the macroscopic level. That is, we present a precise way to tune the dynamic mechanical and thermal properties of dynamic covalent polyimines via the electronic effect of dianiline monomers based on the Hammett equation. This allows for a direct and quantitative correlation of a simple, molecule-based physical parameter (i.e. the monomer’s Hammett parameter, σ) to a range of macroscopic material properties: firstly, the linear correlation of the kinetic activation energy (E_a) for the imine exchange to the σ value, enabled us to tune the E_a from 16 to 85 kJ mol⁻¹. Furthermore, the creep behaviour (γ), glass transition (T_g) and the topology freezing transition temperature (T_v), all showed a strong, often linear, dependence on the σ value of the dianiline monomer. These combined results demonstrate how dynamic material properties can be directly tuned and designed in a quantitative—and therefore predictable—manner through correlations based on the Hammett equation. Moreover, the dynamic nature of the imine bond enabled not only recycling, but also intrinsic self-healing of the materials over multiple cycles without the need for solvent, catalysts or addition of external chemicals. Finally, the effect of polarity within the polymeric structure on the efficiency of imine exchange will be presented as a further molecular handle to control material properties.
Non-isocyanate polyurethane foams derived from 1,1’-carbonyldiimidazole functionalized precursors

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Polyurethanes are some of the most prevalent materials in the industrial sphere because of their versatility. They exhibit exceptional hardness, strength, and flexibility based on chemical structure, affording diverse applications such as coatings, adhesives, foams, elastomers, and fibers. Academia and industry are working towards phasing out isocyanates, which are well known for being toxic, hazardous, and highly reactive. Since isocyanates are one of the two-component polyurethane systems, it is imperative to investigate new routes to polyurethane thermoplastics and foams. There are four major pathways towards non-isocyanate polyurethanes (NIPUs). These include carbonates and carbamates reacting with amines or alcohols, respectively. The Long research group recently discovered a novel method of reacting imidazole-activated diols with amines to produce NIPUs. The products range from thermoplastics to thermoset polyurethane foams based on the reagent functionality and chemical structure. The glass transition temperatures are tunable from below 0 °C to above 130 °C based on differential scanning calorimetry, dynamic mechanical analysis, and thermomechanical analysis. The reaction is highly versatile and is sustainable because it is catalyst-, solvent-, and isocyanate-free.

Isocyanate-free polyurethane foam with scanning electron microscopy image.
Borane catalyzed ring-opening polymerization, copolymerization and depolymerization reactions controlled by Lewis acid strength

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Metal-free catalysts have shown promise as alternatives to transition metal based homogeneous catalysts in a range of ring-opening polymerization and copolymerization reactions, but this area remains quite underdeveloped. We have shown that arylboranes, BPh$_3$ and B(C$_6$F$_5$)$_3$, can be used as catalysts, in the presence of a suitable co-catalyst or as a pre-formed Lewis acid/base adduct, to prepare either cyclic organic carbonate or polycarbonate products from epoxides and carbon dioxide. Selectivity towards cyclic or polymer product is dependent on the substrate used. Lower activity was observed using B(C$_6$F$_5$)$_3$ due to its increased Lewis acidity. Kinetic studies of this metal-free reaction revealed a process that is first order in all reagents with the surprising exception of carbon dioxide, where an inverse dependence was discovered. Following on from this work, we have investigated tandem copolymerization-polymer functionalization reactions where the catalytic borane can hydrosilylate pendent olefin groups along the polycarbonate chain. BPh$_3$ with a suitable nucleophile is also able to copolymerize cyclic anhydrides with epoxides including bioderived limonene-oxide. Due to differences in reactivity between epoxides and anhydrides, block polyester-carbonates can be produced. Further to this, B(C$_6$F$_5$)$_3$ can selectively depolymerize the polycarbonate blocks in these polymers to yield polyester and cyclic carbonate.
1,2,3-triazole based poly(ionic liquids) as polymeric dielectrics
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Polyionic liquids (PIL) are an important addition to polymeric dielectrics in organic electronics due to their versatility. 1,2,3-triazole based PILs are an emerging field among polymeric dielectrics in organic electronics.

The copper-catalyzed azide-alkyne cycloaddition (CuAAC) ‘click’ reaction is a robust and straightforward synthetic route to obtain 1,2,3-triazole based poly(ionic liquids) (PILs) from poly(4-vinylbenzylchloride). Charge in the polymer can be introduced either by alkylating the 1,2,3-triazole group or by using an alkyne that carries a charge. Thusly, the polymer backbone is unaffected, but the charge and the polymer architecture can be manipulated by the choice of alkyne, azide-containing group, and the alkylating group. PIL properties are also affected by the choice of counterions. We prepared both positively and negatively charged PILs carrying either inorganic (Na⁺ or Cl⁻) or organic counterions 1-butyl-3-methyl-imidazolium (C4mim⁺) or 1-butyl-3-methyl-imidazolium (TFSI⁻).

The nature of the counterions had a significant influence on the conductivity of metal-insulator-metal (MIM) capacitors when the dielectric properties were characterized by electrochemical impedance spectroscopy at room temperature. The ion mobility of the positively charged PIL was significantly improved after substituting the Cl⁻ counterion with TFSI⁻, as was the transition frequency of the capacitor, due to the T₉ decreasing from 80 to 8 °C after the ion exchange. For the negatively charged PIL, the counterion exchange from Na⁺ to C4mim⁺ had little effect on the conductivity, as the T₉ of the polymers remained above room temperature.

The tunable aspect of the chemistry, transition frequencies, conductivity, and high capacitance densities make 1,2,3-triazole based PILs desirable dielectrics in organic thin-film transistors, compared to traditional polymer dielectrics.
Accessing chemically recyclable polymers through ring-opening copolymerization/depolymerization of strained monomers with unstrained monomers

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A closed loop cycle for polymer production and disposal is needed to handle the estimated half a billion metric tons a year of polymer that will be used by 2050. Current methods for polymer recycling are insufficient to meet this need. We have demonstrated that the ring-opening copolymerization of an unstrained monomer, γ-butyrolactone, and a strained monomer, ε-caprolactone, produces a chemically recyclable polymer that proceeds with good mass recovery of strained and unstrained monomers. The copolymerization is an enthalpy controlled process driven by the ring-opening of the strained ε-caprolactone monomer. The depolymerization is an entropy controlled process that is driven by the cyclization of the unstrained γ-butyrolactone monomer. Depolymerization of the resulting copolymer yielded greater than 80% and 75% mass recovery of the unstrained and strained monomer, respectively. The recovered monomers can be used without further purification to reproduce the original copolymer, closing the loop for polymer recycling. This proof-of-principle demonstration further diversifies the types of polymers that can be chemically recycled, and provides a strategy that enables tuning of polymer mechanical properties and polymer degradation rates by utilizing two separate monomers to modulate each property independently.
Vanillin and soy derived vinyl monomers copolymerization targeting synthesis of latexes with high bio-based content

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Recently, we reported on synthesis and characterization of new biobased acrylic monomers derived from variety of plant/vegetable oils (soybean, olive, linseed, sunflower, corn, canola etc.) and their application in free radical polymerization. Copolymerization study on plant oil-based monomers (POBMs) with a variety of petroleum-based commodity comonomers demonstrated that incorporation of POBM into macromolecular structure provides internal plasticization, hydrophobization, improves toughness of crosslinked latex polymers and promotes biodegradability of resulted biobased latexes. However, excessive polymers softening was observed when POBM content in the resulted copolymers exceeds 60 wt.\%, making latexes “too soft” and not applicable for film preparation. To be able to increase biobased content without worsening the material properties, alternative biobased counterparts may be considered for copolymerization with POBM. For this, new vanillin-derived 3-allyl-5-vinylveratrole (AVV) was chosen. Having chemical structure similar to petroleum-based Styrene, the AVV can perform as its biobased alternative when incorporated in macromolecular structure. Incorporation of AVV fragments into latex copolymers could balance mechanical properties of the resulted macromolecules by enhancing the materials strength and toughness. In addition, presence of allyl bond in the AVV chemical structure may contribute to its reactivity in free radical reactions, if allyl groups are retained during the polymerization-they can be used for post-polymerization cross-linking. The obtained results show that AVV successfully undergoes free radical homopolymerization and chain copolymerization with POBM (monomer from high oleic soybean oil was used). As determined by $^1\text{H}$ NMR spectroscopy, AVV’s allylic groups remain unreacted under polymerization reaction conditions used in this study. Feasibility of AVV and POBM combination in chain copolymerization was demonstrated. Varying monomers feed ratio, latexes in a broad range of thermo-mechanical properties were synthesized, along with ability to tune tensile properties by crosslinking using allylic groups of AVV fragments.
Design, synthesis and application of precision synthetic biopolymers with defined sequences

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Natural macromolecules (e.g. nucleic acids and proteins) are exactly sequence-defined polymers, and their specifically defined sequences of nucleotides or amino acids create complexity and assure the structural and functional diversity required for living organisms in nature. Particularly, precision sequence control is the most crucial method used by nature for developing molecularly encoded self-replicators, which are the essence of all of life forms. However, most of these reported synthetic polymers are often polydisperse and sequence-uncontrollable in nature, which greatly prevent understanding of fundamental interactions between recently, a number of synthesis approaches have been explored to make discrete synthetic polymers with defined monomer sequence. Well-established solid-phase synthesis enables the fabrication of sequence-defined polymers. Such method is quite efficient for controlling dispersity and monomer sequences of synthetic polymers, but it is greatly limited by low yields, high cost of the solid supports, inability to quantitatively monitor the coupling progress and difficulties of scale up. In comparison, liquid-phase synthesis has long been proposed to overcome these deficiencies, enabling facile and efficient production of sequence-defined synthetic polymers at large scales.

Herein, we aim at creating a flexible and scalable liquid-phase synthesis platform towards producing precision sequence-defined biopolymers with DNA-mimicking information storage and retrieval at the molecular level. A variety of functional sequence-defined synthetic biopolymers with fully controlled molecular structures, monomer sequences and specific functions have been acquired using such liquid-phase synthesis method. These polymers will be readily endowed with diversified properties and functions via the site-selective modification approach, further showing great potential for widespread applications in nanotechnology and pharmaceutical fields. When a specific stimulus is applied, these exogenous or intrinsic properties and functions of these polymers can also be effectively or even precisely regulated, thereby bringing promising site-specific response into these polymeric materials.

Fig. 1. (a) Plot of sequence purity as a function of molecular weight for natural biopolymers, conventional synthetic polymers and precision synthetic polymers. (b) Sequence-defined synthetic polymers with well-defined monomer sequence and diverse chemical bonds. (c) Site-selective multi-functionalization of sequence-defined synthetic polymers.
Highly selective cationic co-polymerization of 2-MeTHF to bio-based polyether polyols

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Polyethers with defined end group functionalities are indispensable building blocks to produce polyurethane based materials and high-performance adhesives. Currently polyether polyols are obtained by the poly- and oligomerization of cyclic ethers from petrochemical feedstocks, e.g. propylene oxide (PO), ethylene oxide (EO) and tetrahydrofuran (THF). The lack of bio-based alternatives prompted us to investigate 2-methyl tetrahydrofuran (2-MeTHF), thus far mainly used as a solvent or fuel additive, as co-monomer. In contrast to THF, 2-MeTHF is regarded as non-polymerizable. However, we present the first reported methodology to co-polymerize 2-MeTHF with PO to hydroxy terminated polyethers. The obtained materials are low in cyclic oligomers, which is otherwise difficult to achieve in cationic polymerization.

Initial investigations showed that with strong Lewis acids, with or without a nucleophile as initiator, mostly cyclic oligomers were obtained; these presumably form via a backbiting reaction, a common side reaction in cationic ring opening polymerization. On the other hand, with only 0.02 mol-% phosphotungstic acid as catalyst the incorporation of 2-MeTHF and the molecular weight of the polymer could be directly controlled by the ratio between the initiator alcohol and PO, i.e. a living copolymerization (Figure 1); of the investigated bifunctional alcohols 1,4-butandiol (1,4-BDO) performed best.

NMR and ESI-MS studies proved the absence of cyclic oligomers and an average incorporation of 2-MeTHF up to 43 mol-%, which is close to the theoretical maximum of 43.3%. Subsequently, we performed a scale-up producing 300g of copolymer. Crosslinking experiments with 4,4-methyl phenyl isocyanate show promising applicability in two component adhesives.

Yield= 80-85%, f(2-MeTHF)=38-42 mol-%
Mₐ(Theor.)=1446 g/mol
Mₐ(NMR)=1390(±130) g/mol
Mₐ(GPC)=1381(±70) g/mol D=1.4
Mₐ(OH-V)=1560(±44) g/mol

Scheme 1: Methodology for the copolymerization of 2-MeTHF and PO to OH terminated polyether polyols.

Figure 1: Predicted vs. experimental Mₐ at different ratios of fed PO and 1,4-BDO
Regioregularity effects on the thermotropic liquid crystalline phase transitions of poly(3-dodecylthiophene)

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Liquid crystalline (LC) interactions of conjugated polymers (CPs) allow to yield an effective route for preferred morphologies for organic electronics. However, systematic understanding and control of the LC interactions decoupled from other parameters have been difficult to achieve. Herein, the thermotropic LC phase transition of regioregularity-controlled poly(3-dodecylthiophene) (P3DDT) is investigated. Controlling regioregularity (RR) of the P3DDT from 95% to 65% provides significantly altered strength of the LC interactions while maintaining the chemical structures the same. As the RR reduces, the P3DDT exhibits progressively decreased phase transition temperatures under polarized microscopy (POM) due to weaker interchain interactions. In the X-ray scattering and thermal analysis, it is founded that the melting of side-chain and backbone lead to entering the nematic and isotropic phase, respectively. Furthermore, as RR decreasing, the ratio of Form II/Form I polymorphs is increased. Considering the faster breakdown of Form II upon heating, larger Form II/Form I can promote lower transition temperature. Molecular design of the RR provides an effective approach to controlling LC interactions of CPs and to obtaining a desired LC phase and morphologies.
Synthesis and characterization of Azulene incorporated polymers as dielectric materials

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With the increasing demand on energy, new materials and techniques are created to improve the energy conversion and the energy storage density. Capacitors play a crucial role by storing energy and releasing them on-demand and are containing dielectric material between two conductive electrodes. Dielectric materials are insulators which allow electric flux via polarization that is coupled to the electric field through permittivity. Compared to inorganic materials, organic polymers have many advantages as dielectric materials due to their high flexibility, good manufacturability, high dielectric breakdown strength, and low dielectric loss. Unfortunately, the applications of polymer based dielectric materials are limited because of the low dielectric permittivity of those polymers. Therefore, there is a high demand for polymeric materials with high dielectric permittivity at high electric field.

Azulene, a 10-$\pi$-electron isomer of naphthalene, has an intrinsic large dipole moment of 1.08 D, which is unusual for hydrocarbon compound. It is a polarized compound induced by the aromatization of the structure. Recent work has focused on tuning electronic properties of the azulene compounds and their applications in non-linear optics, liquid crystals, field effect transistors and photovoltaics. Polymers and copolymers containing Azulene units in their main chains and side chains have been reported mainly through Azulene’s 1 and 3 positions with limited studies of functionalization through 2 and 6 positions. The large resting dipole, easy synthesis, functionalizability and solution processability renders azulene compounds as ideal materials to improve the dielectric properties of the polymers. In this study, the polarizability of Azulene will be obtained by modifying azulene with electron donating and electron accepting groups at 2 and 6 positions. By incorporating these modified azulene derivatives as pendent groups to polymers, new dielectric materials can be achieved. Here, the chemical composition of these novel polymeric materials and their dielectric performances will be presented.
Materials informatics to accelerate polymer research
Corinne Lipscomb, Presenter

Deposition of synthetic and bio-based polycations onto negatively charged solid surfaces: Effect of the polymer cationicity, ionic strength, and the addition of an anionic surfactant
Professor Eduardo Guzman Solis, Presenter; María Hernández-Rivas; Laura Fernández-Peña; Andrew Akanno; Andrew Greaves; Lionel Bureau; Fabien Leonforte; Francisco Ortega; Ramon Rubio; Gustavo Luengo

Highly active zinc bisguanidine catalysts for the production of biodegradable polyesters
Alina Hermann, Presenter; Sonja Herres-Pawlis

Recycling of hard to recycle materials
Robert Peoples, Presenter

Application of cross-linked polyrotaxanes for oil well construction
Hasmukh Patel, Presenter; Roland Martinez; Kenneth Johnson

Innovative applications of polymers in downhole applications
S. Sherry Zhu, Presenter; Marta Antoniv; Hsieh Chen; Ayrat Gizzatov

Suspension polymerization of poly(octadecyl acrylate) powders for powder bed fusion of phase change materials
Ren Bean, Presenter; Emily Wilts, Presenter; Camden Chatham, Presenter; Julia Pimentel, Presenter; Jose Sintas, Presenter; Christopher Williams, Presenter; Timothy Long, Presenter

Properties of waterborne pressure-sensitive adhesives with a poly(acrylic acid)-block-poly(butyl acrylate) diblock copolymer additive
Kylie Manning, Presenter; Joseph Binder; James Defelippis; Johnpeter Ngunjiri; Saswati Pujari

Integrated fluorescent carbon dots for various biomedical applications
Ranju Kandra, Presenter
Materials informatics to accelerate polymer research

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Over the last two years, 3M has been developing digital tools for data visualization and sharing, as well as advanced statistical and machine learning modeling specifically for materials development. A case study using these tools within the polymer domain will be discussed.
Deposition of synthetic and bio-based polycations onto negatively charged solid surfaces: Effect of the polymer cationicity, ionic strength, and the addition of an anionic surfactant

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The deposition of layers of different polycations (synthetic or derived from natural, renewable resources) onto oppositely charged surfaces has been studied using ellipsometry and quartz crystal microbalance with dissipation monitoring (QCM-D). Information about the thickness of the deposited layers and their water content was ascertained. The adsorption of the different polycations onto negatively charged surfaces was found to be a complex process, which is influenced by the chemical nature of the polymer chains, ionic strength, polymer concentration and the addition of additives such as surfactants. The experimental picture shows a good agreement with theoretical calculations performed using the Self-Consistent Mean Field (SCF) approach. The results show that the electrostatically-driven deposition can be tuned by modifying the physico-chemical properties of the solutions and the chemical nature of the adsorbed polymer. This versatile approach is a big step forward in aiding the design of new polymers for many industrial applications and, in particular, the design of sustainable washing formulations for cosmetic applications.
Highly active zinc bisguanididine catalysts for the production of biodegradable polyesters

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Polylactide is a well-known bioplastic which is both bio-based and biodegradable. It is one of the most widely produced bioplastics and the growing production rate of this material has the potential for capturing high market shares in the coming decade. In general, the end-of-life of biodegradable plastics gives an environmental advantage. The current problem for some bioplastics also including polylactide is the industrially used toxic tin-catalyst (tin(II)-2-ethylhexanoate) for the production of the polymers. Currently, accumulation of bioplastics in the environment leads to soil contamination through catalyst remaining in the polymer. In order to solve this problem and make the complete life cycle of this polymer sustainable, a specially designed robust zinc-bischelate complex with triflate anions was synthesized and investigated. The results showed that this non-toxic zinc-catalyst has the highest activity in the bulk polymerization of lactide so far. It polymerizes technical grade racemic lactide in melt with fast rate constants, high molar masses and yields in a short time. Additionally, e-caprolactone was also polymerized with this specific zinc catalyst, for which the industrially based tin catalyst could be replaced likewise. Here, the high activity of the zinc catalyst led to colorless polymer with high molar masses. Further, this catalyst is the first guanidine-based catalyst that is also able to polymerize lactide in solution. The catalyst is therefore a valuable addition to both the production of biodegradable monomers and the ecotoxicity reduction of plastic waste.
Recycling of hard to recycle materials

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Plastic waste is receiving well-deserved and unprecedented interest from a recycling perspective. Mechanical and, in particular chemical recycling, offer a proven way to provide closed-loop mechanisms for many materials. Polymer streams that are totally or primarily homogenous are obvious priority candidates for recycling. However, complex assemblies of polymers and systems make the challenge much more difficult, both technically and economically.

This talk will present results on harder to recycle products such as paint, mattresses, and especially carpet. After 20 years of effort, a major recession and now the pandemic, carpet recycling in the United States, like many recycling operations, has reached a crisis point. Outside of California, carpet recycling has contracted. To better understand the challenges, we will focus in technologies, economics, products and markets which impact the recycling of such materials. In particular, efforts in California will be compared to those of other commodities in the state. Good progress has been achieved despite the pandemic after extensive capital investment in infrastructure and on-going large subsides paid. What have we learned and how can this be translated to other systems will also be discussed.
Application of cross-linked polyrotaxanes for oil well construction

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During what is known as the primary well cementing process, cement is placed in the annulus between the rock formations of the wellbore and the steel casing, in order to provide an impermeable seal. This seal achieves what is regarded in well construction as zonal isolation. In order for the well construction process to be successful, the cement must have the mechanical properties to insure a pressure tight seal between casing and formation in the high pressure and high temperature environment of the well. The differential pressure on the casing during production creates stresses on the cement sheath. These concentrated stresses generate cracks or fractures in the cement and result into serious consequences, e.g., safety, reduced production and eventually decreases the total lifespan of the oil well. Adding elastic polymers improves the set cement's resistance to such stresses, providing better long-term zonal isolation. Current technology in the field uses traditional polymers or rubbers as cement additives, which tend to lose their efficacy over time and do not effectively address the materials requirements for our downhole environments. Furthermore, conventional and commercially available additives detrimentally affect the compressive strength of the cement. To address these issues, we have developed a novel polymeric additive based on the pulley-principle – cross-linked polyrotaxanes, which redistributes localized stresses throughout the cement matrix to minimize the formation of cracks, yielding a cement endowed with exceptional mechanical properties. We have observed consistent reduction in Young’s modulus for cement with cross-linked polyrotaxanes compared to control cement sample at different temperatures. This characteristic proves that blending of cross-linked polyrotaxanes into wellbore cement enables the uniform distribution of stresses and contributes toward enhanced elastic properties in cured cement.
Innovative applications of polymers in downhole applications

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Polymers have been widely applied in oil and gas industry. Most polymers are used as friction reducers, viscosifiers, diverters, etc. in hydraulic fracturing, drilling, and enhanced oil recovery. The harsh downhole environment – a porous media filled with fluids of oil and saline water at high temperature and high pressure – poses challenges to efficiently transport and maintain polymers’ long-term stability. These unique challenges provide opportunities for innovative applications of polymers. Here we will present some examples of innovative polymer applications in the downhole environment. The examples include polymers with transient stability as cost-effective diverters, stabilizing polymeric nanoparticles in high salinity fluids, polymeric nanoparticles as mud logging tags for accurate cutting depth correlation, and low retention polymers in porous formation rocks (simulation and experiments).
Suspension polymerization of poly(octadecyl acrylate) powders for powder bed fusion of phase change materials

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Powder bed fusion (PBF) is a layer-wise additive manufacturing (AM) process that produces 3D parts through selectively melting polymer powders with an infrared (IR) laser beam. Despite its long-standing use to produce end-use parts for industrial applications, the large majority of PBF research has been limited to a select few thermoplastics, with a primary focus on nylon. This work describes the use of a novel low-melting (< 80 °C) polymer for PBF, poly(octadecyl acrylate) (POA), and suspension polymerization to produce particles for application as a phase change material. Suspension polymerization is underutilized in the PBF literature producing spherical particles with controlled sizes while only using water, a non-toxic solvent, for the process. Tuning stabilizer amounts, poly(vinyl alcohol), in suspension polymerization varied the particle sizes of the POA and varying temperatures controlled crosslinking percentages. 2 wt % stabilizer produced particles with a 148 µm mean size and 60 % gel fraction, which represented the smallest sizes and gel fractions of the series. The high degree of crosslinking may oppose coalescence of particles during printing and thus solution-made POA was also added via dry mixing. Static and dynamic powder flowability experiments determined Hausner ratio and avalanche angle of 100% solution-polymerized, 100% suspension-polymerized, and 50:50 mixture powders. All fell within the common range of powder properties for PBF, but 50:50 was chosen to attempt 3D parts based on zero-shear viscosity. The 50:50 mixture produced multi-layered 3D parts thus proving this system’s potential for a novel material and particle manufacturing method for PBF. Differential scanning calorimetry (DSC) also measured latent heat and stability over 50 heat-cool-heat cycles of a printed part to confirm the effectiveness as a phase change material.
Properties of waterborne pressure-sensitive adhesives with a poly(acrylic acid)-block-poly(butyl acrylate) diblock copolymer additive

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A common issue when designing polymers for pressure sensitive adhesive (PSA) applications is an inverse relationship between shear strength (cohesion) and both peel and tack (adhesion) properties. A high shear resistance can be obtained by increasing the stiffness of an adhesive. However, an increase in modulus can lead to poor wetting and limited fibrillation during debonding. High tack and peel strength require an increase in viscous properties that negatively effects shear strength.

Acrylic acid (AA) is often polymerized as a comonomer in waterborne pressure sensitive adhesives (PSA) to aid in latex stability by electrostatic repulsion at neutral pH and improve adhesive performance. The adhesive strength is greatly affected by the location of the acrylic acid moieties on the latex particle. Introduction of AA to a polymer particle also allows for a strategy to adjust PSA performance by adjusting pH.

In the present study, a commercial PSA with 0% or 1% acid in its backbone was formulated with an amphiphilic diblock copolymer, poly(acrylic acid)-block-(butyl acrylate) (pAA-b-pBA), synthesized by reversible-addition fragmentation chain-transfer (RAFT) polymerization. It was hypothesized that the diblock copolymer would adsorb onto the soft acrylic latex particles in the emulsion state. Formation of a thin hard layer in the film state can produce a percolated network, increasing PSA cohesion without decreasing adhesion. Film drying conditions can also alter the morphology of the final film. The pH of the nanocomposites was also varied to evaluate changes in PSA properties with respect to the ionization of the AA portion of the diblock copolymer.
Integrated fluorescent carbon dots for various biomedical applications

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We are reporting novel protocol for the synthesis of carbon quantum dots using BTCA as an organic source. Carbon dots (Cdots) have become a potential material for biosensing, drug delivery and bioimaging because of their excellent optical properties, high biocompatibility and low toxicity. Thus, the preparation, properties and applications of Cdots have drawn great attention. In this review, Cdots were classified into two groups: graphenenanodots and carbon nanodots, based on the difference in precursors and preparation methods. The synthetic methods of Cdots were summarized and their luminescence mechanism was analyzed. The applications of Cdots in biosensing, drug delivery and bioimaging were also discussed. The issues and challenges of Cdots were analyzed for their further development. These can be characterized by FTIR, HRTEM XRD XPS. The objective of the study that how carbon dot and chitosan influence the growth of the plant at various concentration. Secondly, as well as drug release study of chitosan carbon dot nanocomposite film
Joseph C. Salamone Symposium: Revolutionary Innovation
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William Daly, Organizer, Presider; Dana Garcia, Organizer, Presider; Timothy Long, Organizer, Presider; Ann Beal Salamone, Organizer, Presider

Disruptive chemistry intertwined with biology to tackle wound healing obstacles
Ann Beal Salamone, Presenter

Convergent, translational research to improve human health
Joseph DeSimone, Presenter

Multi-messenger time-domain astronomy: GW170817 and the future
Alessandra Corsi, Presenter

Membrane-based water purification to help alleviate global water scarcity
Judy Riffle, Presenter

From basics to experiments and products; and unto the marketplace: An early history of polyisobutylene in medicine
Joseph Kennedy, Presenter; Len Pinchuk

Creative innovations in POLY
William Daly, Presenter

Climate science discoveries, trends, and insights, 1930-2019
Jeremy Hoffman, Presenter

Asking more from our networks: From 3D printing carbonaceous objects to supramolecular elastomers
Timothy Long, Presenter; Clay Arrington; Boer Liu; James R Brown; Johanna Vandenbrande

Technical opportunities associated with producing plant-based meat
Tasha Hermes, Presenter

Technologies at the bleeding edge of ophthalmology and wearable diagnostics
Dr. Jeffrey Linhardt, Presenter

Diastolic dysfunction and cognitive impairment
Dr Alicia S Parker, MD, Presenter
Disruptive chemistry intertwined with biology to tackle wound healing obstacles

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Two areas of current innovation highlight and honor my beloved husband, Dr. Joseph C. Salamone as well as the scientific team at Rochal Industries.

While the SARS-Cov-2/COVID-19 pandemic invaded our lives in 2019, chronic wound infection pandemics have been with humans since the beginning of humanity (e.g., leprosy). In the USA, chronic wounds are suffered by 6.7 million people with at least 90% being infected with microbes in a biofilm state. Wound infection exacerbates poor wound healing. Within a few hours of attaching to a surface, bacteria and fungi synthesize complex protective structures composed of at least polysaccharides, proteins, humic substances, lipids and nucleic acids which are strengthened by electrostatic interactions, hydrogen bonding and London dispersion forces. Biofilms are created to provide microbe sustainability in the experienced environment which means every biofilm is different in construct composition, density, and conformation. A synergistic set of chemicals was created and introduced to the market (2019/2020) to deconstruct diverse biofilms found in chronic wounds and kill the encased microbes using multiple chemical methods - without harming human cells/tissue. More recently, longer lasting deactivation of human coronavirus, including SARS-CoV- 2, on skin and other surfaces has been observed.

Further, for wounds to heal, necrotic tissue must be removed as this dead tissue is not only a microbe food source but also catalyzes further tissue degradation. Surgical methods, mechanical techniques, and current enzymatic products for debridement remove necrotic tissue but also remove and damage healthy tissue. Through out-of-the-box thinking, a completely different chemistry has been put into use to selectively remove dead tissue. Not only is the chemistry unique but the test methods for determining efficacy are unique.

![Graph showing mature biofilm microbe survival](image)

Mature biofilm microbe survival
Convergent, translational research to improve human health

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This lecture will describe nano-/micro-fabrication and 3D printing technologies that we have invented and employed to advance human health. In 2004 we invented Particle Replication in Non-wetting Templates (PRINT), a high-resolution imprint lithography-based process to fabricate nano- and micro-particles with precise and independent control over particle parameters (e.g. size, shape, modulus, surface chemistry). PRINT led us to launch Liquidia Technologies (NASDAQ: LQDA) and opened new research paths, including to elucidate the influence of specific particle parameters in biological systems, and to inform the design of vaccines and targeted therapeutics. In 2015 we reported the invention of Continuous Liquid Interface Production (CLIP), which overcame limitations in polymer 3D printing—slowness, a very limited range of materials, and an inability to create parts with the mechanical and thermal properties needed for widespread utility. CLIP is transforming how products are made. In medicine, for example, to help address shortages, CLIP enabled a new COVID-19 nasopharyngeal testing swab to go from concept to market in 20 days, followed by a 400-patient clinical trial at Stanford. Academic labs are also using CLIP, including to create IVRs that optimize drug delivery, and implantable chemotherapy absorbers to limit toxic side effects. Vast opportunities also exist in next-generation devices. For example, the fabrication of an iontophoretic device we invented several years ago to treat hard-to-reach solid tumors is now being optimized for clinical trials with CLIP. We are also pursuing new advances including software treatment planning for digital therapeutic devices in pediatric medicine, as well as the design of a single-digit micron resolution printer to advance microneedle designs for vaccine applications. Our impact in human health relies on our ability to foster a convergent research program that allows for new connections to be made among traditionally disparate disciplines and concepts, and to maintain a consistent focus on the translational potential of our advances.
Multi-messenger time-domain astronomy: GW170817 and the future

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On 2017 August 17, the field of multi-messenger astronomy made the big leagues with a dazzling discovery. After several detections of gravitational waves from binary black hole mergers with no convincing electromagnetic counterparts, advanced LIGO and Virgo scored their first direct detection of gravitational waves from a binary neutron star merger, an event dubbed GW170817. Soon after the gravitational wave discovery, GW170817 started gifting the astronomical community with an electromagnetic counterpart spanning all bands of the spectrum. Since then, the hunt has been on for more multi-messenger detections of these cosmic fireworks. In this talk, I will review what we have learned from GW170817, what questions remain open, and what are the prospects for future multi-messenger studies of the transient sky.

Images of the GW170817 field from Jansky VLA data (PI: Corsi). The radio afterglow of GW170817 is marked with a white open circle. The central panel shows the discovery of a 6 GHz radio glow! The right image taken 6 d later confirmed this discovery. On the left is a pre-discovery image of the field.
Membrane-based water purification to help alleviate global water scarcity

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I am elated to present this discussion in honor of Joe Salamone, a distinguished revolutionary scientist, businessman and friend. There is widespread recognition that the world’s supply of clean water is in great jeopardy, and that the key to solving the scarcity lies largely in membrane processes for removing salt and other contaminants, and in learning how to purify and reuse water. The dominant technology for reverse osmosis membranes is a layered composite comprised of an ~100-nm thick non-porous aromatic polyamide atop a porous polymeric mechanical support with a textile backing. The membranes are rolled into a spiral wound configuration and placed in a tube where the tubes are connected in series to introduce contaminated water under pressure and exit a portion as clean water. The flux of water must be high to transport large volumes efficiently, the rejection of angstrom level contaminants should be >99%, they must not clog, and ideally they should last for years with minimum operating downtime devoted to keep them clean. Requirements for the composite membranes are challenging and depend on both the thin non-porous barrier layer and the thicker porous substructure, as well as the interface between them. The chemical structure, hydrophilicity and topology of the barrier layer, and the pore morphology in the support, are critical. As one defines new chemistries for barrier layers, one must also provide an economical means for processing such composites. NALA is focused on developing chemically resistant sulfonated polysulfone barrier layers to avoid the problem of biofouling that has plagued polyamide membrane users for decades. The new membranes cannot be processed with current in-situ interfacial polymerization technology, so their implementation also requires a new manufacturing process.
From basics to experiments and products; and unto the marketplace: An early history of polyisobutylene in medicine

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We are honored to be part of this Symposium memorializing the accomplishments of Joseph C. Salamone, inventor and innovator extraordinaire, and dedicate our presentation to his memory. This work began in the 1970-ies when JPK decided to emulate Michael Szwarc's epochal discovery of living anionic polymerization of olefins, by developing living cationic polymerization of isobutylene, an olefin that cannot be polymerized by anionic means. To accomplish this objective took over 10 years of dedicated research by JPK and coworkers. By the mid 1980-ies the objective was reached and polyisobutylenes not only with precisely predictable molecular weights having narrow dispersities were synthesized but also well-defined telechelic polyisobutylenes and polyisobutylene block polymers, such as poly(styrene-b-isobutylene-b-styrene) (SIBS). SIBS has no cleavable groups and the polyisobutylene backbone prevents embrittlement and cracking under flexion. LP will focus on the practical consequences of this basic discovery and will outline four medical devices enabled by living cationic polymerization: (1) The world’s most successful drug eluting stent coated by SIBS (TAXUS, Boston Scientific Corporate Research, Marlboro, MA, United States) that prevents restenosis; (2) PRESERFLO MicroShunt (Santen Pharmaceutical Co. Ltd., Osaka, Japan), based on the discovery that SIBS provokes insignificant inflammation and encapsulation in the eye, the MicroShunt lowers intraocular pressure and stops the progression of vision loss from glaucoma; (3) Crosslinked polyisobutylene intraocular lens (Xi’an EyeDeal Medical Technology Co., Ltd. Xi’an, China) that eliminates glistening and halos; and (4) Crosslinked SIBS heart leaflet valves (Polynova Cardiovascular Inc. Stony Brook, NY, United States) that allows percutaneous implantation of heart valves. We foresee a rich future of polyisobutylene-based biomaterials as polyisobutylene is the most bioinert, enzymatically, hydrolytically and oxidatively stable synthetic elastomer known to man.
Creative innovations in POLY

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Joseph Salamone’s strong motivation to provide service to professional organizations was inculcated in graduate school by his PhD advisor, Charles G. Overberger. Joe joined the Polymer Chemistry Division (POLY) in the early 60’s. Upon election to division treasurer in 1974, Joe Salamone began to enhance the impact of POLY. Joe’s entrepreneurial skills motivated the organization of the first topical workshop in 1979, an endeavor that established one of POLY’s most successful business ventures. To promote education in polymer science, he participated in the formation of the Joint Polymer Education Committee (POLYED) with the Organic Coatings and Plastics Division (PMSE) in 1974. The Industrial Sponsors group was formed in 1979, which further strengthened POLY’s service to its members. During his tenure in office the first POLY poster session was held in 1980. He influenced the creation of the Herman F. Mark Award (1976), the Carl S. Marvel Creative Polymer Chemistry Award (1981) and the Paul J. Flory Polymer Education Award (1982). In 1982, POLY won the ACS Outstanding Division Award for the first time.

Joe served on the organizing committee of the Pacific Polymer Federation (PPF) when it was conceived in 1984 and helped organize the first Pacific Polymer Conference (PPC) meeting in Maui in December 1989. He served as President of PPF in 1995.

Joe Salamone’s intellect and persistent drive transformed POLY and the ACS. Joe’s innovations established POLY as a financially sound organization with international prominence. His professional accolades include election to the National Academy of Engineering (NAE) and the National Academy of Inventors. He was one of POLY’s most distinguished members. We appreciate his dedication and service.
Climate science discoveries, trends, and insights, 1930-2019

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Building on foundational theory and observations of the greenhouse gas effect, evidence of recurrent ice ages, and advancements in observational and computational technology, the field of climate science has grown rapidly throughout the 20th and early 21st century, revolutionizing our understanding of how human activities interact with and directly influence the atmosphere, cryosphere, biosphere, and hydrosphere around us. In keeping with this Symposium's aim to celebrate the life of accomplished scientist Dr. Joseph C. Salamone, in this presentation I will present major advancements in the field of climate science in the context of Dr. Salamone's lifetime and achievements. These milestones will familiarize Symposium attendees with climate models, paleoclimatology, phenology, and urban microclimatology. I will conclude with a vision of how talented thinkers and makers like Dr. Salamone are leading the charge in adapting to and mitigating the impacts of climate change on our communities today and into the future.
Asking more from our networks: From 3D printing carbonaceous objects to supramolecular elastomers

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Sustainable chemistry together with green chemistry continue to provide an overarching motivation for our discovery of advanced materials and advanced manufacturing, addressing end-of-product-life challenges for polymeric products with a circular economy paradigm. Our research integrates green synthetic methods and sustainable vision as a cross-cutting initiative. This lecture will highlight recent advances in polymer design with a “molecules to manufacturing to marketplace” perspective, and crosslinking plays a major role in the design of elastomers for 3D stereolithographic printing, polyimides for vat photopolymerization, and novel polymer architectures for binder jetting of water-soluble adhesives. Pyrolysis of fully aromatic polyimides that result from vat photopolymerization yield complex geometries of carbon with desirable conductivity and thermal resistance. In addition, recent efforts in thermoplastic elastomer design with block and segmented copolymers illustrate the complementary nature of the physical crosslink versus the covalent crosslink. This lecture will illustrate various crosslinking strategies where the crosslinks are susceptible to reversibility using various external stimuli, ranging from heat and pH to photo-irradiation and ionic salts. This lecture honors Joe Salamone for his continuing legacy of functional polymer design at the interface of photochemistry and the impact of network structure on emerging technology. Moreover, his steadfast dedication to translational polymer science and engineering will continue to impact our field for decades to come. The following figure depicts acetal-containing polyether crosslinking agents for the preparation of network structures that are susceptible to acid-cleavage, suggesting impact in 3D printed elastomers and drug delivery applications.
Technical opportunities associated with producing plant-based meat

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It is not new news that the plant-based meat protein category is growing. The category has seen strong growth and billions of dollars of investment resulting in strong advancement of category and product performance. The goal for the category shifted from being simply a vegetarian or vegan option to mimicking the experience of the animal incumbent, bringing in a new flexitarian consumer who is trying to reduce meat consumption to the category. Progression of taste, texture, appearance and even store placement of plant-based meat proteins to replicate the animal offering has brought more consumers to the category and helped reduced perceived gaps between the incumbent meat and plant-based offerings. Although the progress made is truly a feat, meat eaters still note sacrifices when choosing plant-based. Further progress is needed to close this gap and remove the perceived sacrifices made by meat eaters when choosing plant-based meat options. What are the sacrifices and research opportunities? Through experience with industry development, manufacturing for plant-based meat, as well as customer conversations and proprietary customer research, it has been shown that the specific gaps differ by product type (i.e., plant-based patties mimicking beef vary from plant-based patties mimicking chicken but have the overarching goals in common). The largest opportunities to continue advancing the category include but are not limited to texture, flavor, appearance and the label impact of those solutions. The opportunities are large for this category and the purpose of this message is to begin discussing the technical opportunities in the plant-based meat category that we can unlock together to elevate the entire category.
Technologies at the bleeding edge of ophthalmology and wearable diagnostics

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In addition to being a prolific inventor, entrepreneur, and technologist; Dr. Joseph C. Salamone was an extraordinary mentor who instilled scientific curiosity and fostered creativity in all those who worked with and for him. In this lecture, I would like to honor Joe by discussing several technologies that have their roots in the Salamone Research Group and beyond. Polymer and material scientists have long known that small changes in the chemical structure of a polymer or formulation can induce large changes in their macroscopic properties. By specifically tailoring polymers and formulations our team was able to develop hydrogels that had superior water retention properties, inherent surface wettability, and tunable refractive index modification. Several products and projects that came from these discoveries will be presented.

More recently, the fields of smart contact lenses and wearable sensing systems have seen considerable growth. These technologies sit at the interface of microelectronics, life science, materials, optics, and big data. Multidisciplinary teams of researchers have made significant developments in system level assembly, communication and data transfer, chemical and electrochemical sensing, and custom designed electronic components. Efforts toward the development of a glucose sensing contact lens will be highlighted as well as learnings that have spawned projects in other areas. Body worn sensors capable of analyzing interstitial fluid will also be presented with an emphasis on the role that polymer science plays in sensor development.
Diastolic dysfunction and cognitive impairment

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The relationship between diastolic dysfunction and cognition is undefined. Diastolic dysfunction is common, disproportionately affects females, and is increasing in the community. If diastolic dysfunction is found to be associated with cognitive impairment, that would suggest diastolic dysfunction is a novel modifiable risk factor for the development of dementia.

Echocardiographic, MRI and neuropsychological data collected by the Framingham Heart Study, Offspring Cohort, at Exam 8 was reviewed. Data from 1438 participants showed that increasing E/E' ratio, indicating increasing diastolic dysfunction, was associated with increased executive function impairment in the Similarities ($\beta \pm SE: -0.29 \pm 0.09, p < 0.002$) and FAS Phonemic Fluency ($-1.27 \pm 0.33, p < 0.001$) tasks. Those with moderate to severe diastolic dysfunction performed more poorly on Logical Memories ($-0.70 \pm 0.34, p < 0.036$) and FAS Phonemic Fluency ($-2.75 \pm 1.11, p < 0.014$), and trended towards increased impairment on Similarities ($-0.59 \pm 0.30, p < 0.052$) (Table 1). Data from 1217 participants showed that those with mild diastolic dysfunction trended towards increased white matter hyperintensities ($0.11 \pm 0.07, p < 0.105$); participants with moderate-to-severe diastolic dysfunction had increased white matter hyperintensities ($0.30 \pm 0.09, p < 0.001$). Data from 1415 participants showed that increasing E/E' ratio was associated with increased incident mild cognitive impairment (HR 1.29 [95%CI: 1.01, 1.66], $p < 0.04$). Diastolic dysfunction was associated increased incident mild cognitive impairment. Increased diastolic dysfunction was associated with impaired executive function and verbal memory on neuropsychological testing, along with increased cerebral small vessel disease as demonstrated by white matter hyperintensities on MR imaging. An amnestic impairment was also seen, such as can occur in Alzheimer's disease. This study suggests that diastolic dysfunction is a novel modifiable risk factor for the development of dementia.

Table 1. Diastolic Function and Neuropsychological Evaluation

<table>
<thead>
<tr>
<th>Echocardiographic Index</th>
<th>PC1</th>
<th>LMM</th>
<th>TrB-Tm<em>A</em></th>
<th>SIM</th>
<th>FAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>E/E' ratio*1</td>
<td></td>
<td></td>
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<tr>
<td>Model 1</td>
<td>-0.03±0.02(0.254)</td>
<td>0.01±0.10(0.963)</td>
<td>-0.001±0.01(0.919)</td>
<td>-0.29±0.09(0.022)</td>
<td>-1.27±0.33(&lt;0.001)</td>
</tr>
<tr>
<td>Model 2</td>
<td>-0.01±0.02(0.543)</td>
<td>0.01±0.10(0.921)</td>
<td>-0.001±0.01(0.933)</td>
<td>-0.26±0.09(0.005)</td>
<td>-1.12±0.34(&lt;0.001)</td>
</tr>
<tr>
<td>Model 3</td>
<td>-0.01±0.02(0.706)</td>
<td>0.05±0.11(0.647)</td>
<td>0.002±0.01(0.719)</td>
<td>-0.25±0.09(0.008)</td>
<td>-1.06±0.36(&lt;0.002)</td>
</tr>
</tbody>
</table>

Diastolic Dysfunction

| Model 1                  |     |     |           |     |     |
| Normal                  | Ref |     |           |     |     |
| Mild                    | -0.05±0.06(0.446) | -0.04±0.25(0.006) | -0.70±0.34(0.036) | Ref | Ref |
| Moderate to Severe      | 0.16±0.08(0.055) | Ref | 0.01±0.02(0.817) | Ref | Ref |
| Ref                     |     | 0.22±0.02(0.321) | 0.55±0.30(0.052) | Ref | Ref |
| 2.90±0.80(0.013) |     |     |           |     |     |

Model 2

| Normal                  | Ref |     |           |     |     |
| Mild                    | -0.03±0.06(0.519) | -0.02±0.25(0.949) | -0.89±0.30(0.043) | Ref | Ref |
| Moderate to Severe      | 0.13±0.08(0.129) | Ref | 0.01±0.02(0.808) | Ref | Ref |
| Ref                     |     | 0.25±0.02(0.295) | -0.50±0.31(0.017) | Ref | Ref |
| 2.16±0.80(0.007) |     |     |           |     |     |

Model 3

| Normal                  |     |     |           |     |     |
| Mild                    | -0.02±0.06(0.736) | -0.03±0.25(0.868) | -0.51±0.35(0.141) | Ref | Ref |
| Moderate to Severe      | -0.06±0.08(0.271) | 0.01±0.02(0.810) | 0.004±0.02(0.856) | 0.25±0.20(0.272) | 0.43±0.31(0.174) |
| Ref                     |     |     |           |     |     |
| 2.90±0.81(0.010) |     |     |           |     |     |

* Natural log transformed to normalize the distribution. Standardized to mean=0 and variance=1.

Model 1: adjusted for age, age squared, interval between exam and NP, sex, education and prevalent AF

Model 2: model 1 plus systolic blood pressure, treatment for hypertension and prevalent CVD

Model 3: model 2 plus diabetes mellitus, smoking, total cholesterol to HDL ratio, lipid lowering Fx, triglycerides and body mass index

PC1: Global Cognitive Score; LMM: Logical Memories - Delayed Recall; TrB-Tm*A: Trail making test (B – A); SIM: Similarities; FAS: Total score from Verbal Fluency - exclude Animals.

Table 1. Diastolic Function and Neuropsychological Evaluation
Macromolecular Science at the Dawn of its Second Century
Timothy Lodge, Organizer; Krzysztof Matyjaszewski, Organizer; Peter Zarras, Organizer

Macromolecular Science at the Dawn of its Second Century
April 5, 2021

Rapid synthesis of polymeric libraries
Craig Hawker, Presenter

The selective synthesis of polymers utilizing selective catalysts
Robert Grubbs, Presenter

Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets
Jacob Lessard; Georg Scheutz; Michael Sims; Seung Hyun Sung; Thomas Epps; Prof. Brent S Sumerlin, Presenter

New methods for the synthesis of sustainable polymers
Geoffrey Coates, Presenter

Sustainable polymer science and technology: A shared responsibility
Marc Hillmyer, Presenter

Hybrid bonding polymers: Integration of covalent and noncovalent bonds
Samuel Stupp, Presenter

Molecular genetics in the second century of macromolecular chemistry
David Tirrell, Presenter

Digital manufacturing of polymer products
Joseph DeSimone, Presenter

Balancing precision and randomness: A tale of random heteropolymers
Ting Xu, Presenter

Coming full circle: Adapting controlled radical polymerization for organic synthesis
Michelle Coote, Presenter; Alfred Fung; Vincent Doan; Chelsey Hammill; Benjamin Noble

Self-growing of double network hydrogels by mechanical training
Takahiro Matsuda; Tasuku Nakajima; Jian Ping Gong, Presenter

Luminogenic polymers with bright future
Prof. Dr. Ben-Zhong Tang, Presenter

Macromolecular Science at the Dawn of its Second Century
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Transforming thermoplastics into vitrimers
Renaud Nicolay, Presenter

Designing polymers for bio-applications
Molly M Stevens, FREng FRS, Presenter

Synthetic informational polymers: Steps toward artificial life
Jean-Francois Lutz, Presenter

New synthetic strategies for on-demand degradable polymeric materials
Jeremiah Johnson, Presenter

Functional nanoparticles via “living” crystallization-driven self-assembly
Prof. Ian Manners, Presenter
Nanoscopic measurement of the glass transition in nanostructured macromolecules
Rodney Priestley, Presenter

Polymers designed to recover lithium from aqueous streams
Samual Warnock; rahul Sujanani; Everett Zofchak; Shou Zhou; Theodore Dilenschneider; Kalin Hanson; Sanjoy Mukherjee; Venkat Ganesan; Benny Freeman, Presenter; Mahdi Abu-Omar; Christopher Bates

Macromolecular Science at the Dawn of its Second Century
April 7, 2021

From bio-inspired polymers to life-like systems
David Ng; Tanja Weil, Presenter

Can a material perform as an engine?
Dr. Martin Moller, Presenter

C1, C3 and C5 polymerizations: Towards unprecedented polymeric materials
Nikos Hadjichristidis, Presenter

The second century: Polymers from an industrial perspective
Prof. Dr. Sebastian Koltzenburg, Presenter

Precise microstructures in ionomers: New morphologies for improved properties
Karen Winey, Presenter

Polymeric Ionic Liquids: A platform for metal ion conduction
Prof. Rachel Segalman, Presenter

Design-by-architecture: Encoding tissue mechanics in synthetic polymers
Prof. Sergey Sheyko, Presenter
Rapid synthesis of polymeric libraries

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

A versatile and scalable strategy is reported for the rapid generation of block copolymer libraries spanning a wide range of compositions starting from a single parent copolymer. This strategy employs automated and operationally simple chromatographic separation that is demonstrated to be applicable to a variety of block copolymer chemistries on multigram scales with excellent mass recovery. The corresponding phase diagrams exhibit increased compositional resolution compared to those traditionally constructed via multiple, individual block copolymer syntheses. Increased uniformity and lower dispersity of the chromatographic libraries lead to differences in the location of order–order transitions and observable morphologies, highlighting the influence of dispersity on the self-assembly of block copolymers. Significantly, this separation technique greatly simplifies the exploration of block copolymer phase space across a range of compositions, monomer pairs, and molecular weights (up to 50000 amu), producing materials with increased control and homogeneity when compared to conventional strategies.
Olefin Metathesis has become a tool for the synthesis of complex organic molecules and materials. The key to the development of these applications has been the discovery and study of organometallic complexes that will efficiently catalyze the reaction in the presence of standard functional groups.

In addition to the synthesis of complex organic molecules, the catalysts can be used to construct well defined polymer structures that have an array of functions. Key to the synthesis of these materials has been the understanding of the mechanisms of the polymerization process and the development of catalysts that allow careful control of the microstructure of the materials.
Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets

Jacob J. Lessard¹, Georg M. Scheutz¹, Michael B. Sims¹, Seung Hyun Sung², Thomas H. Epps², Brent S. Sumerlin¹, sumerlin@chem.ufl.edu. (1) Department of Chemistry, University of Florida, Gainesville, Florida, United States (2) Chemical Engineering, University of Delaware, Newark, Delaware, United States

The classical division of polymeric materials into thermoplastics and thermosets based on covalent network structure often implies that these categories are distinct and irreconcilable. Yet, the past two decades have seen extensive development of materials that bridge this gap through incorporation of dynamic crosslinks, enabling them to behave as both robust networks and moldable plastics. Although their potential utility is significant, the growth of covalent adaptable networks (CANs) has obscured the line between “thermoplastic” and “thermoset.” This presentation will emphasize that the unique properties of CANs generally emerge from the specifics of the network chemistry/structure while highlighting the promise of controlled architecture (co)polymers for the construction of vitrimer materials.
New methods for the synthesis of sustainable polymers

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

In this presentation, new catalytic routes to polymers from commodity monomers will be presented, with a focus on biodegradable materials, renewable feedstocks, polymers for upcycling and improved properties.
Sustainable polymer science and technology: A shared responsibility

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

Over the past century, numerous natural polymers like rubber from the Hevea brasiliensis tree and modified natural polymers like cellulose acetate have been mainstays of modern life. However, their prevalence prior to World War II has been outstripped by petroleum-based compounds with the advent of modern polymers that, almost entirely, are derived from finite stores of fossil resources. Synthetic polymer production from petrochemicals was at its infancy when I was, and over the past 50+ years the global production of polymers has increased by more than a factor of 100, while the population on Earth increased by only factor of two. This rapid and continued growth of the polymer industry has led to innumerable useful technologies and, unfortunately, staggering levels of synthetic polymer trash. This waste is all too visible and the degradation-resistant plastic refuse we don’t routinely encounter, for example in our oceans, is wreaking ecological damage far and wide. As polymer scientists and engineers, we have a shared responsibility to reverse course and more carefully consider the origins and fates of the materials that we have a common passion for studying. The challenge is all the more daunting because polymers will continue to play important positive rolls in modern society, and we cannot compromise on performance when it comes the materials of tomorrow. Basic research in field of sustainable polymers is of paramount importance to tackle this challenge. Undoubtedly, the basic research discoveries of today will lead to the packaging, construction, household, clothing, automobile, and energy materials of tomorrow. Nobel Laureate Al Gore recently proclaimed, “the evidence now indicates that we are in the early stages of a sustainability revolution that will achieve the magnitude of the Industrial Revolution and the speed of the digital revolution” (New York Times; nyt.ms/32QaBCk). As polymer scientists and engineers, we should lead the way in positively contributing to our slice of such a revolution. In this presentation, I will emphasize the work being carried in the NSF Center for Sustainable Polymers that is focused on this important goal for our shared future.
Hybrid bonding polymers: Integration of covalent and noncovalent bonds

Samuel I. Stupp, s-stupp@northwestern.edu. Northwestern University, Evanston, Illinois, United States

Supramolecular polymers with their energy-tunable noncovalent bonds among structural units have inherent potential to form highly ordered but dynamic structures. The possibility of programming interactions in these systems through self-assembly enables design of materials that respond rapidly to external stimuli, dissolve or melt into monomeric liquids for limited life cycles that avoid pollution, and reversible changes in structure and function. On the other hand, covalent polymers with their rich array of known architectures form mechanically robust soft materials but only with limited recycling capacity and limited ability to structurally morph reversibly. Thus in the second century for polymers, a useful strategy for innovation in soft materials could involve the chemical integration of covalent and supramolecular polymers. The concept of “hybrid bonding polymers” (HBPs) in which both components coexist is proposed in this lecture and illustrated with several specific examples. Covalent and noncovalent polymerizations in systems to be described can occur simultaneously, sequentially, or independently. HBPs have led us to discover supramolecular strategies to catalyze covalent polymerization, novel biomaterials, and robotic materials that emulate living matter.
Molecular genetics in the second century of macromolecular chemistry

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Molecular genetics offers unique advantages in the programming of macromolecular structure and function. This lecture will explore the use of artificial genetic information to direct the synthesis of novel macromolecular systems. Examples may include the synthesis of conducting polymers, the control of mechanical properties in thin bacterial films, and the use of protein unfolding to map mechanical stress fields in macromolecular networks.

A molecular stress sensor for artificial protein networks
Digital manufacturing of polymer products

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The production of polymer products relies largely on age-old molding techniques. Casting arose roughly 7,000 years ago. Polymer materials were first used in injection molding 150 years ago. Since then, the basic approach to manufacturing polymer products at scale has not fundamentally changed. Despite the ascent of 3D printing technologies starting in the 1980s, additive methods have not delivered a meaningful alternative to traditional processes.

In this talk, I will describe Continuous Liquid Interface Production (CLIP) technology, which embodies a convergence of advances in software, hardware, and material science to enable a powerful approach to polymer additive manufacturing. CLIP uses software-controlled chemistry to produce commercial quality parts rapidly and at scale by capitalizing on the principle of oxygen-inhibited photopolymerization to generate a continual liquid interface of uncured resin between a forming part and a printer’s exposure window. This allows layerless parts to ‘grow’ continuously from a pool of resin, formed by light. A wide range of polymers that give rise to desirable properties—including silicones, epoxies, biocompatible polyurethanes, and elastomeric polyurethanes—have been developed for use with CLIP.

CLIP brings the digital revolution to polymer manufacturing and opens major opportunities for industrial production across diverse industries. Previously unmakeable products are already being manufactured at scale with CLIP, given its combination of performance, speed, and material choice. Examples include the large-scale production of midsoles for the adidas Futurecraft 4D shoes, mass-customized dental products, next-generation football helmets by Riddell, and parts on Ford production vehicles. CLIP also creates valuable opportunities for product light-weighting and de-materialization, accelerated product design cycles, and local-for-local manufacturing.
Balancing precision and randomness: A tale of random heteropolymers

Ting Xu, tingxu@berkeley.edu. Material Sci Eng, UC Berkeley, Berkeley, California, United States

Realization of protein-like behavior synthetically has been actively pursued to meet material demands in the life science, environment, and energy areas, but remains challenging for the scientific community. It has been long believed that the precise protein sequence and folding generate the protein structure and chemical diversity, both of which are essential toward functionalities seen in natural systems. However, the emerging knowledge of unstructured proteins and sequence homology leads to new opportunities to corroborate the known static protein structures with various functions requiring movements, as well as the level of sequence specificity with common sequence homology. The immediate question is, what level of precision in sequence and structural control is needed to synthetically recapitulate the selectivity and efficiency of natural proteins? I am going to discuss our journey to pursue these questions starting from model peptide/protein-polymer conjugates to understand protein-polymer interaction, to engineering random heteropolymers as intrinsically disordered protein mimetic and to recent findings that sequence heterogeneous random heteropolymers can behave like a selective proton channel. These studies demonstrate the importance of (1) the adaptability enabled by the statistical similarity and (2) the modularity afforded by monomer chemical diversity to achieve uniform behavior in heterogeneous systems. It also validates statistical randomness as an unexplored approach to realize protein-like behavior in a predictable manner.
Coming full circle: Adapting controlled radical polymerization for organic synthesis

Michelle Coote, michelle.coote@anu.edu.au, Alfred Fung, Vincent Doan, Chelsey Hammill, Benjamin Noble. Chemistry, Australian National University, Canberra, Australian Capital Territory, Australia

Controlling radical polymerization has been arguably one of the most important developments in polymer chemistry of the last few decades. The key processes, such as ATRP, NMP and RAFT, were invented by taking established small molecule chemistry but using it in a novel way — to reversibly trap growing polymer radicals as dormant species so as to minimize termination. Since their inception, intensive research has led to massive improvements in control and scope through, for example the development of ATRP catalysts with increased activity, or the development of control agents that respond to alternative stimuli such as light, electricity or pH. These developments in turn offer new opportunities in small molecule synthesis. This presentation will outline two such opportunities. First, we will show how ATRP catalysts can be used to improve Cu-based cross-coupling techniques. As part of this work, we will describe our recent efforts to increase ATRP catalyst activity, with advantages for both polymerization and synthesis. Second, we will show how alkoxyamine cleavage can be triggered electrochemically, and that this in turn can be harnessed to develop safer in situ on demand methylation and alkylation procedures.
**Self-growing of double network hydrogels by mechanical training**

Takahiro Matsuda, Tasuku Nakajima, **Jian Ping Gong**, gong@sci.hokudai.ac.jp. Hokkaido Univ, Sapporo, Hokkaido, Japan

Biological tissues are dynamic, open systems in which structural transformations to adapt to the surrounding environment are constantly occurring through metabolic processes. For example, skeletal muscles hypertrophy and strengthen due to repeated mechanical exercise. The exertion destroys the fibril structure, whereas the nutrition (amino acids) supply and constructive chemical reactions grows new muscle. By contrast, synthetic materials are static, closed systems, with no structural reconstruction and substance exchange with surroundings. Usually, repetitive mechanical loading leads to damage and even failure of materials.

Herein, we present a principle for creating metabolic-like hydrogels that self-grow and strengthen by repetitive mechanical stimuli. We show that the double-network hydrogels exhibit sustained strength increase along with size increase under repetitive loading in monomer (nutrition) solution. This metabolic-like phenomenon of double network hydrogels is through a repetitive structural destruction and reconstruction of the brittle network by mechanochemical transduction. This mechanism endows the hydrogels to achieve new functions at specific time and position triggered by mechanical stimuli. This work might inspire new strategies for developing self-adaptable and sustainable materials.

Illustration of molecular mechanism for self-growing double network hydrogel.
Luminogenic polymers with bright future

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Polymers with aggregation-induced emission (AIE) characteristics are a class of materials that show weak light emission in dilute solutions but become intensively emissive in the aggregated state. They have attracted tremendous attention in the past decades due to their good processability, efficient solid-state emission, high sensitivity in fluorescence sensing, unique mechanical properties, diverse topological and morphological structures, etc. In this talk, the recent research progress on the synthesis, structures and functionalities of AIE-active polymers will be introduced. Moreover, new AIE-active systems (clusteroluminescent polymers) without conventional chromophores will also be discussed. A general method for the synthesis of AIE-active polymers is to incorporate AIE-active luminogens (AIEgens) into the side chain, main chain, or center/terminal of a polymer structure. By using different polymerization or post-modification strategies, a large variety of AIE-active polymers with linear, star-shaped, dendritic, hyperbranched, cross-linked, or three dimensionally ordered structures have been constructed. The combination of AIE effect and the polymer characteristics enables AIE-active polymers to find a wide range practical applications, including fluorescence chemosensing, bioprobing, bioimaging, as well as light emitting device fabrication. We hope this talk could provide some insight into the design strategy and the structure-property relationship of AIE-active polymers to benefit the further advancement of this area, and to show a picture of the bright future of luminogenic polymers.
Transforming thermoplastics into vitrimers

Renaud Nicolay, renaud.nicolay@espci.fr. ESPCI Paris - PSL, Paris, France

Thermoplastics are ubiquitous in everyday life because of their low cost and desirable physical properties. Nevertheless, a difficult choice between durability and reprocessability continues to hamper efforts to design synthetic organic polymers to be more recyclable. A new class of materials, vitrimers, has emerged as an intriguing approach to circumvent this tradeoff. Vitrimers are permanent networks of polymer chains connected via dynamic covalent bonds, which allow the network to change its topology while maintaining a constant number of chemical bonds at all temperatures. Their synthesis in solution or in the melt, using various grafting chemistries, will be presented. The effect of the functionality and topology of the polymer network on the viscoelastic properties of vitrimers, as well as the ability of these materials to be processed multiple times with thermoplastic techniques will be discussed. Finally, the thermomechanical and chemical resistances of these vitrimers will exemplified and compared to that of their thermoplastic precursors.

Schematic of the rearrangement of the network’s topology in a thermoplastic-based vitrimer
Designing polymers for bio-applications

Molly Stevens, m.stevens@imperial.ac.uk. South Kensington Campus, Imperial College London, London, United Kingdom

This talk will present our recent advances in designing polymer materials for tissue engineering and drug delivery applications. We are developing biointerfaces with interesting features such as the incorporation of biological and topographical cues to enhance tissue regeneration and cell differentiation, and hydrogel-based materials with shape-memory and self-healing properties. We are exploiting the use of remote fields including acoustic and magnetic waves to manipulate cells and nanoparticles to obtain 3D structures that more closely resemble natural tissues. We are developing high-throughput synthesis of polymersomes with exciting applications as drug and vaccine delivery vehicles. Advances in microfabrication and 3D printing strategies will be discussed.
All known terrestrial Life-forms are operated by informational polymers, such as DNA and RNA, that can store and transfer information. Such Life-supporting macromolecules have been long thought to be unique and, so far, synthetic analogues have not been successfully developed. Indeed, artificial biological systems have been currently only reported with slightly-modified nucleic acids (i.e. nucleic acids analogues containing non-canonical monomers or modified backbones), which are conceptually and structurally very close to Natural genetic polymers. However, in theory, Life could be attained with other types of macromolecules. In order to support Life, a macromolecule shall exhibit at least the three following properties: (i) the ability to store information at the molecular level, (ii) the capacity to transfer its information to other molecules and (iii) the possibility to induce information variations through random or programmed mutations. Besides nucleic acids analogues discussed above, there is currently no man-made macromolecule that combines all these properties. Yet, in recent years, significant progress has been made for the synthesis of abiotic informational macromolecules. In addition, artificial self-replication has been demonstrated with small model molecules. Mutability has also been described for some abiotic sequence-defined polymers. Thus, technically speaking, the design of artificial Life-supporting macromolecules appears feasible. Yet, artificial Life is not only a matter of molecular design, but also a question of non-equilibrium thermodynamics. Therefore, the creation of Life-supporting macromolecules shall combine advances in polymer synthesis and systems chemistry. In this lecture, I will describe future challenges and directions toward polymer-based artificial Life.
New synthetic strategies for on-demand degradable polymeric materials

Jeremiah A. Johnson, jaj2109@mit.edu. MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Strategies for controlled polymer degradation have enabled the development of novel functional materials and have provided deep insight into the properties of polymeric networks. This talk will highlight our recent efforts to design degradability into new and old classes of materials. Specifically, triggering polymer degradation through the photocontrolled and reversible self-assembly of metal-organic cages/polyhedra, as well as through the use of cleavable comonomers, will be described.
Functional nanoparticles via “living” crystallization-driven self-assembly

Ian Manners, imanners@uvic.ca. Chemistry, University of Victoria, Victoria, British Columbia, Canada

Molecular, and more recently, macromolecular synthesis has evolved to an advanced state allowing the creation of remarkably complex organic molecules and well-defined polymers with typical dimensions from 0.5 nm - 10 nm. In contrast, the ability to prepare materials in the 10 nm – 100 micron size regime with controlled shape, dimensions, and structural hierarchy is still in its relative infancy and currently remains the virtually exclusive domain of biology.

In this talk recent developments concerning a promising “seeded growth” route to well-defined 1D and 2D nano- and microparticles termed “living” crystallization-driven self-assembly (CDSA), will be described. Living CDSA can be regarded as a type of “living supramolecular polymerization” that is analogous to living covalent polymerizations of molecular monomers but on a much longer length scale (typically, 10 nm – 5 microns). Living CDSA also shows analogies to biological “nucleation-elongation” processes such as amyloid fiber growth.

The building blocks or “monomers” used for living CDSA consist of a rapidly expanding range of crystallizable amphiphiles such as block copolymers, homopolymers with charged termini, or planar p-stacking molecules with a wide variety of chemistries. The seeds used as “initiators” for living CDSA are usually prepared from preformed polydisperse 1D or 2D micelles by sonication.

Recent results indicate that living CDSA is scalable, which will help enable applications in areas such as optoelectronics, catalysis, and biomedicine, and recent examples of work by our group and our collaborators in these areas will be discussed.
Nanoscopic measurement of the glass transition in nanostructured macromolecules

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Many technological advances are driven by the ongoing emergence of nanostructured macromolecules as the key component to enable innovation. Yet, from a materials design perspective, we cannot presume that the bulk properties of macromolecules define their behavior when physically confined to nanoscale dimensions. This is, in fact, not true, as there is now convincing evidence that the nanoscale properties of macromolecules, including the glass transition temperature, can be profoundly different from the bulk. The precise origin of these effects remains unsettled, but a primary factor must be the presence of interfaces. Achieving breakthrough in this scientific problem is especially acute because, unlike atoms or small molecules, there is a presence of multiple competing length scales near these interfaces. At macromolecule interfaces, the dimensions of a single chains can exceed 10 nm, such that a gradient in properties can be long-range and dependent on chain conformation. An enduring barrier to establishing the needed fundamental understanding of macromolecular interfacial behavior, and thereby, nanoscale confinement behavior, has been the challenge to directly probe gradients in properties at site specific locations, and with nanometer resolution. In this talk, I will discuss how we have exploited polymer chemistry to enable a better understanding of how geometric confinement and interfaces modify the glassy properties of nanostructured macromolecules in homogenous and mixed systems.

Nanoscale Distribution of Glass Transition Temperatures in Block Copolymers
Polymers designed to recover lithium from aqueous streams

Samual Warnock, rahul Sujuanani, Everett Zofchak, Shou Zhou, Theodore Dilenschneider, Kalin Hanson, Sanjoy Mukherjee, Venkat Ganesan, Benny D. Freeman, freeman@che.utexas.edu, Mahdi M. Abu-Omar, Christopher M. Bates. (1) McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States (2) Chemistry, University of California Santa Barbara, Santa Barbara, California, United States (3) materials Department, University of California Santa Barbara, Santa Barbara, California, United States (4) Materials Research Laboratory, University of California Santa Barbara, Santa Barbara, California, United States (5) Chemistry and Biochemistry, UCSB, Santa Barbara, California, United States (6) Materials and Chemical Engineering Departments, University of California, Santa Barbara, Santa Barbara, California, United States

Lithium is a valuable element used in contemporary energy applications, but its isolation from natural reserves is plagued by time-consuming and costly processes. While polymer membranes could in principle circumvent these challenges by efficiently performing aqueous separations, they currently exhibit poor ion-specific selectivity. Here, we introduce a tunable poly(norbornene) membrane platform that can separate lithium ions from aqueous solutions by copolymerizing: (1) 12-crown-4 ligand that impart a mechanism for selectivity, (2) poly(ethylene oxide) side-chains to control water content, and (3) a crosslinker to form robust solids at room temperature. Salt transport measurements indicate these materials exhibit unprecedented reverse permeability selectivity (~2.3) of Li$^+$ over Na$^+$—the highest documented to date for a polymer membrane under aqueous conditions to date. As demonstrated by molecular dynamics simulations, this effect originates from the ability of 12-crown-4 to bind Na$^+$ ions more strongly than Li$^+$ in an aqueous environment, which acts to reduce the mobility of Na$^+$ relative to Li$^+$ and offsets increases in Na$^+$ solubility. These results reveal new insights into the design of advanced membranes for solute-specific separations and establish a promising strategy for lithium recovery.
From bio-inspired polymers to life-like systems

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Nature serves as source of inspiration for the design of polymers and nanomaterials of comparable dimensions, structural precision and functionality as cellular biopolymers. DNA nanotechnology has emerged as a powerful tool to precisely position polymerization initiators or DNA catalysts on perfectly folded DNA origami nanostructures. The combination of the DNA origami technology and polymerizations initiated by visible light has provided access to distinct photo-patterned 3D nanostructures with dimensions far below 100 nm and much smaller than the wavelength of light. In addition, unfolded, denatured proteins have served as macromolecular templates for the preparation of bottlebrush polymers with functionalities at distinct locations along the main chain.

Besides mimicking nature’s strategies to design defined polymeric nanostructures, controlling structure formation inside cells could give entirely new perspectives on how synthetic architectures could affect a living system. We have formed peptide nanostructures inside living cells by multi-step chemical reactions occurring in different cellular compartments and based on natural triggers. The formation of synthetic nanostructures inside the cytosol of cancer cells significantly affects cell viability. Controlling cellular responses such as apoptosis through structure formation opens great opportunities for medical applications.
Can a material perform as an engine?

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Synthetic microswimmers are small objects with the size of micrometers. Autonomous motion, i.e., driven and directed (i) rotation, (ii) vibration/oscillation or (iii) translation (locomotion), requires the particles to do work. Our example exploits a controlled body shape deformation for the motility, mimicking the locomotion of bacteria. Because of the low Reynolds number conditions, the forward stroke must be different from the shape recovering stroke. The repetition is firstly controlled from outside in a second approach generated autonomously.

For this we designed a LCST-hydrogel system, in which the motion is affected by volume change and bending of the micro object. It is controlled precisely by the (i) design of the geometrical shape, (ii) the widely variable material properties and (iii) by the energy intake via infrared irradiation. We attempted and succeeded to cause the repetitive deformation by continuous irradiation. This required the introduction of an autonomous feed-back mechanism by which the energy uptake ceased upon raising the temperature and a hysteretic bistability by which we could prevent that the system could adopt a shape corresponding to a steady state equilibrium. The volume-phase transition is affected by strictly localized heating inside the particles. For this purpose, the gels were equipped with 1-4 gold nanorods per mm\textsuperscript{3} that absorb light at 780 nm and convert it practically instantaneously to heat. The critical phase segregation occurs within milliseconds and that the dynamics and the change in shape can be designed by the geometrical hydrogel structure.

A tapered helix from poly(NIPAM) containing gold nanorods beats upon pulsed irradiation with IR-light and moves forward by repetitive body shape deformation.
C1, C3 and C5 polymerizations: Towards unprecedented polymeric materials

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In contrast to the well-known C2 polymerization of vinyl monomers (chains are growing by two carbons at a time) and C4 polymerization of dienes (chains are growing by four carbons at a time), the borane-initiated polymerization of sulfoxonium and arsonium ylide monomers are leading to C1 (chains are growing by one carbon at a time), C3 (chains are growing by three carbons at a time) and C5 (chains are growing by five carbons at a time) polymers.

By designing/synthesizing suitable ylide monomers and alkylborane initiators we were able to direct the polymerization to C1 (dimethylsulfoxonium methylide), C3 (methylallyltriphenylarsonium ylide), or C5 (dienyltriphenylarsonium ylide) mode. These findings open new horizons for the synthesis of unprecedented polyethylene (PE)-, polymethylallyl- and polymethylpentadienyl- based polymeric materials. Some examples are given in Scheme 1.

Results from the initial studies on the properties of these polymeric materials, as well as their potential applications, will also be discussed.

Scheme 1. Some examples of PE-, polymethylallyl- and polymethylpentadienyl-based polymeric materials.
The second century: Polymers from an industrial perspective

Sebastian Koltzenburg, sebastian.koltzenburg@basf.com. BASF, Ludwigshafen, Germany

100 years after the discovery of macromolecular chemistry by Hermann Staudinger, polymeric materials have taken on an unprecedented triumphal march through all areas of our daily lives. Today, macromolecular science is an established interdisciplinary science at the boundaries of chemistry, physics, biology, medicine and engineering, to name but a few.

A whole range of properties make polymers a unique and therefore irreplaceable material class today:

Material properties can be engineered in a wide range, e.g. by copolymerization

Polymers are usually non-equilibrium systems and often capable of stabilizing complex systems outside their thermodynamic equilibrium in a metastable state 100 years after Staudinger's sensational discovery, the way in which we deal with polymers in industry and academia has developed rapidly. To be successful in this field today, it is no longer enough simply to master the synthesis of macromolecules. The future lies in knowing exactly what the desired polymer is capable of doing in the target application - and why. This requires a scientific qualification that goes far beyond classical chemical education (especially in areas such as biophysics or electronics) and the ability to work in teams with ever new tools, especially with respect to digitization. Against this background, a stronger integration of academia and industry is becoming increasingly important.

The downside of undifferentiated and in part irresponsible use of plastics must also be mentioned in this context. In particular, the so-called microplastics represents a challenge to macromolecular research, which cannot be overestimated. Bio-based and biodegradable polymers will become increasingly important here. However, these will not be able to solve the entire problem completely, so that further recycling and recovery options have to be designed and consistently implemented.

**Microbial colonization**

*Polyester (PBAT) in agricultural soil*
Precise microstructures in ionomers: New morphologies for improved properties


Polymer synthetic chemistry can now provide remarkable control over polymer microstructures, include the placement of associating functional groups in ionomers. We have studied precise and nearly-precise polymer architectures synthesized by acyclic diene metathesis, ring opening metathesis and step-growth polymerization. After a short synopsis of prior work, this talk will focus on precise sulfophenylated polyethylene ionomers with a neutralized functional group on every 5th carbon (p5PhSA-X, where X is H+, Li+, Na+, etc.) and (ii) segmented ionomers containing polar units with neutralized sulfonate groups separated by a precise number (x = 10, 12, 18, 23, 48) of methylene groups (PESx-X). Through a combination of X-ray scattering and atomistic molecular dynamics the p5PhSA-X ionomers exhibit percolated ionic aggregate morphologies. When the acid form is hydrated the conductivity exceeds that of Nafion. When neutralized with metal cations, the electrochemical impedance spectroscopy demonstrates decoupled dynamics between the cations and polymer backbone. While the ionic aggregates are irregular in p5PhSA-X, the PESx-X ionomers exhibit exceptional long-range order and order-order transitions reminiscent of block copolymers. The most promising of these ordered structures is the gyroid structure, which exhibits higher ionic conductivity than the isotropic layered or hexagonal morphologies. Innovative molecular designs of ionomers are building robust structure-property relationships for transport in these hierarchical materials to provide continuous pathways for improved ion transport.
Polymeric Ionic Liquids: A platform for metal ion conduction

Rachel A. Segalman, segalman@engineering.ucsb.edu. Chemical Engineering, UCSB, Santa Barbara, California, United States

While polymer electrolytes hold the promise of improving safety and mechanical durability of electrochemical devices, most suffer from relatively low ionic conductivities especially at ambient temperature. This combination of challenges becomes even more pronounced in the conduction of the multivalent metal ions likely to be necessary for next generation, high energy density energy storage devices where the ions are likely to have complex, multi-functional interactions with the polyelectrolyte matrix. Ionic liquids (IL’s) have been suggested for applications as diverse as solubilizing cellulose, antimicrobial treatments, and electrolytes in batteries due to their molten salt properties. Polymeric ionic liquids are not just solid counterparts to IL’s, but are excellent vectors for the inclusion of a variety functionalities ranging from multi-valent ion conductivity for batteries to magnetism into a polymer membrane. Polymeric ionic liquids capable of conducting multivalent ions are based on transient metal-ligand coordination interactions and the conductivity is related to both the segmental motion of the backbone and the lifetime of the metal-ligand bond. In this talk, I will discuss the roles of polymer backbone chemistry, metal-ligand coordination, and ion concentration on ion conductivity and mechanical properties.

Ion conductivity in PIL systems is reliant on salt dissolution, metal-ligand bond lifetime, and segmental motion.
Design-by-architecture: Encoding tissue mechanics in synthetic polymers

Sergey Sheyko, sergei@email.unc.edu. Chemistry, UNC Chapel Hill, Chapel Hill, North Carolina, United States

Mimicking the mechanical behavior of living tissues is vital for medical implants, tissue engineering, soft robotics, and wearable electronics. However, the oxymoronic combination of biological softness, strength, and firmness is difficult to recreate in synthetic materials. Current design strategies are predominantly based on exploratory mixing of assorted polymers, crosslinking schemes, and solvents, which is both inflexible in application and imprecise in property control. We present a universal materials design platform that leverages precision engineering of brush-like network architectures to program biological mechanical properties in solvent-free elastomers. By accurately controlling a multiplet of independent architectural parameters, we replicated stress-strain response of essential tissues ranging from a supersoft fat tissue to a strong skin. This design-by-architecture approach lays the foundation for a configurable synthetic engine that will be capable of encoding a broad range of mechanical phenotypes within any desired chemistry. We will discuss different principles of brush network assembly including permanent and reversible cross-link that emulate distinctive features of biological networks. Further, a concept of injectable elastomers will be presented opening prospective for additive manufacturing of biomedical devices and tissue models. Taking advantage of myriad chain-end functionalities, we are able to control the curing time from seconds to days, which benefits a range of biomedical applications from tissue fixation to body implants, respectively.
Paul J. Flory Education Award in Honor of Kris Matyjaszewski
April 8, 2021
Dr Rigoberto Advincula, Organizer, Presider; Kathryn Beers, Presider

Watching micelles break into two
Timothy Lodge, Presenter

Soft bottlebrush networks to promote contact with rough surfaces and support quantification of cleaning delicate surfaces
Kathryn Beers, Presenter; Teresa Duncan; Edwin P Chan

Ring-opening radical polymerization of cyclic disulfides as a tool for the synthesis of (bio)degradable polymers
Nicolay Tsarevsky, Presenter; Mojdeh Raeisi; Sophia Bianchi; Houliang Tang

Utilizing accelerating reactions to develop new polymerization systems with fine polymer structure
Dr. Haifeng Gao, Presenter

Soft materials designed using synergies of dynamic bonds and complex architectures
Dominik Konkolewicz, Presenter

How we see and sense bottlebrushes
Prof. Sergey Sheyko, Presenter

Catenated and knotty macromolecular systems
Dr Rigoberto Advincula, Presenter

Learning and teaching ATRP
Krzysztof Matyjaszewski, Presenter
Watching micelles break into two

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

Block copolymer micelles are often prepared or used in a non-equilibrium state, but remarkably little is understood about the mechanisms by which these micelles relax toward equilibrium. We examine the fragmentation kinetics of spherical micelles formed by a 1,2-polybutadiene-block-poly(ethylene oxide) copolymers in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide-based ionic liquids. In this system, the core-forming block is 1,2-polybutadiene (and the corona-forming block is poly(ethylene oxide). Using a direct dissolution technique, initial micelles are prepared that are significantly larger than equilibrium. A combination of techniques is used to follow the subsequent decrease in size, including dynamic light scattering, small-angle X-ray scattering, and especially liquid-phase transmission electron microscopy. Experimental variables include the interfacial tension between the core and the solvent (modulated through the solvent cation structure), annealing temperature, and copolymer concentration and molecular weight. Consistent results are obtained among the various experiments, but in several respects the results are quite surprising, as will be discussed.

Cartoon of the fragmentation process, and TEM image near the transition state
Soft bottlebrush networks to promote contact with rough surfaces and support quantification of cleaning delicate surfaces

Kathryn Beers, beers@nist.gov, Teresa T. Duncan, Edwin Chan. Materials Science and Engineering Division, NIST, Bethesda, Maryland, United States

Cleaning delicate surfaces depends on a number of conditions being met, including conformal contact with particulates on a surface, and favorable chemical interactions to promote release from the substrate. These conditions were demonstrated with a series of studies identifying conditions for optimal contact on surfaces of varying topology both with and without model ‘dirt’. A range of materials were necessary to explore a broad variable space in the properties of the networks or gels, including modulus and adhesion energy with hydrophobic particulates. Commonly used cleaning gels were complemented with soft bottlebrush networks to quantify particulate removal using image analysis. This informs guidelines to materials selection for conservators to promote efficient cleaning while minimizing disruption of underlying substrates. For a single application, cleaning efficiency up to 40% was achieved, while greater that 70% efficiency was obtained for multiple treatments of the same area.

Particulate removal from rough surfaces
Ring-opening radical polymerization of cyclic disulfides as a tool for the synthesis of (bio)degradable polymers

Nicolay V. Tsarevsky¹, nvt@mail.smu.edu, Mojdeh Raeisi¹, Sophia Bianchi¹, Houliang Tang². (1) Department of Chemistry, Southern Methodist University, Dallas, Texas, United States (2) Southern Methodist University, Richardson, Texas, United States

Cyclic di- and polysulfides readily undergo radical ring-opening polymerization, which leads to the formation of macromolecules with multiple reductively degradable disulfide groups in the backbone. Lipoic acid is a naturally occurring cyclic disulfide, which is of particular interest as a monomer for the preparation of linear, branched, and network biocompatible and biodegradable polymers. For example, the thermal radical copolymerizations of mono- and dilipoate esters (e.g., ethyl lipoate and the sugar-derived isosorbide dilipoate), conducted in the presence of radical initiators, affords gels, which degrade in the presence of reducing agents, such as thiols and phosphines. Importantly, the copolymerizations can be carried out in miniemulsion and the obtained nanoparticles can be employed as carriers of various substances (dyes, drugs), which are released upon reduction. The radical ring-opening polymerization of ethyl lipoate is reversible and is characterized by a ceiling temperature of 137 °C. Due to the reversibility of the polymerization, polylipoates degrade upon heating with formation of the parent monomers. Further, lipoic acid and its derivatives copolymerize easily with vinyl monomers, e.g., acrylates. When a lipoate and acrylate moieties are present in the same molecule, its radical polymerization affords partially biodegradable branched and eventually network polymers, containing both disulfide and thioether bonds in the backbone. Systematic kinetic studies of the radical ring-opening polymerization of lipoates will be presented, along with some applications of the synthesized disulfide-containing polymers.

![Chemical structures and reactions](image.png)
Utilizing accelerating reactions to develop new polymerization systems with fine polymer structure

Haifeng Gao, hgao@nd.edu. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States

Carefully reading Paul J. Flory’s classic textbook of “Principles of Polymer Chemistry” always inspires new ideas to develop polymerization methods that can effectively overcome the synthetic challenges in dendrimers, hyperbranched polymers and linear polymers. This presentation discusses our recent interest on utilizing efficient organic reactions, such as copper-catalyzed azide-alkyne cycloaddition reaction and Friedel-Crafts hydroxyalkylation reaction, to develop new methods for syntheses of hyperbranched polymers with well-defined nanostructures and linear polymers with high molecular weights. These polymers are successfully applied as unimolecular nanocontainers for encapsulation and as membrane materials for transportation.
Soft materials designed using synergies of dynamic bonds and complex architectures

Dominik Konkolewicz, d.konkolewicz@gmail.com. Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

Polymer networks containing consist of long polymer linked together using crosslinking points, making them strong and tough materials, but often at the expense of recyclability or adaptability. 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. This enables dynamic materials be reused, remolded and reprocessed. 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 talk 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. Polymer architecture is a further tool that can be used to enhance and tune material properties, with both macromolecular and network architecture explored.
How we see and sense bottlebrushes

Sergey Sheyko, sergei@email.unc.edu. Chemistry, UNC Chapel Hill, Chapel Hill, North Carolina, United States

Molecular conformation and macroscopic properties of brush-like polymers are controlled by well-defined architectural parameters including side-chain length, grafting density, and crosslink density. Loosely grafted comb-like macromolecules behave as flexible linear chains that overlap and entangle, whereas densely grafted bottlebrushes behave as worm-like filaments possessing distinct shape and self-disentangled organization. Relatively large dimensions and discrete assembly of bottlebrushes allowed imaging of individual molecules both as single species and within dense films by atomic force microscopy (Figure a). Steric repulsion between long and dense side chains may induce conformational transitions and even cause scission of covalent bonds. In block-copolymer bottlebrushes, the same steric repulsion regulates dimensions of microphase separated domains and generates structural coloration (Figure b). Herein we will first present assorted visuals of different bottlebrush systems and then discuss their implications for fundamental understanding and practical applications of these unique macromolecules. From many interesting applications such as membranes and drug delivery, the ability of brush elastomers to precisely replicate the deformation response of soft tissues is particularly noteworthy. Brush architecture imposes significant shifts in mechanical properties of bottlebrush assemblies such as melts, elastomers, and gels. We will discuss the distinct tactility of brush materials by examining quantitative correlations between the brush parameters and specific materials mechanical characteristics such as modulus, elongation-at-break, strength, and firmness.

a. Imaging of individual bottlebrush macromolecules by atomic force microscopy. b. Structural coloration due to microphase separation of linear-brush-linear triblock copolymer.
Catenated and knotty macromolecular systems

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Controlled polymer architectures are a part of the versatility of macromolecular materials in new synthesis and design. There is high interest in new polymer synthesis routes, topologies, mechanisms, and applications.

The most common choices for synthesis go from linear, grafted, and hyperbranched systems. However, there are many other topologies that are of high interest because of their relevance: from understanding entanglement behavior to a practical understanding of polymer viscosity limits. It is also of interest to control composition (blocks, random, alternate) in order to enable interaction parameter control. Macromolecular architectures based on cyclic polymerization routes can be achieved by ring-closure or ring-expansion routes. This talk will focus on our approach to the macromolecular synthesis of catenanes, macrocycles, and knots based on a rational design of supramolecular macroinitiators that template the ring closure and ring expansion in the living polymerization mechanism. We utilize a number of macromolecular, interphase, and surface characterization and modeling studies to define successful synthesis strategies. The end goal is to produce higher throughput synthetic methods that can unlock the utility of rationally entangled and knotted polymers.
Learning and teaching ATRP

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

Atom transfer radical polymerization (ATRP) has been successfully used to synthesize various nanostructured polymers with controlled composition, topology and functionality. Fundamental kinetic and mechanistic aspects of ATRP will be presented together with some review of special properties of polymers prepared by ATRP.
The POLY/PMSE awards reception was held on Wednesday evening, April 14, 2021, during the virtual ACS National Meeting honoring outstanding achievements by its members. A list of award recipients is below. Timothy Lodge (University of Minnesota), opened the event with a Plenary Lecture titled, “Pillars of Polymer Science” (abstract on next page). 2021 POLY Chair, Andrea Kasko (UCLA) and 2021 PMSE Chair, Timothy Bunning (Air Force Research Laboratory) had the pleasure of congratulating this year’s presenter.

**POLY Awards:**
- ACS Award in Polymer Chemistry in Honor of Ken Wagener
- ACS Award in Pure Chemistry in Honor of Rebekka Klausen
- 2021 POLY Fellows - Luis Campos (Columbia Univ.), Thomas Epps (Univ. of Delaware), Wei Gao (Dow, Inc.), Frank Leibfarth (UNC, Chapel Hill), Carmen Scholz (Univ. of Alabama, Huntsville), Karen Winey (Univ. of Pennsylvania)
- Paul J. Flory Polymer Education Award - Krzysztof Matyjaszewski (Carnegie Mellon Univ.)
- Carl S. Marvel Award for Creative Polymer Chemistry - Richard Hoogenboom, (Ghent Univ.)
- Distinguished Service Award - Hayley Brown (Dow, Inc.)
- POLY Past Chair - Mike Meador (NASA-Retired)
- Excellence in Graduate Polymer Research & Undergraduate Research in Polymer Science
- POLY Session Organizer Recognition
- POLY Poster Awards - Jerika Chiong (Stanford Univ.), Shashini Diwakara (Univ. of Texas - Dallas), Xue Liu (Technical Univ. of Denmark)

**Thank You POLY Program Chairs and Organizers**

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Pillars of Polymer Science

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

As we celebrate the centenary of Hermann Staudinger’s ground-breaking paper in 1920, at a time when macromolecular chemistry has never been more important to science and technology, it is appropriate to recollect some of the most important advances in the field. I will present a very brief summary of the major milestones that have brought us to the current state of the art, along with a smattering of possibly interesting footnotes.
Charged electrostatically assembled nanoparticles for targeted delivery
Dr. Paula T. Hammond, Presenter

Time evolution of colloidal stratification in a drying droplet
Joseph Jiang, Presenter; H Daniel Ou-Yang; Chong Shen; Lanfang Li

Kinetics of mesoglobules formation and disintegration in solutions of thermo-responsive polymers after fast pressure jumps
Bart-Jan Niebuur; Leonardo Chiappisi; Florian A. Jung; Xiaohan Zhang; Alfons Schulte; Prof. Christine M. Papadakis, Presenter

Functionalization of kinetically trapped micelles to enable constant core size
Taylor Larison, Presenter; Morgan Stefik

Radioluminescent crystalline colloidal arrays: Fine-tuning color characteristics via X-ray induced, sequential Förster resonance energy transfer (FRET)
Haley Jones, Presenter; Iurii Bandera; Eric Zhang; Stephen Foulger

Tutorial on modeling of multi-phase latex morphology development
John Tsavalas, Presenter

Expanding the scope of RAFT polymerization for (multi)block copolymer synthesis by exploitation of the nanoreactor concept in emulsion polymerization
Dr Thiago Guimaraes; Murtaza Khan; Robert Richardson; Glenn Clothier; Steven Thompson; Graeme Moad; Sebastien Perrier; Professor Per B. Zetterlund, Presenter

Step-growth radical thiol-ene emulsion polymerizations: Synthesis of highly functionalized nanoparticles
Kyle J Cassidy; Meagan Arguien; Devon Shipp, Presenter

Radical-mediated thiol-ene suspension polymerizations stabilized by using colloidal silica
Kyle J Cassidy, Presenter; Devon Shipp

Nano-engineered multiblock copolymer particles via RAFT emulsion polymerization
Dr Thiago Guimaraes, Presenter; Murtaza Khan; Glenn Clothier; Steven Thompson; Graeme Moad; Sebastien Perrier; Professor Per B. Zetterlund

Colloids for energy storage: Visualizing energy transport in redox-active colloids and using colloids as templates for 3D-structured li-ion battery electrodes
Paul Braun, Presenter
Colloidal nanosphere lithography: Templating electropolymerizations and applications  
Dr Rigoberto Advincula, Presenter

Functional polyphosphazene colloids  
Andrij Pich, Presenter

EDTA mimicking polymers and their ability to form Zr(IV) chelation mediated nanostructures  
Dr Meike Nicole Leiske, Presenter; Thomas Davis; Kristian Kempe

Organic X-ray radioluminescent crystalline colloidal arrays encapsulated in poly(ethylene glycol) methacrylate-based hydrogel films with a tunable emission  
Sarah Mell, Presenter; Haley Jones; Iurii Bandera; Stephen Foulger

Nanocomposite microgels prepared by seeded emulsion polymerization  
Daisuke Suzuki, Presenter; Takumi Watanabe; Yuichiro Nishizawa; Haruka Minato; Chihong Song; Kazuyoshi Murata

Investigation for formation process of hydrogel microspheres during precipitation polymerization  
Yuichiro Nishizawa, Presenter; Haruka Minato; Takumi Inui; Takayuki Uchihashi; Daisuke Suzuki

Evaluation of thermoresponsive behavior of charged hydrogel microspheres with different charge distributions  
Takumi Inui, Presenter; Yuichiro Nishizawa; Daisuke Suzuki

Liquid crystal peptide/DNA coacervates in the context of prebiotic molecular evolution  
Tony Jia, Presenter; Tommaso Fraccia

Near-infrared emitting polymer dots for multiplexed cellular imaging  
Connor Riahin, Presenter; Adam Meares; Erin Lavik; Marcin Ptaszek; Zeev Rosenzweig

Highly efficient photochromic tungsten oxide@PNIPAM composite spheres with a fast response  
Ruxiu Wang, Presenter; Qi Zhang; Yamiao Lu; Yayun Wu; Jinghe Yuan; Jiguang Liu

Polymer Colloids: Synthesis, Analysis, Modeling & Application  
April 14, 2021

Analysis of colloidal particles and emulsion polymers with asymmetric flow field flow fractionation and related techniques  
Wei Gao, Presenter

Development of two-dimensional offline coupling of asymmetrical flow field-flow fractionation (AF4) and capillary electrophoresis  
Meng Jing, Presenter; Wei Gao; Paul Hutchins

Time-resolved small-angle X-ray scattering studies during aqueous emulsion polymerization  
Adam Czajka, Presenter; Steven Armes

Combining suspension polymerization free radical copolymerization and click chemistry towards cross-linked polymer microparticles with tunable surface properties
Yoanh Moratille, Presenter; Muhammad Arshad; Céline Cohen; Abdelhamid Maali; Elisabeth Lemaire; Nathalie Sintes-Zydowicz; Eric Drockenmuller

**Synthesis, computer simulation and NMR study of novel peptide dendrimers with arginine and histidine spacers designed for drug and gene delivery**
Igor Neelov, Presenter; V Bezrodnyi; O Shavykin; S Mikhtaniuk; I Tarasenko; N Sheveleva; D Markelov

**One-step synthesis of responsive cavity-forming zwitterionic colloids**
Heather Hamilton, Presenter; Laura Bradley

**Silicone dispersions by conventional polymerization or soft matter engineering**
Dr Francois Ganachaud, Presenter

**Thermodynamics: The invisible arbiter of emulsion structure; insight from an examination of three-phase emulsions**
Dr. Yihan Liu, Presenter; Ibrahim Eryazici; Anirudha Banerjee; Jennifer Reil; Xiangyi Zhang

**Entropy-driven assembly behavior in 3D confined nanoparticle/block copolymer hybrid system**
MENG XU, Presenter; Hongseok Yun; Bumjoon Kim

**Controlled scalable nanofabrication of new classes of colloidal polymer morphologies in sheared liquids**
Rachel Bang, Presenter; Austin Williams; Sangchul Roh; Orlin Velev

**Development of polymeric stabilizers for the mechanical dispersion process**

Thomas Kalantar, Presenter; Mladen Ladika; Gary Strandburg; Mechelle Churchfield; Adam Safir; Steven Zong

**Polymer Colloids: Synthesis, Analysis, Modeling & Application**
April 15, 2021

**Diverse and unique colloidal particles assembled from polydisperse liquid crystalline oligomers**
Shu Yang, Presenter

**Mechanistic Study on crosslinking in seeded emulsion polymerization: Effect of monomer feed rate on gel formation**
Chang Liu, Presenter; Dr. Amit Tripathi; John Tsavalas

**Design and synthesis of colloidal unimolecular polymers**
Ashish Zore, Presenter; Peng Geng; Michael VanDeMark

**Effect of charge density on surface tension behavior of colloidal unimolecular polymers**
03:05pm - 03:15pm USA / Canada - Pacific - April 15, 2021
Ashish Zore, Presenter; Peng Geng; Michael VanDeMark

**Self assembly and characterization of novel photochromic particles**
Ruxiu Wang, Presenter; Qi Zhang; Jiguang Liu

**Preparation of non-spherical polymer particles via simple approaches**
Dr. Amit Tripathi, Presenter; Yung-Chun Lin; John Tsavalas, Presenter
Stealth polymer nanorods: Living crystallisation-driven self-assembly of poly(2-oxazoline)s in pure water
John Finnegan, Presenter; Thomas Davis; Kristian Kempe

Three-dimensional confined assembly of bottlebrush block copolymers: the effect of molecular weight on the particle morphology
Eun Ji Kim, Presenter; Jaeman Shin; Taeyang Do; Juhae Park; Su-Mi Hur; Jeung Gon Kim; Bumjoon Kim

Waterborne multi-lobed particle morphology for directed-assembly towards 3D hierarchical structures
Yung-Chun Lin, Presenter; Dr. Amit Tripathi; John Tsavalas

Shape-changeable block copolymer particles driven by photo-isomerizable surfactants
Jinwoo Kim, Presenter; Hongseok Yun; Kang Hee Ku; Bumjoon Kim
Charged electrostatically assembled nanoparticles for targeted delivery

Paula T. Hammond, hammond@mit.edu. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

A layer-by-layer (LbL) technique toward construction of nanostructured nanoparticles provides a unique platform approach for drug delivery and nanomedicine. We have generated LbL outer layers that provide effective stealth properties, with long systemic plasma blood half-lives and higher tumor accumulation over time, and demonstrate efficacy in advanced breast and lung cancer models in which siRNA targets have been delivered with chemotherapy drug in the same nanoparticle system. We are now examining new siRNA and drug combinations in ovarian cancer. By staging release of different drug components via the adaptation of the nanoparticle structure, we can achieve highly synergistic release behavior in these systems. We have found that certain LbL nanoparticle formulations traffic differently in cells based on the negatively charged polypeptide, and are exploring ways to utilize these differences in affinity for more selective tumor cell binding and deliver within cells. Ongoing work includes addressing barriers to transport of these nanoparticles relevant to tumor or other tissue penetration, and will be discussed, including new work involving the understanding of these trafficking patterns and a means to leverage them toward the delivery of cytokines for activation of the immune system against cancer. Finally, we have also begun investigating how these polymeric colloidal systems undergo release mechanisms when in the tumor microenvironment.
Time evolution of colloidal stratification in a drying droplet

Joseph Jiang¹, zhj216@lehigh.edu, H Daniel Ou-Yang¹, Chong Shen², Lanfang Li¹. (1) Physics, Lehigh University, Bethlehem, Pennsylvania, United States (2) Beijing University of Chemical Technology, Beijing, China

In a droplet drying, uniformly mixed colloidal particles with two differ sizes could separate either due to the difference in particle diffusion or the convection flow induced by difference in buoyancy. The role for each mechanism causing the stratification is unclear if we only watch the final distribution of particles after drying. To distinguish how each mechanism stratifies the particles, we need to control diffusiophoresis and convection by varying size ratio of big to small particles and the degree of density mismatching respectively. We record time evolution of distributions for two-sized particles to understand how particles are stratified by each mechanism. The experiments are designed into a droplet drying process confined between two parallel plates where fluorescent particles are tracked by a confocal fluorescence microscopy and analyzed by MATLAB imaging processing. The results show the two-type particles accumulate at different locations when the direction of the convection flow changes. This talk will present the spatiotemporal evolution of the concentration for small and big particles and show the stratification can be controlled by adjusting the convection and diffusiophoresis.
Kinetics of mesoglobules formation and disintegration in solutions of thermo-responsive polymers after fast pressure jumps

Bart-Jan Niebuur¹, Leonardo Chiappisi², Florian A. Jung¹, Xiaohan Zhang¹, Alfons Schulte³, Christine M. Papadakis¹, papadakis@tum.de. (1) Physik Dept, Soft Matter Physics, Tech Univ Munchen, Garching, Germany (2) Institut Laue-Langevin, Grenoble, Rhône-Alpes, France (3) Department of Physics, University of Central Florida, Orlando, Florida, United States

Polymeric nanoparticles are used in many fields, e.g. for drug delivery. Poly(N-isopropylacrylamide) in aqueous solution forms nanoparticles (“mesoglobules”) above its cloud point. The coexistence line of this system in the temperature-pressure frame is an ellipse with a maximum at ~60 MPa and 35 °C. We investigate the formation and growth of mesoglobules as well as their dissolution after rapid pressure jumps across the coexistence line, both at low (below 20 MPa) and high pressures (above 101 MPa). Time-resolved small-angle neutron scattering at instrument D11 (ILL Grenoble) gives structural information on a large range of length scales and in a time range from 50 ms to ~1650 s after the jump.

In the low-pressure regime, we find that, initially, growth proceeds via diffusion-limited coalescence, but this process is later slowed down by the appearance of a dense and rigid shell from dehydrated polymers. The further away the target pressure from the coexistence line, the earlier the slowing-down sets in and hinders further growth. In contrast, in the high-pressure regime, the chains stay hydrated and mobile, and the diffusion-limited coalescence proceeds without hindrance during the entire measuring time.

The dissolution of mesoglobules is studied by pressure jumps from the two-phase into the one-phase region. Varying the target pressure allows altering the osmotic pressure of the solvent. At a target pressure close to the coexistence line, the release of single polymers from the surface of the mesoglobules is the dominating mechanism, whereas for target pressures deeper in the one-phase regime, the swelling of the mesoglobules by water prevails. The dissolution time decreases with increasing jump depth. The results point to the importance of the osmotic pressure of water.
Functionalization of kinetically trapped micelles to enable constant core size

Taylor Larison, tlarison@email.sc.edu, Morgan Stefik. Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

Polymer micelles have found significant uses in areas such as drug/gene delivery, medical imaging, nanostructured materials, and as templates. For many of these applications size of the polymer micelle and functionalization of the micelle play a critical role in overall performance. To date, however, these parameters have been fundamentally linked where altering the functionalization of equilibrating micelles causes a change in the micelle core size due to equilibration. Through proper synthetic design we demonstrate one can independently tune the functionalization of a micelle corona without eliciting a change to the micelle aggregation number. This is achieved through kinetic entrapment of polymer micelles prior to chemical modification of the corona to enable constant micelle core size. Specifically, Poly(cyclohexyl methacrylate-b-[(diethoxyphosphoryl)methyl methacrylate]) (PCHMA-b-PDEPMMA) was micellized and kinetically trapped in an aqueous solution prior to quantitative hydrolysis of the phosphonated ester groups in order to functionalize the micelle corona with a desired number of acid groups. Further processing of the newly modified micelles by changing the pH of the solution led to an increase in the overall charge density of each micelle. Using $^{31}\text{P}-\text{NMR}$ we are able to demonstrate quantitative hydrolysis of the micelle corona, while statistically significant TEM measurements quantify the micelle core size. It was shown that kinetic entrapment of polymer micelles prior to chemical modification was necessary to preserve constant micelle aggregation number under diverse conditions.
Radioluminescent crystalline colloidal arrays: Fine-tuning color characteristics via X-ray induced, sequential Förster resonance energy transfer (FRET)

Haley W. Jones\textsuperscript{2,1}, hwjones@clemson.edu, Iurii Bandera\textsuperscript{2,1}, Eric Zhang\textsuperscript{2,1}, Stephen H. Foulger\textsuperscript{2,1,3} (1) Materials Science and Engineering, Clemson University, Clemson, South Carolina, United States (2) Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Anderson, South Carolina, United States (3) Bioengineering, Clemson University, Clemson, South Carolina, United States

X-ray radioluminescent crystalline colloidal arrays (CCAs) with highly tunable emission colors are synthesized using an emulsion polymerization procedure. An anthracene monomer is copolymerized with styrene and propargyl acrylate monomers to generate a CCA that exhibits the typical luminescence characteristics of anthracene (Anth). These nanoparticles are able to spontaneously self-assemble into FCC structures due to the electrostatic repulsive forces between the particles. By synthesizing highly stable, monodisperse colloidal particles that exhibit X-ray radioluminescence (RL), the intensity of emitted light from the particulate system can be manipulated by photonic means. The rejection wavelength of the CCA can be shifted across the visible spectrum by the addition or removal of DI water which corresponds to a change in the interplanar spacing. When the rejection wavelength of the CCA is outside of the RL spectra, typical Anth emission behavior is detected with an emission spanning 400 – 515 nm and a maximum at 420 nm. When the rejection wavelength is within the RL spectra of the CCA, a decrease in spontaneous emission is observed. In this system, the decrease in spontaneous emission corresponding to the rejection wavelength of the CCA can be shifted across the RL spectra of Anth. Furthermore, the color of emitted light from the CCA can be adjusted to span the visible spectrum by incorporating organic fluorophores that form Förster resonance energy transfer (FRET) pairs with each other and the scintillator. A naphthalimide derivative that absorbs in the blue region where Anth emits can be integrated within the particles such that the CCA possesses an overall green emission with a maximum at 535 nm. Additionally, a rhodamine B derivative that absorbs in the green region where naphthalimide emits can be integrated within the green-emitting particles such that the CCA possesses an overall red emission with a maximum at 630 nm. The color of emitted light from the green- and red-emitting CCAs can similarly be manipulated by photonic means to fine-tune the emission of the liquid systems.
Tutorial on modeling of multi-phase latex morphology development

John Tsavalas, john.tsavalas@unh.edu. Chemistry, University of New Hampshire, Durham, New Hampshire, United States

Modeling of polymer colloid formation is a complex endeavor, even for a single homogeneous composition. The particles, typically synthesized by emulsion polymerization, result from a complex overlay of reactions that occur simultaneous in the aqueous phase, the organic particle phase, and at their interface. Often, the locus of radical formation is in the aqueous phase where oligomeric chains form until surface active, adsorb to particles, and upon further growth solubilize and propagate within that new phase. Kinetics for the same reactants can be orders of magnitude different in these two phases, further complicated if pH sensitive or able to dimerize. This complexity is exacerbated when multiple polymer phases are involved, for example in seeded emulsion polymerization, towards composite multi-phase particle morphologies. Too often, focus is on the final state of equilibrium, where practical synthetic approaches are more often kinetically limited by diffusion. This tutorial will emphasize the critical importance of properly defining the parameters and reaction conditions that influence the ability of each polymer phase to diffuse. Glass transition temperatures, relative to the reaction temperature and influenced by hydroplasticization and unreacted monomer present, play a crucial role. Process conditions, such as the monomer feed rate to the reactor, serve not only as engineering parameters but also dramatically impact morphology. Diffusion is proportional to chain length and thus impacted by termination, crosslinking, and long chain branching. Modeling offers insights into how each of these individual topics play a role in a highly interdependent system, often enabling insights too complex for our natural intuition. This tutorial highlights examples of such modeling efforts to emphasize not only the complex interplay but also some enlightening discoveries resulting from such pursuits.
Expanding the scope of RAFT polymerization for (multi)block copolymer synthesis by exploitation of the nanoreactor concept in emulsion polymerization

Thiago R. Guimaraes¹, Murtaza Khan¹, Robert A. Richardson², Glenn K. Clothier¹, Steven W. Thompson¹, Graeme Moad³, Sebastien Perrier², Per B. Zetterlund¹, p.zetterlund@unsw.edu.au. (1) Cluster for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, University of New South Wales, Sydney, New South Wales, Australia (2) University of Warwick, Coventry, United Kingdom (3) Manufacturing, CSIRO, Clayton, Victoria, Australia

RAFT polymerization is a versatile technique for synthesis of polymers of a range of complex architectures. Multiblock copolymers composed of polymer segments of sufficiently high molecular weight such that microphase separation and self-assembly can occur offer a pathway to a myriad of nano-engineered nanoparticles and materials (Fig. 1). In the present work, we demonstrate how aqueous RAFT emulsion polymerization can be used to significantly expand the synthetic capabilities of RAFT polymerization by understanding and exploiting kinetic and mechanistic features of polymerization within nanoreactors (i.e. polymeric nanoparticles).

The degree of livingness (chain-end fidelity) in RAFT polymerization for a given degree of polymerization can be markedly increased in a compartmentalized system such as (mini)emulsion polymerization. This is a consequence of a reduced rate of bimolecular termination caused by physical segregation of propagating radicals in submicron size particles (nanoreactors). Exploitation of this feature makes it possible to prepare multiblock copolymers comprising slowly propagating monomers such as styrenes and methacrylates, which is not possible in the corresponding homogeneous (solution/bulk) system. Another important intrinsic feature of emulsion polymerization is that the polymerization occurs in submicron size polymer particles with monomer being supplied from micron size monomer droplets via diffusion through the aqueous phase. Consequently, the ratio of monomer to RAFT end groups within the particles is lower than in the corresponding homogeneous system. This enables (macro)RAFT agent / monomer pairs with chain transfer coefficients that are too low for efficient RAFT control to be employed successfully in emulsion polymerization, contrary to in the corresponding homogeneous systems. This has important implications in regard to polymer synthesis; for example, it significantly expands the range of synthetically accessible multiblock copolymers as the restriction of “monomer order” in block synthesis is markedly relaxed.

Fig 1. Graphic illustration of multilayered nanoparticle obtained via sequential RAFT emulsion polymerization.
Step-growth radical thiol-ene emulsion polymerizations: Synthesis of highly functionalized nanoparticles

Kyle J. Cassidy, Meagan N. Arguien, Devon A. Shipp, dshipp@clarkson.edu. Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States

Recent developments in radical-mediated thiol-ene polymerizations include the application of these polymerizations in emulsion, dispersion, and suspension polymerizations. These step-growth polymerizations have several significant advantages over traditional chain-growth (e.g., acrylic or styrenic) polymerizations. In particular, they allow for easy functionalization through simple stoichiometric adjustments of the monomers used in the polymerization; for example, adding a slight excess of thiol monomer produces colloidal polymer particles replete with thiol functionality. Furthermore, the subsequent use of thiol-ene (and thiol-yne) and other ‘click’ chemistries can lead to the facile production of biodegradable and bio-functionalized colloids.

Our early publications showed that radical-mediated thiol-ene polymerizations can easily be performed in suspension, mini-emulsion and dispersion polymerizations. In each of these cases, the initiator is oil (monomer) soluble, and thus particles grow either from the monomer droplets (in the cases of suspension or mini-emulsion systems), or from the precipitation of the growing polymer (in dispersion polymerizations). Recently, we have shown that by using a water-soluble initiator, such as potassium persulfate (KPS), it is possible to perform thiol-ene polymerizations under conditions that essentially mimic those of traditional vinyl monomer emulsion polymerizations. Furthermore, the formation of nanoparticles that may be uniform in size is possible. Results from this study will be discussed, along with approaches to modify and functionalize these nanoparticles.

Radical-mediated thiol-ene emulsion polymerizations.
Radical-mediated thiol-ene suspension polymerization stabilizations by using colloidal silica

Kyle J. Cassidy¹, cassidkj@clarkson.edu, Devon A. Shipp². (1) Chemistry, Clarkson University, Potsdam, New York, United States (2) Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States

Pickering stabilization has been shown as a method to create core-shell composite particles. Using “hard” inorganic particles, such as silica, to reduce surface energy at the interfacial boundary between monomer droplets and continuous phase during suspension polymerization. This yields polymer particles that are coated with inorganic particles. The monomers commonly used are traditional styrenics, acrylics and methacrylics, all of which undergo chain-growth radical polymerization. Using the recently developed approach of performing step-growth radical-mediated thiol-ene polymerization in suspensions, we found that Pickering stabilization yielded core-shell composite particles, wherein the poly(thioether) colloids are coated in silica nanoparticles. Through the addition of various co-stabilizers, it was shown that the amount of silica needed to stabilize and retain the same distribution could be decreased. This approach to composite particle synthesis can lead to many different applications, ranging from biomaterials to surface-enhanced Raman spectroscopy (SERS)-based sensing applications.
Nano-engineered multiblock copolymer particles via RAFT emulsion polymerization

Thiago R. Guimaraes\textsuperscript{1}, thiago.guimarois@gmail.com, Murtaza Khan\textsuperscript{1}, Glenn K. Clothier\textsuperscript{1}, Steven W. Thompson\textsuperscript{1}, Graeme Moad\textsuperscript{2}, Sebastien Perrier\textsuperscript{3}, Per B. Zetterlund\textsuperscript{1}. (1) Cluster for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, University of New South Wales, Sydney, New South Wales, Australia (2) Manufacturing, CSIRO, Clayton, Victoria, Australia (3) University of Warwick, Coventry, United Kingdom

Block copolymers comprising chemically incompatible blocks that undergo microphase separation have to date been largely explored for nano-structured films. This process is mainly governed by the Flory-Huggins interaction parameter ($\chi$) and degree of polymerization (N), whereby the MW of the comprising blocks must be sufficiently high for microphase separation to occur. Such microphase separation can also be observed within particles prepared in heterogeneous systems, which results in nano-engineered particles displaying sophisticated morphologies.

Recently we reported an environmentally friendly approach for the preparation of multiblock copolymers via sequential RAFT emulsion polymerization. The compartmentalization effect, i.e. how the radicals propagate within the particles reducing the termination rate, was exploited not only to obtain rate enhancement of the system, but also to generate chains with high-degree of chain end fidelity. Amphiphilic block copolymer of low MW was initially prepared via RAFT solution polymerization. After purification and solubilization in water, macroRAFT-assisted emulsion polymerization of hydrophobic monomers (styrene (S) or butyl methacrylate (BMA)) was then performed, generating polymeric nanoparticles (“nanoreactors”). Successive sequential RAFT polymerizations of different monomers were subsequently performed, generating a wide range of multiblock copolymer particles (Fig. 1). Due to the compartmentalization effect, polymers exhibiting high MW (>100,000 g mol\textsuperscript{-1}) could be synthesized in a relatively short period of time (~6h). Furthermore, given that the RAFT-moieties are located in the core of the particle, the successive growth of incompatible block copolymers from within the particle centre leads to the formation of multilayered particles. In addition, the number and the composition of each layer was readily controlled due to the great versatility of RAFT polymerization and the judicious choice of monomers. This demonstrates how RAFT conducted in emulsion polymerization can be a very powerful tool for the preparation of tailored-made multilayered particles.

Fig 1. Multilayered nanoparticle obtained via sequential RAFT emulsion polymerization
Colloids for energy storage: Visualizing energy transport in redox-active colloids and using colloids as templates for 3D-structured Li-ion battery electrodes

Paul V. Braun, pbraun@illinois.edu. Univ of Illinois, Urbana, Illinois, United States

We have made considerable advances in using colloidal particles as templates for electrodeposited three-dimensionally structured battery electrodes, and in understanding energy transport within dense suspensions of redox active colloidal particles. We have found that by using colloidal templating, we can design 3D structured battery electrodes with the appropriate free volume to accommodate the large volume changes present during cycling of high energy density alloying-based (e.g., Si and Sn) Li-ion anodes, as well as provide the required pathway for efficient lithium ion and electron transport to provide good rate performances. In a related area, we have been investigating energy transport in redox-active colloids (here the colloids serve as the energy storage material, rather than as a sacrificial template). Somewhat unexpectedly, we discovered that the fluorescence of ethyl-viologen derivatized redox active colloids was a strong function of the colloid’s electrochemical state. Using this, we are able to follow the inter-colloidal energy transport in a dense array of redox-active colloids over distances exceeding 20 microns as the colloids undergo reversible oxidation and reduction. These colloids have been proposed as the basis of flow battery energy storage systems, and understanding energy transport in dense suspensions of redox active colloids is an important requirement to advance the application of these materials.
Colloidal nanosphere lithography: Templating electropolymerizations and applications

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The preparation of new polymers and nanomaterials require hierarchical levels of ordering and structuring: from molecular to macroscopic. The tools and methods available for evincing this order require design principles that start from non-covalent interactions all the way to object patterns that can be manipulated by non-lithographic methods. The ability to synthesize and fabricate layered ordered systems result in new material stimuli-responsive properties. This talk will highlight the research methods in colloidal nanosphere lithography used by our group to produce systems that include: 1) conjugated polymers, 2) electropolymerized molecularly imprinted sensors, 3) electronanopatterning, and 4) polymer brush lithography. What is also important is the use of surface sensitive spectroscopic and microscopic analytical tools applied rationally to highlight evidence of order and function.
Functional polyphosphazene colloids

Andrij Pich, pich@dwi.rwth-aachen.de. Functional and Interactive Polymers, DWI-Leibniz-Institut für Interaktive Materialien, Aachen, Germany

Phosphazene-based polymers have raised great interest in many different scientific fields due to their excellent thermal properties, biocompatibility and biodegradability. These outstanding features turn polyphosphazenes into one of the most interesting hybrid inorganic-organic materials. Cyclo-matrix type polyphosphazene colloids can be synthesized by crosslinking of the cyclic compounds, such as hexachlorocyclotriphosphazene (HCCP), with bi- or multifunctional reagents. Cyclo-matrix polyphosphazenes are promising candidates as carriers, adhesives or flame-retardant polymer additives.

Recently we developed a versatile precipitation polycondensation method to synthesize polyphosphazene colloids with variable chemical structure, crosslink density and size. Starting with hexachlorocyclotriphosphazene (HCCP) and different multifunctional amines or phenols crosslinked cyclo-matrix polyphosphazene particles were synthesized. In this contribution we will focus on synthesis of hybrid colloids based on HCCTP and natural polyphenol tannic acid (TA). We demonstrate that the combination of two reactive building blocks allows flexible control of the chemical structure for hybrid polymer colloids. The influence of varying reagent ratios on the chemical composition and the morphology of the polymer particles was systematically investigated. Obtained hybrid particles were analysed by FTIR spectroscopy, dynamic light scattering, X-ray photoelectron spectroscopy, elemental analysis as well as $^{31}$P MAS NMR. The optimized synthesis process allows control of the particle size in extremely broad range (from 100 nm to 5 μm), variation of crosslink density, modification of chemical structure and efficient particle transfer into aqueous phase.

Obtained polyphosphazene/TA colloids exhibit extraordinary properties like high thermal stability, degradability and reactive surface. The application of phosphazene colloids in flame-retardant coatings, antimicrobial agents or catalyst supports will be discussed.
EDTA mimicking polymers and their ability to form Zr(IV) chelation mediated nanostructures

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Over the last two decades the radioisotope zirconium-89 (⁸⁹Zr) has emerged as highly suitable component of nuclear imaging agents used in positron-emission tomography owing to the relatively long radiolytic half-life (78.41 h) that matches the biological half-life of many polymeric species.¹ Novel ⁸⁹Zr chelating polymers were synthesised by reversible addition-fragmentation chain-transfer polymerisation of a new ethylenediaminetetraacetic acid (EDTA) mimicking monomer bearing two carboxylic acids bridged by a tertiary amine group (Figure 1A).² The monomer presented is accessible in a simple two step strategy and can be polymerised in a controlled fashion enabling the synthesis of defined homopolymers (dispersity < 1.3) and the chain extension of a N-acryloyl morpholine chain transfer agent to afford block copolymers of tailored composition. Upon deprotection of the carboxylic acid groups, the polymers showed similar pKₐ values as EDTA and were able to efficiently complex Zr(IV) in aqueous solution. Specifically, complexation studies using block copolymers revealed the formation of defined nanostructures (Figure 1B and C), which were stable in serum containing cell media for at least 24 h. Their negligible cell toxicity and ability to encapsulate ⁸⁹Zr render the polymers and nanostructures presented suitable candidates for future diagnostic and radiotherapeutic applications in biomedicine.

Figure 1. A: Schematic representation of the preparation of ⁸⁹Zr loaded polymer nanostructures. B: TEM image of Zr(IV) chelation mediated nano-assembly of PNAM₅₈-b-AEAP₁₆ with 2 eq. of Zr(IV) at pH = 5 in MQ. C: Magnification of B indicating the mean length and width of the nanostructures.
Organic X-ray radioluminescent crystalline colloidal arrays encapsulated in poly(ethylene glycol) methacrylate-based hydrogel films with a tunable emission

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A fully organic, fluorescent crystalline colloidal array (CCA) was synthesized by an emulsion copolymerization of styrene, anthracene methyl methacrylate (AMMA), and propargyl acrylate (PA) to form monodisperse nanoparticles. Once polymerized, Coulombic electrostatic repulsive forces cause the nanoparticles to self-assemble into FCC crystal structures which can be encapsulated within a poly(ethylene glycol) methacrylate-based hydrogel network. The radioluminescence of the copolymer CCA system is derived from the inherent scintillating properties of the anthracene monomer. By coupling the radioluminescence and the rejection wavelength of the CCA, the emission characteristics, such as intensity, of the liquid system can be customized. The rejection wavelength of the CCA, which is in the visible light spectrum, is directly related to the interplanar spacing in the crystal. The rejection wavelength can be tuned by diluting the CCA mixture with DI water prior to forming the hydrogel, which adjusts the initial interplanar spacing. Once the CCA is encapsulated within the hydrogel, the film can be swelled and dried to again alter the interplanar spacing, allowing the reflectance to be shifted across the visible spectrum.

Figure 1: a) Schematic of a CCA reflecting visible (green) light and b) corresponding reflectance spectra (rejection wavelength).
Nanocomposite microgels prepared by seeded emulsion polymerization

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Hydrogel microspheres, or microgels, are water-swollen nanomaterials composed of crosslinked amphiphilic polymer chains. Due to a variety of their advantages compared to solid microspheres, microgels have much attention in many applications such as sensors, catalysts, and coatings. To develop microgels with advanced properties, the fabrication of (nano)composite structures is an efficient approach. So far, we have discovered a series of hydrogel/solid nanocomposite microgels, which were synthesized by seeded emulsion polymerization (SEP) in the presence of microgels. As the properties of nanocomposite microgels are strongly correlated to their nanostructures, accurate nanostructural analysis is required. In the present study, we precisely determined the 3D structure of a series of solid/hydrogel nanocomposite microgels by cryo-electron tomography (cryoET) analysis, in addition to scanning electron and transmission electron microscopy, using the synthesized composite microgels with a variety of well-defined structures. The obtained images of cryoET provided important insights into interactions between hydrophobic molecules such as styrene and microgels. It was also discovered that hydrophobic monomers can recognize different microenvironments within microgels. Thus, SEP in the presence of microgels allows hydrophobization of water-swollen hydrated microgels and the formation of unprecedented multilayered nanocomposite microgels. We are convinced that our results of this study should lead to the development of noteworthy research on nanocomposite microgels.
Investigation for formation process of hydrogel microspheres during precipitation polymerization

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Water-swollen hydrogel microspheres (microgels) are soft colloidal particles composed of cross-linked hydrophilic or amphiphilic polymer chains. Because of their fascinating properties, which combine the features of hydrogels and colloids, microgels are expected to find use in numerous applications such as careers for drug delivery and molecular separation. The development of microgels for a variety of applications has been achieved as the result of the discovery of a preparation method capable of producing uniformly sized microgels in a flask, i.e., aqueous free-radical precipitation polymerization. However, although techniques to produce uniform-sized hydrogel microspheres (microgels) by aqueous free-radical precipitation polymerization are well established, the details of the polymerization process remain mysterious. In this study, the structural evolution and thermoresponsiveness of the developing microgels during the polymerization were evaluated using temperature-controlled high-speed atomic force microscopy (TC-HS-AFM). This analysis clarified that the swelling properties of the precursor microgels formed in the early stages of the polymerization are quite low due to the high incorporation of cross-linkers, and that non-thermoresponsive decanano-sized spherical domains are already present in the precursor microgels. Furthermore, we succeeded in tracking the formation of nuclei and their growth process, which has never been fully understood, in aqueous solution using real-time observations (Figure). These findings will help us to design functional microgels with the desired nanostructures via precipitation polymerization.

Figure. Direct visualization of the formation process of the hydrogel microspheres during precipitation polymerization by TC-HS-AFM. reprinted from [Y. Nishizawa, H. Minato, T. Inui, T. Uchihashi, D. Suzuki, Langmuir 2020, https://doi.org/10.1021/acs.langmuir.0c02654] with permission from American Chemical Society.
Evaluation of thermoresponsive behavior of charged hydrogel microspheres with different charge distributions

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As stimulus-responsive polymeric materials undergo dramatic changes in their structure/shape and physical/chemical properties in response to changes in the environment, they are also called “smart materials”. The key factors and requirements for stimulus-responsive materials to undergo changes are to be fast, reversible, complex, and robust in response to the external stimuli. One type of stimulus-responsive materials with the potential to fulfill the aforementioned requirements is hydrogel microspheres (microgels). Microgels are colloidal particles that can respond rapidly to external stimuli because of their microscopic dimensions. Owing to their rapid stimulus-responsiveness, microgels have been used for numerous applications in, for example, molecular separation, drug-delivery vehicles, sensors, and actuators. So far, the stimulus-responsive properties of microgels have been mainly evaluated by scattering techniques, calorimetry, sensors, and so forth. However, these techniques provide ensemble-averaged signals for the entire system. Therefore, undesired artifacts such as unexpected morphology changes in microgels induced by external stimuli might be included in the obtained data, which would hamper the correct interpretation of the data. More reliable data and a deeper insight into the stimulus-responsive behavior of individual microgels should be obtained from real-time direct observations of microgels, which should provide accurate and relevant information on the morphological changes experienced by microgels. In this context, we have achieved a direct visualization of thermoresponsive morphological changes in individual microgels in real time in aqueous solution using high-speed atomic force microscopy (HS-AFM). In this study, we have investigated how highly water-swollen microgels respond to temperature changes using light scattering, electrophoresis and temperature-controlled HS-AFM.
Liquid crystal peptide/DNA coacervates in the context of prebiotic molecular evolution

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Liquid–liquid phase separation (LLPS) phenomena are ubiquitous in biological systems, as various cellular LLPS structures control biological processes. Due to their ease of in vitro assembly into membraneless compartments and their presence within modern cells, LLPS have been postulated to be one potential form of the first cells on Earth. Recently, liquid crystal (LC)-coacervate droplets assembled from aqueous solutions of short double-stranded DNA (s-dsDNA) and poly-L-lysine (PLL) were reported. LC-coacervates conjugate the advantages of associative LLPS with the relevant long-range ordering and fluidity properties typical of LC, which reflect and propagate the physico-chemical properties of their molecular constituents. Here, we investigate structure, assembly, and function of DNA LC-coacervates in the context of prebiotic molecular evolution and the emergence of functional protocells on early Earth. We observe through polarization microscopy that LC-coacervate systems can be dynamically assembled and disassembled based on prebiotically available environmental factors including temperature, salinity, and dehydration/rehydration cycles. Based on these observations, we discuss how LC-coacervates can in principle provide selective pressures effecting and sustaining chemical evolution within partially ordered compartments. Finally, we speculate about the potential for LC-coacervates to perform various biologically relevant properties, such as segregation/concentration of biomolecules, catalysis, and scaffolding, potentially providing additional structural complexity, such as linearization of nucleic acids and peptides within the LC ordered matrix, that could have promoted more efficient polymerization. While there are still a number of remaining open questions regarding coacervates, as protocell models, including how modern biologies acquired such membraneless organelles, further elucidation of the structure and function of different LLPS systems in the context of origins of life and prebiotic chemistry could provide new insights for understanding new pathways of molecular evolution possibly leading to the emergence of the first cells on Earth.
Near-infrared emitting polymer dots for multiplexed cellular imaging

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Near-infrared (NIR) fluorophores are highly desirable for applications involving biological samples because they offer reduced optical interference from autofluorescence of biomolecules and increased penetration depth due to reduced optical scattering compared to visible emitting fluorophores. Organic dye molecules are the most widely studied and used NIR fluorophores in biological applications, but they suffer from several key weaknesses, including poor photostability, and low water solubility without functional modifications that often further reduce their emission quantum yield. Recently, semiconducting polymer nanoparticles (Pdots), have gain increasing attention due to several desirable optical properties, including high photostability, high water solubility, and exceptionally high brightness due to high absorption coefficient and high emission quantum yield. One of the most useful properties of Pdots is that their emission properties can be tuned by doping the polymer matrix with different NIR hydrophobic organic dyes. Here we present Pdots doped with a series of hydrophophyrin dyes with peak emission wavelengths ranging from 640 nm to 820 nm. The inclusion of a dye in the polymer matrix results in highly efficient energy transfer from the polymer to the dye molecules, effectively shifting the Pdots' emission properties to those of the dye. The dye-doped Pdots feature significantly narrower and red-shifted emission peaks compared to the undoped Pdots while also enhancing the water-solubility of the hydrophophyrin dyes. Using confocal fluorescence microscopy, we demonstrate the potential of hydrophophyrin-doped Pdots for multiplexed cellular imaging.

Undoped PFBT polymer dots (left) and PFBT polymer dots doped with a hydrophophyrin dye (right)
Highly efficient photochromic tungsten oxide@PNIPAM composite spheres with a fast response

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Coloration efficiency and a fast response are important in developing materials for optical switching. A novel, highly efficient photochromic tungsten oxide@poly(N-isopropylacrylamide) (PNIPAM) hybrid sphere is reported, whose colors can be rapidly converted between yellow and blue under different lights. The color change can be seen clearly even if the tungsten oxide content in the hybrid sphere is very low, exhibiting outstanding coloration efficiency of tungsten oxide. A photochromic mechanism is proposed in which the amide group in PNIPAM spheres participates in electron injection and the transition of valence states between W⁵⁺ and W⁶⁺ in the photochromic process. The interaction between tungsten oxide and PNIPAM plays a key role in enhancing the coloration efficiency of tungsten oxide and accelerating the switchable speed of color transformation, which is very useful in developing new photochromic materials. These hybrid spheres can be used in rewritable record displays and have wide potential applications in controlling energy transmittance in smart windows or in detecting UV light in optical sensors.
Analysis of colloidal particles and emulsion polymers with asymmetric flow field flow fractionation and related techniques

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Polymer colloids are usually defined as dispersions of submicron polymer particles in liquid (typically aqueous) media. A wide variety of processes are used to prepare polymer colloids. The most often utilized method is emulsion polymerization, which is the basis of a massive global industry. These materials are employed at large scale in a wide range of well-established applications such as coatings, adhesives, home and personal care along with many emerging applications including medicine, biotechnology and energy. In addition to financial value, the shift from solvent to waterborne dispersions has yielded large and measureable sustainability benefits.

The analytical capabilities for the characterization of colloidal particles and the polymers made by emulsion processes are essential to product development, quality control, intellectual property protection, and fundamental research. Asymmetrical flow field-flow fractionation (AF4) with on-line advanced detectors such as multi-angle light scattering (MALS), dynamic light scattering (DLS) and differential refractive index (dRI) have proven their strength in colloid particle characterization. In this presentation, we will review the principles of Field Flow Fractionation (FFF) techniques, the capability of AF4-related techniques, and will use real industrially relevant examples to demonstrate what AF4-MALS-DLS-RI can offer in terms of particle size distribution, particle quantification, particle mass, particle morphology information, and probing the interaction and stability of the particles. In addition for particle characterization, AF4-based techniques exhibit advantages over gel permeation chromatography based techniques for polymer molecular structural characterization, especially for highly branched and microgel containing emulsion polymers. Meanwhile, challenges in characterizing these colloidal systems and emulsion polymers will also be discussed to stimulate future developments in this area.
Nanoparticles (NPs) have a broad range of applications in the chemical industry including paints, home & personal care products, and various plastic products. The physical and chemical properties (i.e. size, shape, and surface composition and charge) are critical to understanding their behavior in product development and application. Although numerous techniques have been explored for particle characterization, most of these focus on size and shape. Capillary electrophoresis (CE) separates particles based on electrophoretic mobility, which is related to both surface charge and particle size. Although CE is a highly efficient separation technique, particle peaks are typically broad and unresolved due to the convoluted distributions of size and charge. Therefore, we apply a two-dimensional off-line coupling of asymmetrical flow field-flow fractionation (AF4) and CE to separate and characterize NPs. The AF4 in the first dimension separates particles according to hydrodynamic diameter and hence reduces the impact of size distribution in CE separation, allowing sharper peaks in the second dimension CE electropherogram and improved resolution of the 2D contour plot as compared to either 1D separation. One major challenge in the application of this 2D technique is the large sample dilution after the AF4 fractionation leading to poor sensitivity for the CE. Multiple approaches have been explored in our research in order to bridge this gap, including ultracentrifugation and large volume sample stacking (LVSS). Also, we have developed Java code to extract and align CE data and perform baseline subtraction in order to obtain 2D contour plots. The improved separation and data processing platform is reproducible and robust, and holds great potential for characterization of a variety of industrial products with NPs components.
Time-resolved small-angle X-ray scattering studies during aqueous emulsion polymerization

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The persulfate-initiated aqueous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) is studied by time-resolved small-angle X-ray scattering (SAXS) at 60 °C using a stirrable reaction cell. TFEMA was preferred to styrene because it offers much greater X-ray scattering contrast relative to water. The evolution in particle size is monitored by both in situ SAXS and ex situ DLS in the absence or presence of an anionic surfactant (sodium dodecyl sulfate, SDS). Post-mortem SAXS studies confirmed the formation of well-defined spherical latexes, with volume-average diameters of 353 ± 9 nm and 68 ± 4 nm being obtained for the surfactant-free and SDS formulations, respectively. \textsuperscript{1}H NMR spectroscopy studies of the equivalent laboratory-scale formulations indicated TFEMA conversions of 99% within 80 min and 93% within 60 min for the surfactant-free and SDS formulations, respectively. Comparable polymerization kinetics are observed for the in situ SAXS experiments and the laboratory-scale syntheses, with nucleation occurring after approximately 6 min in each case. After nucleation, scattering patterns are fitted using a hard sphere scattering model to determine the evolution in particle growth for both formulations. Moreover, in situ SAXS enables identification of the three main intervals (I, II, and III) that are observed during aqueous emulsion polymerization in the presence of surfactant. These intervals are consistent with those indicated by solution conductivity and optical microscopy studies. Significant differences between the surfactant-free and SDS formulations are observed, providing useful insights into the mechanism of emulsion polymerization.
Combining suspension polymerization free radical copolymerization and click chemistry towards cross-linked polymer microparticles with tunable surface properties

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Recent studies on the rheological behavior of concentrated non-Brownian suspensions (NBS) have highlighted the role of interparticle frictional contacts. To investigate these solid contact forces, surface-functionalized polymer microparticles with diameter of ca. 80 μm and tunable surface properties were prepared by the combination of suspension free radical copolymerization, covalent anchoring of a variety of azide-functionalized moieties by copper(I)-catalyzed azide-alkyne cycloaddition and subsequent N-alkylation of the 1,2,3-triazole groups. The resulting cross-linked microparticles were thoroughly characterized by light scattering, differential scanning calorimetry, as well as by optical, confocal fluorescence, scanning electron and atomic force microscopies (Figure 1). Finally, the impact of surface properties and volume fraction on the viscosity of concentrated suspensions of the different microparticles were studied by rheometry.

Figure 1. Optical microscopy (a), scattering electron microscopy (b and c) and confocal fluorescence microscopy (d) of cross-linked azide-functionalized microparticles (a, b and c) and fluorescently labelled microparticles (d).
Synthesis, computer simulation and NMR study of novel peptide dendrimers with arginine and histidine spacers designed for drug and gene delivery

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Dendrimers are macromolecules regularly branched from central core. Their repeating units have a fork-like structure usually with two (rarely with three or more) prongs. Due to this reason, the number of atoms in them doubled (or tripled) in each generation. They have spherical shape, precise size and many terminal groups capable to interact with other biological molecules. Lysine dendrimers and peptide dendrimers were used as carriers for drug and gene delivery as well as for many other biomedical applications. We performed here synthesis, characterization and computer simulation of two novel peptide dendrimers with the same AlaLys core, Lys2Arg and Lys2His repeating units and charged terminal Lys aminoacid residues. Temperature dependences of equilibrium characteristics and orientational relaxation times of terminal, main chain and side CH2 groups in the temperature interval T=283K-343 K were studied. It was demonstrated that size and density distribution of these dendrimers almost do not depend on temperature. Temperature dependences of relaxation times and spin-lattice relaxation time T1H of CH2 groups of all dendrimers were calculated and it was shown that they are very close to experimental results obtained for these dendrimers by NMR.
One-step synthesis of responsive cavity-forming zwitterionic colloids

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The study of composite colloids offers diverse research opportunities encompassing both fundamental principles of soft matter and practical applications in bionanotechnology, environmental sensing and remediation, advanced coatings, and emulsion stabilization. Functional polymer chemistries, such as polyzwitterions, can enhance the utility of this material class by imparting stimuli-response, biocompatibility, and anti-fouling properties. However, the bottom-up integration of polyzwitterions into multicomponent colloids remains a challenge because polyzwitterions are difficult to process with the traditional chemistries and fabrication methods used by colloidal scientists. This contribution demonstrates a one-step synthesis of zwitterionic colloids by the dispersion copolymerization of styrene and sulfobetaine methacrylate in a solvent mixture of alcohol and water. The resulting composite colloids exhibit responsive cavity formation by environmentally benign triggers. We examine the effect of the monomer feed ratio and solvent composition on the colloid morphology and polymer solubility. This study utilizes model chemistries to drive fundamental inquiry into the mechanism of formation for these responsive cavity-forming zwitterionic colloids.

Scanning electron microscopy (SEM) images of colloids isolated in isopropyl alcohol after synthesis (left) and after a subsequent water wash (right). Corresponding transmission electron microscopy (TEM) images (insets) show the formation of a cavity after the water wash. Scale bars indicate 500 nm.
Silicone dispersions by conventional polymerization or soft matter engineering

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The generation of silicone latexes by Ring Opening Polymerization (ROP) of cyclosiloxanes has been widely documented first in patents, and now more and more in academic articles. The polymerization proceeds either by an anionic or a cationic mechanism, in a complex set of 8 different reactions which locations influence severely the state of final polymers and particles. In this lecture, I propose to summarize 20 years of research in this field that I carried out in different labs in France. First, I will explain what mechanisms are at stake when proceeding to conventional ROP in model miniemulsion droplets. Then, I will show that by using different types of soft matter templates (liposomes, microemulsions, functional particles), we can produce original dispersions in a facile manner. Finally, I will summarize the main hurdles still to be passed in the years to come.

Water-filled nanocapsules obtained by vesicle-templated ROP of D4H
Thermodynamics: The invisible arbiter of emulsion structure; insight from an examination of three-phase emulsions

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Emulsions provide a means to deliver mutually immiscible liquids in a macroscopically uniform manner. Multiple-phase emulsions in particular provide a useful template for fabrication of composite materials. The challenge in synthesizing multiple-phase emulsions or composites lies in the ability to design and control the morphology of the multiple-phase system in order to arrive at the desired properties. Multiple emulsions with sophisticated and precisely controlled structures have been well demonstrated via microfluidic techniques that generate one droplet at a time from a capillary. Large scale industrial production of emulsions, on the other hand, relies on the rapid mixing of large quantity of fluids at scales of metric tons instead of grams. Being able to predict and control multiple-phase emulsion structure in this latter case is therefore commercially pivotal. The morphology in a multiple-phase emulsion is governed by equilibrium tensions and volume fractions in accordance with thermodynamic principles. This has been well demonstrated in academic studies but under-appreciated in the formulation world. Equilibrium properties tend to escape the formulator’s mind, as emulsions, after all, are kinetically stabilized systems. This talk brings attention to two types of 3-phase emulsions to demonstrate practical value of (thinking) thermodynamics as well as to illustrate additional insights previously not recognized. The first type of 3-phase emulsion is formed from aqueous suspension polymerization of a solution mixture of silicone and acrylate monomers, which upon polymerization phase separates into two phases within each emulsion droplet. The morphology as well as detailed geometry of the hybrid particle are uniquely defined by the composition of the formulation. The second type of 3-phase emulsion is formed from mechanical dispersion of two immiscible oils in water. In this latter case the morphology of the hybrid droplet is defined by the equilibrium tensions, but specific geometry varies from droplet to droplet owing to random volume combination during the disruptive dispersion process. In both cases, predicted emulsion structure based on equilibrium properties is shown to agree with experimental observations.
Entropy-driven assembly behavior in 3D confined nanoparticle/block copolymer hybrid system

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Generating organic/inorganic hybrid materials with well-defined morphologies is of great importance as spatial alignments highly affect the integrated properties of hybrid nanomaterials. Herein, we investigated the assemblies of polystyrene-grafted Au nanoparticles (Au@PS) within onion-like polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) block copolymer (BCP) particles depending on four parameters: 1) molecular weight ($M_n$) of PS ligands (N), 2) core size of Au@PS, 3) grafting density of PS ligands, and 4) $M_n$ of PS-b-P4VP matrix (P). We observed transitions of hybrid particles between alternate-layered onions, seeded onions, and crusted onions depending on the effect of the aforementioned four parameters on interfacial interactions between ligands and matrix chains. To account for the phenomena, a modified swelling ratio ($P/N_{\text{SDPB}}$) is proposed by considering the ligands in the semi-dilute polymer brush (SDPB) regime as the only brushes available for interfacial interactions with BCPs. The modified parameter successfully explains structural transitions. Furthermore, we take the effect of NP overall size ($d$) into account as a complementary for evaluating the interfacial interactions.
Controlled scalable nanofabrication of new classes of colloidal polymer morphologies in sheared liquids

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By combining key concepts from polymer precipitation and interfacial polymerization with multiphasic fluid shear, we introduce a new method of fabricating a plethora of polymer micro- and nanostructures. This new soft matter nanofabrication technique is versatile, easily tunable, and scalable. A polymer solution is injected in non-solvent medium and precipitated at the interface of the formed multiphasic system under varying liquid shear and interdiffusion conditions. While the liquid shear-driven process is very simple, various combinations of its parameters lead to formation of myriad amazingly diverse colloidal morphologies out of almost any type of polymer. Our previous research on sheared liquid precipitation revealed the formation of microrod, fiber, and “dendricolloid” morphologies. Here, we demonstrate that these are just a few of the multitude of colloidal polymer structures that this liquid nanofabrication technique can produce. To exemplify, we will present data on up to 12 distinctive structures made from the same polymer, polystyrene. The results are interpreted and generalized based on a model which delineates the physical processes into three stages: hydrodynamic shear, mechanical response, and precipitation rate. These insights in the fundamental mechanisms underlying this method allows for tuning of material structure towards an “all-in-one” scalable nanofabrication platform.
Development of polymeric stabilizers for the mechanical dispersion process

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The Mechanical Dispersion (MD) process, a method of making low viscosity aqueous dispersions of polyolefins (and other polymers that do not emulsion polymerize), is enabled by a variety of dispersing materials, including small molecule surfactants and polymeric stabilizers such as ethylene-acrylic acid (EAA) polymers. The polymeric stabilizers are particularly useful at high temperature, but there is a limited range of EAA materials available commercially. The purpose of this preliminary study is to demonstrate that useful dispersing polymers can be prepared from hydrophobic (meth)acrylate/acrylamide monomers copolymerized with sulfonic acid functional moieties. Using high throughput polymer synthesis tools, the potassium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was copolymerized with a series of hydrophobic (meth)acrylate/acrylamide monomers at a range of carbon number to charge ratios to prepare a series of candidate dispersing polymers. The polymers were screened on the basis of high temperature water solubility, molecular weight and, using a novel small-scale MD process, for their ability to enable the dispersion of polyolefin resins to stable aqueous dispersions. Polymers with molecular weight 5,000 – 10,000 Da prepared from AMPS and t-octyl acrylamide, lauryl acrylate, and 2-ethylhexyl acrylate over a wide range of carbon number per charge appeared, in this preliminary work, to be effective. More extensive effort will be needed in order to elucidate detailed polymer structure-dispersion property relationships.
Diverse and unique colloidal particles assembled from polydisperse liquid crystalline oligomers

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Polymeric colloidal particles play important roles in applications including coatings, adhesives, paintings, drug delivery, and personal cares. Often they are prepared from emulsion polymerization with well-controlled chemical compositions of surfactants and monomers. Polydispersity tends to impede self-assembly processes and the control of particle morphologies. In contrast, nature provided us diverse examples of microparticles that have unique surface textures comprised of spikes, stripes, and holes as seen on fungal spores, pollen grains and insect cuticles, from mixtures of polypeptides. Further, shape transformation from one state to another is not uncommon in biology.

Here, we report two examples of self-assembled colloidal particles from nematic liquid crystal oligomers (LCOs), where polydispersity of the chain lengths is a feature. In the first example, we synthesize microparticles using a microfluidic device, followed by solvent evaporation and photopolymerization, leading to with robust, tunable surface patterns. Phase separation of LCOs occurs at the interface of the oil-in-water droplet upon organic solvent evaporation, which is facilitated by the mechanical coupling of LCOs of different chain lengths at the droplet interface. In the second example, we show dramatic shape transition of nematic LCO drops to a rich variety of non-spherical morphologies with unique internal structures upon cooling from the isotropic state to the nematic state. Here, molecular heterogeneity promotes and stabilize the reversible transitions.
Mechanistic Study on crosslinking in seeded emulsion polymerization: Effect of monomer feed rate on gel formation

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Waterborne latex is often called a product-of-process. Here, the effect of semi-batch monomer feed rate on the kinetics and gel formation in seeded emulsion polymerization was investigated for the copolymerization of n-butyl methacrylate (n-BMA) and ethylene glycol dimethacrylate (EGDMA). The gel fraction was strongly influenced by monomer feed rate, even though most of experiments were run under so called starved-fed conditions. More flooded conditions from faster monomer feed rates, including seeded batch reactions, counterintuitively resulted in significantly higher gel fraction. Kinetic Monte-Carlo simulations indicated that the dominant influence on this phenomenon was the sensitivity of primary intramolecular cyclization to the instantaneous unreacted monomer concentration, which is directly impacted by monomer feed rate. This concept has been explored previously for bulk and solution polymerizations, but not for emulsified reaction environments and especially for very low mole fraction divinyl monomer. In addition, while gel fraction could be dramatically manipulated by variations in linear monomer feed rates, it could be markedly enhanced by leveraging non-linear feed profiles built from combination sequences of flooded and starved conditions.
Design and synthesis of colloidal unimolecular polymers

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Colloidal Unimolecular polymer (CUPs) is a single chain polymer nanoparticle made by a process of self-folding or self-assembly of the polymer chain to form a spheroidal particle. The polymer chains consist of both hydrophobic and hydrophilic groups. CUPs are 3-9 nm in size, zero VOC, spheroidal particles that are self-stabilized via electronic repulsion due to the presence of hydrophilic surface charge groups which can be anionic or cationic groups. Each CUP particle is surrounded by a layer of bound or surface water which has different properties like freezing point, density, specific heat capacity as compared to regular water. Designing a CUPs particle to meet ones requirements is extremely easy due to the flexibility and variability it offers in terms of size of the particle, charge density (number of charges per unit area present on the surface) as well as the type of hydrophobic and hydrophilic monomers that can be used to make them. Since each polymer chain collapses into a single particle, the size can be easily controlled by manipulating the molecular weight of the polymer. For the polymer chain to collapse into a CUP particle, a balance of hydrophobic and hydrophilic units is extremely important. Too many hydrophilic groups can cause a change in conformation (from spheroidal to dumbbell or pearl necklace) whereas too few hydrophilic groups can cause aggregation. It is necessary to define the upper and lower limits of the surface charge density as a using a universal parameter that can be easily applied to all types and size of monomers which will greatly simplify the synthesis of these particles. The parameter for a change in conformation from sphere to dumbbell during reduction was verified using particle size measurements, viscosity and surface area calculated using freezing point depression measurements. The design and formation parameters will be defined in this presentation.
Effect of charge density on surface tension behavior of colloidal unimolecular polymers

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Colloidal unimolecular polymer particles, or CUPs, are true nanoscale charged particles of size less than 10 nm that are made from a single polymer chain having a well-balanced number of hydrophobic and hydrophilic units. They are made using a process called water reduction which is a simple and easy method, that allows for preparation of additive-free, zero-volatile organic content (VOC) and stable dispersions. The transformation of polymer chain into a CUP particle is similar to the formation of micelles in surfactants. When water is added to a dilute solution of polymer in a low boiling water loving solvent (e.g. Tetrahydrofuran), the chain collapses because the polymer-polymer interaction exceeds polymer-solvent interaction. The final CUP suspension contains only charged particles, water and counterions. Unlike latex and PUDs, they are free of other additives and surfactants. CUPs have a great potential in field of coatings and in the field of drug delivery, catalyst matrix, etc. Surface tension is an important property in paints and many other applications where CUPs can be used. Studying the surface tension behavior of CUPs is therefore very crucial and will help the understanding of the mechanism by which these nano-size charge particles alter the interfacial tension. CUPs have a mechanism for reducing the surface tension similar to that of surfactants at lower concentration but at higher concentration it is entirely different. Unlike surfactants, CUP particles cannot form micelles at higher concentration. They undergo a phenomenon called counterion condensation which affects its surface tension behavior. In conjunction with surface tension, evaporation rate measurements of these CUP solution was used to derive a model for these particles at the air-water interface. The results show surface tension behavior is primarily affected by charge density and this observation agrees with the predicted model.
Self assembly and characterization of novel photochromic particles

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We have recently prepared a novel organic-inorganic hybrid photochromic particle by free radical polymerization, and its application in discoloration coating was explored. Photochromic particles were assembled on the surface of polyacrylamide microgel and glass slides in different ways, and characterized by confocal laser scanning microscopy (CLSM), scanning electron microscopy (SEM) and ultraviolet-visible absorption spectroscopy (UV-vis). By means of CLSM and SEM, we found that the particles on the gel surface showed multi-layer long range order arrangement. It is found that the particles assembly on the gel surface greatly reduced the transmittance through UV-vis absorption spectrum while assembled onto the surface of the glass, the light transmittance decreased slightly. But both have good discoloration properties. The light transmittance of particles layer will change with the change of illumination time and with the extension of illumination time, the sample has an obvious absorption peak at about 610 nm, which is consistent with the photochromic properties of the photochromic particles themselves.
Preparation of non-spherical polymer particles via simple approaches

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Anisotropic particles have gained significant interest in a wide range of fields including self-assembly, drug delivery, and nanotechnology. The methods to produce such particles can be complex and large-scale production can be a considerable challenge. Here we discuss two complex non-spherical morphologies produced by methods suitable to scaling. In the first, we demonstrate a novel and simple approach for producing hollow spherocylindrical micron-sized particles starting from spherical primary polymer particles. These cylindrical particles also provide an interesting internal morphology. We will also discuss the conditions to tune or control the aspect ratio of these particles. Secondly, we will discuss anisotropic (multi)lobed particles with both shape and surface composition anisotropy. We will demonstrate the application of such particles to create well-controlled multilobed particles via a reactive hetrocoagulative approach for 3-D printing applications.
Stealth polymer nanorods: Living crystallisation-driven self-assembly of poly(2-oxazoline)s in pure water

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The morphology of polymer nanomaterials critically influences their biological interactions contributing to the determination of their in vivo fate.¹ However, currently there is a lack of robust methods for preparing non-spherical particles from biocompatible materials. Here, we combine ‘living’ crystallisation-driven self-assembly (CDSA), a seeded growth method that enables the preparation of rod-like polymer nanoparticles of controlled length, with poly(2-oxazoline)s (POx), a polymer class that exhibits ‘stealth’ behaviour and excellent biocompatibility.²,³ By selecting a thermoresponsive POx core-forming block, the ‘living’ CDSA process could be carried out for the first time in the complete absence of organic solvents, resulting in POx colloidal solutions of nanorods with lengths ranging from 50 to 600 nm. Furthermore, interesting temperature dependent rates of nanorod assembly and disassembly were observed in aqueous environments. In vitro and in vivo studies revealed low immune cell association and encouraging blood circulation times with little difference in the behaviour of POx nanorods of different lengths. The stealth behaviour observed highlights the potential of POx nanorods as a next generation stealth drug delivery platform.

Figure 1. Heat-induced living crystallisation-driven self-assembly of poly(2-oxazoline)s.
Three-dimensional confined assembly of bottlebrush block copolymers: the effect of molecular weight on the particle morphology

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The molecular weights and chain-rigidities of block copolymers (BCPs) can strongly influence their self-assembly behavior, particularly when the BCPs are under confinement. We investigate the self-assembly of bottlebrush block copolymers (BBCPs) confined in evaporative emulsions with varying molecular weights. A series of symmetric BBCPs, where polystyrene and polylactide side-chains are grafted onto the polynorbornene (PNB) backbone, are synthesized with different degrees of polymerization of the PNB (N_{PNB}). Morphological transitions from onion-like concentric particles into striped ellipsoids occur as the N_{PNB} of the BBCP increases, which is also predicted from coarse-grained simulations of BBCP droplets by an implicit solvent model. This transition is understood by the combined effects of i) an elevated entropic penalty associated with bending lamella domains of larger molecular weight BBCP particles and ii) the favorable parallel alignment of the backbone-chains at the free surface. Furthermore, the morphological evolutions of onion-like and ellipsoidal particles are compared. Unlike the onion-like BBCP particles, ellipsoidal BBCP particles are formed by the unique axial development of ring-like lamellae domains on the particle surface, followed by the radial propagation into the particle center. Finally, the shape-anisotropies of the ellipsoidal BBCP particles are analyzed as functions of N_{PNB} and particle volume. These BBCP particles demonstrate promising potential for various applications that require unique rheological, optical, and responsive properties.

(a-c) SEM and (d-f) cross-sectional TEM images of BBCP particles with different molecular weights: (a,d) smallest, (b,e) middle, and (c,f) largest molecular weight. (g-i) Cross-section images of BBCP particles obtained by Monte Carlo simulations by varying the number of beads for the backbone while adjusting the number of beads for the side-chain.
Waterborne multi-lobed particle morphology for directed-assembly towards 3D hierarchical structures

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Particle based building blocks are ubiquitous in applications in material science through to biomedical engineering. Our goal is to produce porous 3D scaffolds through rational design of particles with tunable assembly properties amenable to additive manufacturing techniques. The approach relies on precise control of a non-spherical particle morphology. It is generally challenging to synthesize such particles because surface energy favors spherical shapes to minimize the surface area in contact with the continuous media. We introduced a conventional, two-stage emulsion polymerization to create multi-lobed composite polymer nanoparticles by restricting the polymer chain diffusion on the seed particles. By estimating the diffusion coefficient of the polymers in the system, the size and number of the lobes on the particles could be tuned to a target final morphology. On the other hand, we also studied the pre-clustering behavior of small primary particles to achieve a larger scale of porosity and dimensions in the scaffolds compared to direct assembly of primary particles. Additionally, we developed a family of surface functional groups to trigger self-assembly of these particles on demand, ensure robust fixation, and to study the packing geometries that result on clustering. These are critical to the morphology of the pore network in the ultimate 3D scaffold.
Shape-changeable block copolymer particles driven by photo-isomerizable surfactants

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Shape-transformable particles response to light have been spotlighted for developing active, programmable smart materials. In this work, we report block copolymer (BCP) particles with reversible shape-changing property activated by wavelength-selective light irradiation. For achieving the reversible, shape-transformable BCP particles, we considerably design the spiropyran-based surfactant, which can be isomerized between ring-opening and ring-closing structure by UV or visible light irradiation, respectively. This photoisomerization of the spiropyran surfactant effectively tunes the wetting behavior of BCP chains for a specific wavelength. In the UV light irradiation, spherical BCP particles with hydrophilic outermost layer are generated by the higher hydrophilic interaction of surfactants of ring-opened form. By contrast, surfactants of ring-closed form under visible light provide a neutral surrounding to the BCP particles, producing football- or convex lens-like ellipsoids with axially stacked nanostructures. Importantly, we demonstrate the reversibility of the shape transformations of the BCP particles between spheres and ellipsoids by sequential UV or visible light irradiation, showing the robustness and effectiveness of spiropyran-based surfactants.
Compatible conjugated blends: Impact on the morphology and mechanics of flexible electronics
Zachary Ahmad, Presenter; Luke Galuska; William McNutt; Jianguo Mei; Xiaodan Gu

Effect of precise control of crosslink density on the thermal, mechanical and conductive properties of crosslinked ionene networks
Alexander Thome, Presenter; Kevin Miller

Using ARGET ATRP to synthesize block copolymers containing PDMAEMA and characterizing smart properties using DLS and UV-Vis
Sorfina Suzali, Presenter; Yunyi Huang; Elizabeth Glogowski

Predicting the bandgap of donor-acceptor conjugated polymers
Anna Peterson, Presenter; Jason Azoulay

Preceramic hairy nanoparticles: Investigating monomer variations of polycarbosilane-grafted nanoparticles
Christina Thompson, Presenter; Dr. Kara L Martin; Maria Parvulescu; Subramanian Ramakrishnan; Matthew Dickerson

Simulation-informed rational design of 1D photonic crystals
Clayton Keene, Presenter; Mark Robertson; Zhe Qiang

Stress relaxation through dynamic covalent exchange in polyanhydrides
Rebecca Meacham, Presenter; Ana Witkowski; Kelly Tillman; Patrick Mather; Devon Shipp

Ambient reactive extrusion-additive manufacturing of thermoplastic polyurethanes
Erich G. Loewer IV, Presenter; Aynslie Fritz; PROF Jeffrey Wiggins

Photocurable nanocomposites for the use of synthetic cartilage replacements
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Molecular docking simulations to assess the estrogenic activity of lignin-derivable bisphenol A alternatives and their polymerization via additive manufacturing
Alice Amitrano, Presenter; Jignesh Mahajan; Robert O'Dea; Prof. LaShanda Korley; Thomas Epps

Development of resveratrol/cyclodextrin inclusion complex nanofibrous webs for fast-dissolving dietary supplement
Deniz Tekant, Presenter; Dr. Asli Celebioglu; Tamer Uyar
Synthesis and characterization of glycodendrimersomes for bioimaging applications
Patrick O Aghadiuno, Presenter; Molly Jones; Dr. Davita L Watkins; Sarah Morgan

Electrohydrodynamic encapsulation of curcumin-cyclodextrin inclusion complexes in chitosan/pectin nanofibrous webs
Antonio Saporito, Presenter; Dr. Asli Celebioglu; Tamer Uyar

Reactivity ratios of RAFT polymerization of tert-butyl acrylate and a thiolactone-functionalized acrylamide
Anne Rolsma, Presenter; Yongneng Wu; Devon Shipp

Influencing polymer solubility with thermally-responsive diels-alder monomers
Greg Bisbjerg, Presenter; Ginger W Brown; Kimberly Pham; Ryan de Kock; William Ramos; Jordan Patierno; Natalie Zawalick; Aleyda Bautista; Viviana Vigil; Philip Costanzo
Compatible conjugated blends: Impact on the morphology and mechanics of flexible electronics

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Conjugated polymers show great promise for next generation flexible electronic devices, but there remains a need to balance both mechanical and electrical property. Previously, my lab engineered a partially conjugated polymer (PNDI-C4), which exhibits high ductility upwards of 400% strain, but reduced charge mobility relative to fully conjugated polymer (PNDI-C0). Here, we explore the influence of compatible conjugated blends (PNDI-C4 as the soft matrix and PNDI-C0 as the electrically active component) on polymer morphology, mechanics, and electrical property. We will achieve a fundamental understanding of blend morphology for these similar components by establishing the framework for how they deform with strain. I also intend to supplement this information by examining the effect of tensile chain alignment on the electrical properties of these blend systems. To achieve this, we propose to employ wide-angle x-ray scattering (WAXS) to monitor the crystalline alignment, polarized UV-Vis to monitor the full chain backbone alignment, AFM to monitor surface alignment, and device fabrication to monitor electrical property. Additionally, blends of PNDI-C0 and PDMS will be compared to determine if the partially conjugated polymer is ultimately advantageous as the ductile component, i.e. promotes desired morphology for enhanced mechanics and electrical properties. The overall result of this presentation will clarify the use of flexible partially conjugated polymers as the matrix in blend systems as well as demonstrate fundamental understanding of blend morphology for like components.

Stress vs strain graph for NDI-C4 polymer blended with 2%, 5%, and 10% NDI-C0.
Effect of precise control of crosslink density on the thermal, mechanical and conductive properties of crosslinked ionene networks

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Ionenes are ion-containing polymers where the ionic group is anchored directly into the backbone of the repeating unit. Here, imidazolium groups were incorporated into a covalently crosslinked ionene framework using thiol-ene photopolymerization. The crosslink density was controlled using two synthetic variations: (a) the length of the alkenyl group on the original imidazolium-containing ene monomer and (b) the thiol:ene functional group ratio. In general, networks in which a stoichiometric thiol:ene functional group ratio was employed provided the highest glass transition temperatures and crosslink density, which resulted in the lowest anhydrous ionic conductivities. A combination of increasing the chain length of the ene monomer and a thiol:ene functional group ratio in which excess ene was utilized provided the highest ionic conductivities (~10^{-6} S/m at 20 °C). Overall, this discussion will demonstrate that, with precise control of the network architecture, that the thermal, mechanical and conductive properties can be appropriately tuned.
Using ARGET ATRP to synthesize block copolymers containing PDMAEMA and characterizing smart properties using DLS and UV-Vis

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Smart polymers are polymers that change their properties depending on their surroundings. The smart polymer poly((2-dimethylamino) ethyl methacrylate) (PDMAEMA) is pH- and temperature-sensitive and can switch between being soluble and insoluble in water. Activator ReGenerated Electron Transfer-Atom Transfer Radical Polymerization (ARGET ATRP) was used to synthesize PDMAEMA with a macroinitiator to form tri- and di- block copolymers. ARGET ATRP was used for its environmental benefits, low costs and because of its reduced sensitivity to oxygen as compared to ATRP. Different synthetic conditions were used to obtain various target ratios of the block copolymer. After synthesis, Nuclear Magnetic Resonance (NMR) Spectroscopy and Gel Permeation Chromatography (GPC) were used to determine the relative ratio of PDMAEMA to macroinitiator and the dispersity. Once the target ratio and low dispersity were reached, characterization of smart properties was done by UltraViolet-Visible spectroscopy (UV-Vis) and Dynamic Light Scattering (DLS). Polymer composition and polymer concentration of samples were varied to observe trends. The UV-Vis determined the cloud point, or the temperature at which the polymer switches from being soluble to insoluble in aqueous solution. The DLS determined the change in radius as a function of temperature, from individual polymer chains to micelles or aggregates above the cloud point. Results obtained differed for the various polymer compositions tested. By studying the structure-property relationships of this smart polymer, uses can be optimized in drug delivery and enhanced oil recovery.
Predicting the bandgap of donor-acceptor conjugated polymers

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Donor-acceptor (DA) organic semiconductors (OSC), predicated upon extended $\pi$-conjugation, with open-shell diradical character ($y$) are sought after for their unique quantum phenomena and magnetic interactions where they often serve as the active component in a wide array of next-generation devices. Functionality and utility of OSCs is often defined by the topological arrangement of the electronic structure and configuration of the frontier molecular orbitals (FMOs) (e.g. bandgap). This structure-function-performance relationship highlights the importance of rapid, but accurate, predictions of bandgap ($E_g$) energies for high-$y$ OSCs in the polymeric state towards guiding synthesis. Current computational methods for determining the $E_g$ of a DA conjugated polymer (CP) involve iterative, computationally expensive calculations while only indicating the properties of well-defined structures, requiring extrapolation to describe properties of the polymer. Here, an efficient method was developed to accurately determine the electronic configuration of DA CPs. The $E_g$ values at varying polymer chain lengths were computed using density functional theory (DFT) at the unrestricted-B3LYP/6-311G** level and the trend was used to predict the narrowing $E_g$ expected of an open-shell polymer. These results were used to develop and benchmark the performance of a protocol using periodic boundary conditions (PBC) to describe the electronic configuration along a one-dimensional cell forming an infinite lattice. While many systems were accurately described with PBC, results typically underestimated $E_g$ compared to extrapolated values. Though early results are promising, systems with nearly degenerate FMOs can result in an overpredicted $E_g$, indicating that further development into the exchange, correlation, and mixing parameters is needed.
Preceramic hairy nanoparticles: Investigating monomer variations of polycarbosilane-grafted nanoparticles

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The aerospace industry is perpetually in search of advanced ceramic materials that can withstand higher temperatures and stress while retaining processability. One novel approach to the creation of such high-temperature materials is through the use of hybrid nanoparticles that can be processed like polymers and subsequently converted into ceramics. We have recently created such hybrids, termed hairy nanoparticles (HNPs) that are composed of a preceramic polycarbosilane polymer brush grafted to a silica nanoparticle core. The present class of HNPs is synthesized via platinum(0)-catalyzed hydrosilylation chemistry. This recently developed preceramic hybrid material displays desirable rheological properties and yields inorganic SiO2/SiC nanocomposites upon pyrolysis. In this presentation, we will discuss novel polycarbosilane HNP architectures and their chemical and structural properties, as determined by various analytical techniques, including NMR, GPC, TGA, FTIR, and XRD.
Simulation-informed rational design of 1D photonic crystals

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A one dimensional (1D) photonic crystal (PC) is composed of periodic dielectric layers with mismatched refractive indices, which can reflect electromagnetic waves at designated wavelengths. PC reflectance spectra are determined by the difference in refractive index and thickness of each layer. One common approach to describe the propagating waves through PCs at each interface is using Transfer Matrix Method (TMM). While modeling uniform PCs has been previously demonstrated using this method, a platform to model PCs that accounts for heterogeneity among the layers of the PC that may more accurately depict experimental development of a PC is still lacking. Herein, a MATLAB program is designed to model reflectance behavior of PCs with arbitrary layer thicknesses and refractive indices, as well as involving other user-definable parameters, such as a variety of methods for altering the layer thicknesses and interfacial roughness between distinct layers. Furthermore, this program is built with a Graphical User Interface (GUI) for simplicity and convenience, especially for users with limited programming backgrounds. The application is published alongside a standard operating procedure to help new users navigate the program efficiently. We believe this simulation platform would provide important fundamental insights for informing rational design of 1D PCs in various applications including military defense, advanced coatings, as well as optoelectronics.
Stress relaxation through dynamic covalent exchange in polyanhydrides

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Polyanhydrides are of interest in biomedical applications due to their biocompatibility and linear erosion. This makes them ideal for drug delivery systems. We are also interested in other applications of polyanhydrides such as shape memory and self-healing materials. Previous work in our groups investigated a shape memory elastomeric composite with a polyanhydride permanent phase. The dynamic covalent exchange that occurs between the anhydride groups at elevated temperatures complicated shape memory behavior. The exchange caused stress relaxation in the network, which although this allowed the permanent shape of the polymer to be reconfigured it meant that shape memory behavior was not optimal. It is therefore important to study the exchange process in order to facilitate either shape memory or self-healing in polyanhydrides. In this work, stress relaxation in polyanhydrides made using radical-mediated thiol-ene polymerizations was measured to determine the effect of the crosslink density and temperature on the exchange. Furthermore, a non-composite polyanhydride was investigated as shape memory material and evaluated for its adhesive properties.
Additive manufacturing (AM) has been utilized for multiple decades now and has proved innovative and transformative to the present world; however, not all desired materials can be manufactured using traditional methods of AM. Ambient reactive extrusion (ARE) is a rising alternative method of AM that was developed at the Oak Ridge National Lab. Using this method, the final material polymerizes during and after deposition onto the print bed. This eliminates the issue with traditional AM: mechanical anisotropy. Engineering of the polymer is necessary, especially when using thermoplastic polyurethanes (TPUs). Altering the hard block (HB) to soft block (SB) ratio of TPUs affects the chemorheological properties, but the effect of HB:SB ratio variation on ARE printability is unexplored. Herein, four TPUs of varying HB:SB ratios were synthesized utilizing 4,4’-methylenebis(cyclohexyl isocyanate), 1,4-butanediol, and polytetramethylene ether glycol. The chemorheological properties of the TPU were analyzed via rheology, in conjunction with real-time Fourier transform infrared spectroscopy (RT-FTIR) to observe polymerization. The thermal stability of each polymer was determined through thermal gravitational analysis (TGA), where the effect of altering the HB:SB ratio on degradation was observed. For each TPU, the degree of conversion (DOC) was determined at the time where the storage (G’) and loss modulus (G”) crossed; this provided a baseline of TPU chemorheological properties for ARE printing. It was determined that increasing the HB content decreased G'/G" crossover time, but the effect on DOC requires further evaluation. Future efforts will identify the balance between crossover time and DOC to determine the proper chemorheological properties that dictate successful ARE printing.
Photocurable nanocomposites for the use of synthetic cartilage replacements

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Photocurable nanocomposites have great potential within advanced manufacturing, multifunctional materials, and most specifically tissue engineering. The properties and characteristics of these nanocomposites can be tailored to mimic those of various tissues and/or cartilage, allowing the bio-inspired synthetic materials to replace them. This project investigates the effect of methacrylate-functionalized (MA-SiO₂) and vinyl-functionalized (V-SiO₂) silica nanoparticle loading content on the thermal, mechanical, physical, and morphological characteristics of PEG nanocomposites. It was discovered that both V-SiO₂ and MA-SiO₂ did not considerably impact the glass-transition temperature or hydrophilicity of the material. The gel fraction of composites containing V-SiO₂ decreases with the initial addition of 3.8 wt%, but then displays an increase with further addition (>7.4 wt%) until it reaches a plateau at 10.7 wt%. Whereas the MA-SiO₂ induced no significant changes in gel fraction with increased loading. An increase in mechanical properties was also observed with increasing concentration for both sets of series. However, due to the higher crosslink density, MA-SiO₂ reached its ultimate mechanical stress threshold at a lower concentration of 7.4 wt%, while V-SiO₂ maxed out at 10.7 wt%. Transmission electron microscopy coupled with small-angle X-ray scattering revealed that V-SiO₂ displayed a bimodal size distribution, while MA-SiO₂ displayed only one. Ultimately, the MA-SiO₂ containing composites offer superior mechanical and morphological characteristics in comparison to the V-SiO₂ loaded samples.
Molecular docking simulations to assess the estrogenic activity of lignin-derivable bisphenol A alternatives and their polymerization via additive manufacturing

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Lignin-derivable bisphenols could serve as potentially safer replacements to BPA, a suspected endocrine disruptor. This work focuses on fundamentally understanding the structure-activity relationships of lignin-derivable bisphenols to predict estrogenic activity (EA) and design safer alternatives to existing bisphenols. Binding affinities to estrogen receptor alpha (ERα) were calculated via molecular docking simulations, and a correlation between the median effective concentration (EC₅₀) values of commercially available (bis)phenols and their binding affinities was developed to predict the EC₅₀ values of lignin-derivable bisphenols. On the basis of the correlation curve, lignin-based bisphenols with binding affinities weaker than -6.0 kcal/mol are expected to exhibit no EA. Two methoxy groups on the aromatic rings substantially weaken the binding affinities to ERα (~-6.0 kcal/mol) by blocking the binding pockets. Similarly, the bulkier bridging groups such as ethyl or methoxy on lignin-bisphenols reduce the binding affinities because of steric effects. Several of the lignin-derivable bisphenols with binding affinities weaker than -6.0 kcal/mol were synthesized and incorporated into additive manufacturing resins for stereolithography 3D printing. The thermal (e.g., glass transition temperature, thermal decomposition behavior) and mechanical (e.g., tensile strength, modulus) properties of the printed materials were characterized to elucidate key structure-property relationships. Together, the structure-activity and structure-property relationships developed in this work could be leveraged to design materials that can match or exceed the performance of existing bisphenol-based materials without endocrine disruption potential.
Development of resveratrol/cyclodextrin inclusion complex nanofibrous webs for fast-dissolving dietary supplement

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The encapsulation of food/dietary supplements into electrospun cyclodextrin (CD) inclusion complex nanofibers paves the way for developing novel carrying and delivery substance along with orally fast-dissolving property. Here, the large surface area and highly porous structure of nanofibers ensure readily dissolving or disintegrating of nanofibrous webs upon contact with saliva. On the other hand, cyclodextrins (CDs) classified as cyclic oligosaccharides enhance the water solubility and stability of the poorly soluble bioactive agents by inclusion complexation with their doughnut-shaped cavity. In our study, CD inclusion complex nanofibers of resveratrol were fabricated from the aqueous systems by using the electrospinning technique. Resveratrol is a well-known bioactive agent with its high antioxidant potential and it is commonly used in the formulation of dietary supplements. However, the poor water solubility of resveratrol is a drawback that creates challenges during its practices. Here, the hydroxypropylated (HP) CD derivatives of HPβCD and HPγCD were used for both encapsulation of resveratrol and the electrospinning of free-standing nanofibrous webs. The amorphous distribution of resveratrol in the nanofibrous webs by inclusion complexation and the unique properties of nanofibers have ensured the fast-disintegration and fast-dissolution of nanofibrous webs in the saliva simulation and in an aqueous medium. The enhanced solubility of resveratrol in the case of resveratrol/CD nanofibrous webs has also ensured an improved antioxidant property for resveratrol. The polymeric resveratrol/pullulan nanofibrous webs have been also formed as a control sample in which resveratrol compounds are found in the crystal state. Both CD nanofibrous webs have shown faster dissolution, disintegration, and release profile and higher antioxidant potential compared to resveratrol/pullulan based samples.

Figure 1. (a) Schematic view of the resveratrol/cyclodextrin inclusion complex formation and electrospinning of resveratrol/cyclodextrin inclusion complex nanofibers. (b) The photographs of fast-dissolution and fast-disintegration performance.
Synthesis and characterization of glycodendrimersomes for bioimaging applications

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Bioimaging is a noninvasive process in which biological activity in the human body can be observed using fluorescent dyes and probes. Probes can be made safer by encapsulating them with biocompatible polymers. Glycodendrimersomes (GDs) are hollow spheres with a hydrophilic corona consisting of glycopolymers and a hydrophobic core consisting of dendrimers, which provide an optimal environment for fluorescent probes. Glycodendrons of appropriate composition prepared from reaction of a linear glycopolymer with a dendron will self-assemble to form GDs when exposed to water. In this work, thiol-ene click reactions of glycopolymers with PLA-based dendrons were explored. Glucose-functionalized glycomonomers were synthesized by reacting N-hydroxyethyl acrylamide (HEAm) and acetobromo-α-D-glucose (AcBrGlc) in a stereospecific glycosylation reaction. Linear glycopolymers were synthesized through reversible addition-fragmentation chain transfer (RAFT) polymerization and chain transfer agent (CTA) end groups were removed, resulting in a thiol group, post-polymerization. Dendrons with two focal points were synthesized using ring opening polymerization. The glycopolymer and dendrons were characterized using 600 MHz NMR for end group analysis. Gel permeation chromatography with multi-angle laser light scattering (GPC-MALLS) was utilized to compare changes in the molecular weights of the reagent polymers and the click reaction products.

Figure: pGlcEAM glycopolymer
Electrohydrodynamic encapsulation of curcumin-cyclodextrin inclusion complexes in chitosan/pectin nanofibrous webs

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There is a growing concern in both the pharmaceutical and food industries for developing encapsulation technologies from renewable sources with the intention of packaging, protection, carrying, and delivery of active compounds. Biopolymers have been concerned as an alternative for fossil fuel-based products owing to their non-toxic, sustainable, biodegradable, and biocompatible properties. Chitosan and pectin are attractive types of polysaccharides that can be industrially produced and have received great attention from the food, pharmaceutical, and cosmetic areas. The electrohydrodynamic atomization method of electrospinning is a rather feasible, flexible, and cost-effective tool to fabricate an encapsulation matrix for various active compounds accompanied by many functional and structural advantages. The major features that make electrospinning attractive are the large surface area, 3D continuous structure, and high porosity of ultimate electrospun nanofibers. Cyclodextrin (CD) is a type of cyclic oligosaccharides having truncated molecular structures and capable of forming inclusion complexes with a variety of compounds that leads to enhanced water solubility/stability and different release profiles for various active compounds. In our study, we have fabricated a curcumin-CD inclusion complex incorporated chitosan/pectin nanofibrous webs using the electrospinning technique. The incorporation of inclusion complex structure has made it possible to generate nanofibrous webs from chitosan and pectin polymers which are normally not possible without using an additional spinnable polymer into the electrospinning solutions. Due to inclusion complexation, the amorphous distribution of curcumin crystals has been provided within the nanofibrous webs which provides an enhanced release profile in an aqueous medium for the insoluble molecule of curcumin. Here, the ultimate nanofibrous webs of chitosan/pectin-curcumin-CD have been thermally crosslinked to obtain stable nanofibrous webs in the liquid environment. The structural characteristics and the stimuli-responsive release profiles of webs have been evaluated in the context of the study.

Figure 1. Schematic view of (a) the curcumin-cyclodextrin inclusion complex formation and (b) the electrospinning of chitosan/pectin/curcumin-cyclodextrin inclusion complex nanofibrous webs.
Reactivity ratios of RAFT polymerization of tert-butyl acrylate and a thiolactone-functionalized acrylamide

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The purpose of this work was to determine the reactivity ratios of tert-butyl acrylate (t-BA) and a thiolactone acrylamide (TlaAm) using RAFT polymerization. This was accomplished by initiating the solution polymerization using AIBN and monitoring the reaction by taking samples over time. These were used to determine the molar conversions of the monomers. Gel permeation chromatography (GPC) was used to determine the molecular weight distributions – these were narrow (dispersity <1.3), which indicates that the RAFT polymerization was successful. The molar conversions were then used along with the Kelen-Tudos method to calculate the reactivity ratios; these were $r_{tBA} = 0.96$ and $r_{TlaAM} = 0.84$. 

![Chemical reaction diagram](attachment:image.png)
Influencing polymer solubility with thermally-responsive diels-alder monomers

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Using Diels-Alder (DA) chemistry, two monomers were designed to contain a DA adduct and a polymerizable unit such that cyclo-reversion would yield either the maleimide or the furan unit attached to the polymer chain. These thermally responsive monomers were then copolymerized with N-isopropylacrylamide (NIPAM) via reversible addition-fragmentation chain-transfer (RAFT) polymerization to yield linear copolymer structures. Using UV-Vis Spectroscopy, it was determined that solution-state thermal properties were influenced by a number of variables such as comonomer feed ratio, polymer chain end functionality, polymer backbone length and composition. [figure1]
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Ring-opening polymerizations of cyclic esters by a genuine H-bond donor and Lewis base amine cocatalyst
Degradable poly(β-thioether ester ketal) thermosets: Incorporating hydrolyzable acyclic ketal crosslinks to achieve tunable network dissolution

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In recent years, interest in degradable polymers has risen greatly due to the concerns of plastic waste in the environment and has inspired our investigation into degradable thiol-ene materials. Fully degradable thiol-ene thermosets were synthesized using hydrolyzable monomers in combination with a multifunctional thiol and photoinitiator. A library of different acyclic ketal-based monomers was synthesized using a simple ketalization reaction between various carbonyl containing compounds and alkene functionalized alcohols. All samples were easily cured after only seconds of exposure to UV light. Mass loss vs. time was determined gravimetrically for all thermosets. For each composition, samples were removed from their solution at specific degradation times, lyophilized and weighed. The network degradation rates in acidic solutions were found to be highly tunable based on the stability of ketal building blocks used to construct each monomer.
Self-condensing ring-opening metathesis polymerization: A novel approach to hyperbranched polymers

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A novel approach to prepare hyperbranched polymers was achieved based on the synthesis of a ROMP-inimer, a molecular that acts as both an initiator and a monomer. Self-condensing vinyl polymerization and self-condensing ring-opening polymerization have long been used to prepare hyperbranched polymers using inimers. Ring-opening metathesis polymerization (ROMP) is widely used to make several different polymer architectures, but never hyperbranched polymers by a self-condensation approach. The key advance needed to enable the synthesis of a ROMP inimer is in attaching a ROMP monomer to the catalyst itself without initiating polymerization. In order to achieve this goal, a modified latent-initiating catalyst was synthesized followed by subsequent coupling of a ROMP monomer to the catalyst. This catalyst (a ROMP inimer) enabled hyperbranched polymer synthesis via self-condensing ROMP. This approach enables the synthesis of several hyperbranched polymers with controlled branching, desirable functionality, and potentially enhanced rheological performance. The methods developed in this study will open a new monomer class to making unique hyperbranched polymers.
Conjugated polymers display a wide variety of applications including production of Light Emitting Diodes (LEDs), Field Effect Transistors (FETs) and organic photovoltaics. Our work in the lab focuses on the development of Polymer Solar Cells (PSCs) using various electron donating and electron accepting units to individually tune the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) respectively and produce a small but controlled band gap. This is accomplished through the synthesis of several precursors and their subsequent polymerization using Acyclic Diene Metathesis (ADMET) and Suzuki Polycondensation (SPC).

Moderately strong electron donors, such as phenylene or thiophene compounds, and strong electron acceptors, such as benzothiadiazole and benzoxadiazole, are coupled into donor-acceptor (D-A) moieties in different combinations to tune the band gap. D-A type monomers and polymers are synthesized based on the polymerization technique used. ADMET requires the presence of terminal dienes whereas SPC necessitates the use of halogens and boronic esters. Consequently, the precursors and monomers are developed using different synthetic techniques to produce homologous structures in order to compare the effects of both polymerizations on the resulting molecular weight and photo-physical properties. This work will cover the synthesis and characterization of several D-A polymers using both polymerization techniques to design low band gap conjugated polymers for application in photovoltaics.
Synthesis and analysis of a photo-responsive, degradable polyester

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Stimuli-responsive polymers with degradation capabilities have garnered increased attention over the past few decades due to their ability to controllably break down into small molecules. This transformation produces a fundamental change in the chemical and physical properties of the system. As a result, dynamic polymers such as these have seen applications in a variety of fields, including drug delivery, sensing, lithography, and adhesives. In part, these materials have found such a wide range of applications due to the controllable nature of their degradation. Polymers have been designed to degrade selectively when exposed to specific stimuli such as chemical, biological, thermal, pH, mechanical, or light. While each of these stimuli plays a role, light-responsive materials are particularly desirable due to the extreme degree of control that they can exhibit. We have developed a polyester capable of responding to UV-light and undergoing controlled degradation into small, inert molecules. Upon exposure to light, our polymer undergoes a two-step chemical transformation. Initially, a selective photo-isomerization occurs, which allows for a subsequent transesterification reaction leading to backbone cleavage. This poster will focus on the development, synthesis, and photo-responsive nature of our polyester.
Polymersome assembly by polyglycerol based amphiphilic poly(disulfide)s and glutathione triggered intracellular drug delivery

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Redox responsive functional polymers are highly relevant as targeted drug carriers for cancer cells owing to their degradable nature in presence of glutathione (GSH) which is overexpressed in cancer cells. We have synthesized a linear polyglycerol (LPG) based amphiphilic copolymer architecture LPG-b-PDS-b-LPG (P1) where LPG serve as hydrophilic unit and the poly(disulfide) (PDS) serves as the hydrophobic segment. Fluorescent copolymer P2 was prepared by conjugating fluorescein isothiocyanate (FITC) to the hydroxyl groups of P1. Both P1 and P2 exhibited polymersome assembly in aqueous medium with very high loading efficiency of the anticancer drug doxorubicin (Dox). In presence of glutathione (GSH), the aggregates were disassembled and showed GSH concentration dependent release of the encapsulated guest molecules. MTT assay suggested excellent biocompatibility of the block copolymers in both HeLa and MDA-MB-231 cell line. Live cell fluorescence microscopy and flow cytometry studies revealed the time dependent cellular internalization of the Dox encapsulated polymersome. Cytotoxicity assay of the Dox-loaded polymersome exhibited time and dose-dependent sustained killing of HeLa (IC\textsubscript{50} \sim 4.0 \mu g/mL) as well as MDA-MB-231 (IC\textsubscript{50} \sim 8.7 \mu g/mL) cells. Glutathione reduced monoester (GSH-OEt) is well known to penetrate the cell membrane and enhance the intracellular GSH concentration. Cancer cells pretreated with GSH-OEt were killed at a much faster rate indicating direct impact of the intracellular GSH concentration on the drug release kinetics and consequently killing of the cancer cells. Highlight of these recent results will be presented in the poster.

Representation of glutathione triggered disassembly of polymersome and release of anticancer drug in cancer cells.

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Sustainable epoxy resins derived from syringic acid and mixtures of lignin monomers

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Composites composed of epoxy resins are high strength, yet lightweight alternatives to traditional metal components used in automotive, windmill, and electronics industries. Traditionally, epoxy resins are produced from petroleum-derived bisphenol A (BPA), which is epoxidized and cured with an amine or anhydride hardener. Unfortunately, BPA-based epoxy resins are derived from a non-sustainable resource and are not easily recycled, and BPA itself is a known endocrine disruptor. Lignin, a component of biomass with rigid aromatic structures, offers potential as a more sustainable and less toxic replacement for BPA in epoxy resins. When crude depolymerized lignin was used to produce epoxy resins, the resulting polymers exhibited low glass transition temperatures and moduli compared to commercial petroleum-based resins. In contrast, when individual lignin-derived model compounds were used as precursors for producing epoxy resins, the polymers had superior thermomechanical properties, comparable to commercial resins. Here we present for the first time the use of syringic acid, a product of catalytic depolymerization of lignin, as a precursor for producing biobased epoxy resins. Syringic acid was epoxidized and cured with an anhydride curing agent. We have examined the properties of epoxy resins derived from syringic acid alone, as well as from mixtures of lignin-derived model compounds. These studies have helped us understand how individual lignin monomers or their combinations impact epoxy resin properties and produce targeted epoxy resins with superior properties to petroleum derived resins.
Developing sialic acid-containing antiviral materials

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Sialic acid (N-acetylneuraminic acid) is used by many viruses (influenza, mumps, corona, noro, and rotavirus) to initiate viral replication. This binding between the virus and sialic acid on cell surfaces is mediated by multiple simultaneous interactions (polyvalency). Sialic acid-containing polymers can mimic this natural polyvalent attachment as each repeat unit is capable of binding to the viral surface. Previously synthesized polymeric antivirals support this phenomenon and have significantly enhanced the inhibition of viral infection in comparison to monomeric analogues. Because these tailored polymers act as a decoy for viruses to bind to instead of an otherwise healthy cell, replication, infection, and resultant symptoms are greatly reduced.

Our previous work with sialic acid containing polymers has been geared toward enhanced inhibition of influenza by creating a library of polymers with systematically varied molecular weight, topology, sialic acid content, sialic acid linkage, side chain length, and comonomer identity. These polymers will be tested via a hemagglutination inhibition (HI) assay and analyzed for enhanced inhibition of influenza. These fundamental structure-property relationship studies will serve as a basis for designing and synthesizing future aerosolized anti-influenza materials. Additionally, utilizing that influenza and corona viruses both use sialic acid to initiate replication, we have synthesized sialic acid containing nanoparticles for inhibition of SARS-CoV-2.
Role of length in the ultrasonication of asymmetric polymer topologies

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The utilization of ultrasound to assess mechanically induced chain scission remains an emerging field of study in polymer science, as many of the conditions leading to bond breakage have yet to be elucidated. While work on linear polymers has established a link between an increased rate of scission to longer chain lengths, minimal work has been conducted on more complex polymer architectures. As a result, the contributions of structural factors unique to nonlinear polymers on mechanochemical response (i.e., contour length, side chain length and composition) have yet to be definitively established. Herein, this work systematically investigates the role of topologically asymmetric linear-bottlebrush diblock copolymers to elucidate the role of increasing bottlebrush composition on mechanochemical chain scission kinetics. Specifically, a small library of poly(norbornene polystyrene)-b-poly(norbornene dimethyl ester) (PNBPS-b-PNDME) linear-bottlebrush block copolymers were generated with variable block composition (10, 30 and 50% bottlebrush) and overall backbone length (DPn = 75 or 150). Norbornene-functionalized polystyrene macromonomers (3 kDa) were prepared via reversible addition-fragmentation chain-transfer (RAFT) polymerization. Sequential ring-opening metathesis polymerization (ROMP) of NDME and NBPS a generated the linear-bottlebrush diblock copolymer. Through the aid of a coumarin tag located on the chain end, the location of the scission events along the backbone of the polymer were discerned using size-exclusion chromatography. Importantly, this work demonstrates the influence of complex topology on mechanochemical response that has not yet been extensively explored.
Synthesis of polysulfides using polar monomers to form sulfur-containing hydrogels

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Each year petroleum refining produces millions of tons of elemental sulfur. With few applications, the stock of elemental sulfur continues to grow with each year. This work focuses on the synthesis of polysulfides using polar monomers. Due to their hydrophilic nature, polar monomers are unlikely to be miscible with sulfur. Garlic essential oil, which contains allyl sulfides, allows thiol radical formation at lower temperatures and presents fewer miscibility issues in comparison to elemental sulfur. By inducing radical formation, interaction and potential polymerization is able to take place between the sulfur-containing material and the polar monomer. The polysulfides are synthesized using elemental sulfur or garlic essential oil as the sulfur-containing material and methacrylamide or polyethylene glycol dimethacrylate as the polar monomer. NMR spectroscopy, IR, DSC and TLC are used to characterize each of the polysulfides. The goal of this project is to form a reproducible polymer disk that will allow the examination of the fundamental properties, specifically the swelling properties of these polysulfides. As this project progresses, the goal will be to synthesize a polysulfide hydrogel capable of swelling with water and other solvents. These hydrogels could have potential biomedical applications, for example wound care and therapeutic treatments.
Donor/acceptor interactions of new fluorene based small molecules with P3HT
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Small molecules acceptors (SMAs) using fluorene cores have been used in organic photovoltaics as an attractive alternative to traditional fullerene acceptors. Herein we describe the facile synthesis of four fluorene based cores with terminal phenyl, thienyl and furyl malononitrile groups. The products were obtained from a two-step reaction of 9,9-diocetylfluorene-2,7-diboronic acid with meta or para-bromobenzaldehyde, 5-bromo-2-thiophenecarboxaldehyde and 5-bromo-2-furaldehyde under Suzuki conditions. Subsequent reaction with malononitrile yielded 9,9-diocetylfluorene -2,7 (1-phenyl-3(or 4)-methylen malononitrile) (m-FPM or p-FPM), 9,9-diocetylfluorene -2,7 (2-thienyl-5-methylene malononitrile) (FTM) and 9,9-diocetylfluorene -2,7 (2-furyl-5-methylene malononitrile) (FFM) in good yields respectively. Optical and electronic characterization were performed using, UV-visible and fluorescence spectroscopy, cyclic voltammetry, and DFT calculations. Donor/acceptor interactions between poly-3-hexylthiophene (P3HT) and the SMAs were investigated using fluorescence quenching experiments. P3HT emission reduction was observed in the presence of all SMA with m-FPM and p-FPM having the maximum percent emission reductions of 99.2% and 86.2 % respectively, indicating favorable donor/acceptor interactions. DFT calculations indicate that the planarity of the SMAs have a major impact on the donor/acceptor interactions in solution. Films of P3HT and each SMA were cast from chlorobenzene in 1:1 and 1:4 ratios respectively. AFM indicated the formation of continuous films, however differences in phase separation, network and crystallite formation can be observed at different SMA loadings. The combined results indicate that all of the molecules have the potential to be effective SMAs in organic based photovoltaics.
Fluorescent bio-based films from chitosan and fluorene based small molecules

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Bio-based fluorescent films consisting of a blend of chitosan with fluorene based small molecules were prepared, and their structural, optical, and morphological properties were studied. 9,9-Dioctylfluorene -2,7 (2-thiophene) (FT) and 9,9-dioctylfluorene -2,7 (2-thienyl-5-methylene malononitrile) (FTM) were chosen for their solubility and their large extinction coefficients to produce the fluorescent bio-based films. Films were cast from solutions prepared from 0.5 wt% or 1.0 wt% chitosan dissolved in 1% acetic acid, FT or FTM (0.0078 wt%-0.25 wt%) dissolved in DMSO, and with or without glycerol. Solution cast films were dried at 60 oC. The fabricated bio-based films were characterized using spectroscopic techniques (FT-IR, UV–Vis, and fluorescence), thermogravimetry (DSC and TGA), and atomic force microscopy (AFM). Interestingly, structural interactions between the malononitrile group of FTM and chitosan were observed in the FT-IR even at low wt% in the absence of glycerol, indicating that FTM may be acting as a plasticizer in the absence of glycerol. No interaction of this nature was observed for FT as it does not contain functionality capable of hydrogen-bonding interactions. Optical characterization displayed impressive absorbance and fluorescence intensity in the films even at low wt% FT or FTM in the presence and absence of glycerol. DSC and TGA also showed difference between the films which can mainly be attributed to the presence and absence of glycerol indicating that optical properties of chitosan can be easily modified with little loss of the improvements glycerol provides to the physical/mechanical properties of the films. AFM indicated that surface roughness increased in the absence of glycerol and that an increase in phase separation was observed at higher wt% of both FT and FTM. These newly obtained fluorescent bio-based films are an exciting area of research as we continue to develop new materials that have a wide variety of applications, are inexpensive in nature and have the potential for biodegradable properties.
Trials of quantifying polymer transitions

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Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. Compounds containing Diels-Alder (DA) linkages were prepared and incorporated into polymeric structures using RAFT polymerization techniques, and resulted in an array of properties. This work will articulate the trials and techniques employed to measure different polymer transitions, including successes, failures and lessons learned. [figure1]
Selective precipitation of toxic metal ions by charged polysulfide p(S-DADM)

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Elemental sulfur is produced as a byproduct of the oil refining industry. Although this sulfur has its applications, its rate of consumption falls far short of its rate of production. This excess has prompted an exploration into novel sulfur-based materials, notably, polymers formed by inverse vulcanization. Like sulfur, these polymers tend to be completely insoluble in water, placing severe limitations on its utility. This work explores the properties of the first water-soluble polymer produced by inverse vulcanization. Polymer structure was confirmed by H NMR and further characterized by DSC and GPC. Sulfur selectively adsorbs some toxic heavy metal ions according to the hard-soft acid-base theory. The charged monomer, diallyldimethylammonium chloride (DADM) grants the polymer solubility, thereby maximizing its interaction with aqueous metal ions. The reagents are polymerized for 6 hours in an oil bath at 160 °C, dissolved, then filtered. Poly(S-DADM) with 30, 50, and 70% by weight sulfur were created and tested for solubility. The p(S50%-DADM50%) was also tested with a variety of metal salts in aqueous solution at high concentrations to check for precipitation. Silver, lead, and cadmium were given particular focus, using sodium, calcium, and iron ions as controls to qualitatively determine selectivity. The salt solutions which showed precipitation were also measured quantitatively by atomic absorption spectroscopy to determine the metal binding capacity of the polymer. The selectivity, economy, and simplicity of p(S-DADM) has an advantage over current non-specific filtration methods by binding selectively to certain heavy metal ion contaminants.
Superhydrophobic surface nanomaterials via π-Allylnickel-catalyzed living coordination block copolymerization of allene derivatives under polymerization-induced self-assembly conditions

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The allylnickel-catalyzed living coordination polymerization of allene derivatives gives well-defined polymers containing various functional groups with controlled sequence and molecular weight. This living polymerization method can also be carried out under the dispersion polymerization conditions in polar protic solvents such as alcohols and water to produce well-defined functional polymer microspheres. Based on these remarkable features, we describe herein the block copolymerization of a perfluoroalkyl-substituted allene and a monofunctional hydrophobic allene or a bifunctional hydrophobic allene in fluororous solvents to produce well-defined polymeric nanostructures through the polymerization-induced self-assembly process (Scheme 1).

For example, the living solution polymerization of 2-(perfluorooctyl)ethoxymethylallene (10 equiv.) was carried out by [(π-allyl)NiOCOCF₃]₂ in a fluorous solvent, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane, at ambient temperature for 24 h. To the resulting living polymer solution, phenoxyallene (50 equiv.) was subsequently added to conduct the block copolymerization at ambient temperature for additional 12 h. By the progress of the post-polymerization, the polymerization system gradually turned from the transparent solution to suspension to produce nanostructured polymeric materials. The static contact angle of the water (θ_water) on the thin layer of the polymer micelles, which was prepared by the drop-casting of the copolymer suspension onto a glass substrate, reached 153 degrees, which supported the superhydrophobic nature of the layered polymer micelles (Figure 1).

![Scheme 1](image)

**Scheme 1**

**Figure 1.** a) TEM image of nanostructure of resulting diblock copolymer micelle; b) Photoimage of water droplet on the glass surface coated with copolymer micelles.
Engineered Petasis three-component reaction for the synthesis of poly (α-amino acid)s

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Multi-component reactions (MCRs) have been gathering intensive attentions from polymer community due to their synthetic modularity and click-type reactivity. In this study, we selected the Pteasis three-component reaction (Petasis-3CR), which is a powerful tool to generate the α-amino acids by reacting the aromatic boronic acids, amines, and glyoxylic acids. Despite the synthetic benefits arising from the Petasis-3CR, chemical nature of boronic acids remains problematic for polymer synthesis. To be precise, boronic acids are known to be in equilibrium with their corresponding cyclic trimers of boroxines, suppressing their employment in polymer structures due to the lack of chemical stoichiometry and a potential risk to behave as a cross-linker. Therefore, we have decided to tackle the improvement of the Petasis-3CR aiming the integration with polymer chemistry. In this presentation, the original Petasis-3CR was engineered so that the protocol would be compatible with polymer synthesis, offering an access to poly (α-amino acids) in one-pot manner (Scheme).

Scheme. A modified Petasis three-component reaction for polymer synthesis.
Relay polymerization by concurrent atom transfer radical polymerization and nitroxide radical coupling

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Atom transfer radical polymerization (ATRP) in conjunction with nitroxide radical coupling (NRC) is difficult to achieve due to nitroxide radical’s propensity to terminate radical polymerization. However, this difficulty could be overcome by introducing a functional reagent combining a nitroxide radical and an ATRP active halogen, i.e., a halogen group which can initiate one polymer chain by ATRP. For the reaction to proceed favorably, slow additions of the functional reagent to the reaction system were necessary. As a result, a polymerization with conjugated radical trapping and re-initiation took place resembling a relay race and thus was named relay polymerization. The molecular weight of these polymers increased with time, meanwhile, the molecular weight distribution stayed relatively narrow, $M_w/M_n \approx 1.20$. The relay polymerization introduced dynamic chain linkages displaced among the long-chain polymer which can be used to create alternating block-copolymers by nitroxide mediated polymerization (NMP). This relay polymerization process opens a vast array of macromolecular structures that suit desired architectures and functionalities
Blending electronic and ionic conductive polymers for use in p-doped organic electrochemical transistors

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Electronic and ionic conductive polymers blends were studied for their potential improvement of organic electrochemical transistor device performance. The polymer blend studied was a mixture of charge conductive poly(3-hexyl-thiophene) (P3HT) and ion conductive ROMP based polymer with oligomeric ethylene oxide side chains. Potassium salts with a variety of anions (chloride, hexafluorophosphate, and bis-trifluoromethanesulfonimide (TFSI)) were examined for doping the P3HT. A variety of weight fractions were analyzed using spectroelectrochemistry, atomic force microscopy, X-ray diffraction, and moving front data. AFM topography data indicates an increase in phase separation dimensions with decreased P3HT content. The time constant for polaron formation was reduced for all blends and anions though the effect was most pronounced for chloride compared to pure P3HT. The lamellar spacing is modestly increased for all blends doped with all anions compared to undoped pure P3HT with the TFSI anion expanding the most. This suggests that the ion conductive component primarily facilities ion transport without noticeably changing the structure of the doped P3HT. It is anticipated that transconductance will benefit from blending with this ion conductive polymer.
Low bandgap polymers via direct arylation polymerization: Putting the pressure on past cross-coupling methods

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In recent years, direct arylation polymerization (DArP) has become a leading cross-coupling method in conjugated polymer synthesis. Previously, most cross-coupling reactions were carried out through methods such as Stille, Suzuki, Kumada, Negishi, etc. While these older methods have their utility, stoichiometric amounts of main group elements and/or other reagents are typically required. With this issue comes the problem of increased toxicity and less environmentally friendly syntheses. DArP mitigates this issue by direct activation of the C-H, thus removing the need for such main group intermediates.

Here, the necessary requirements are thus only C-H and a C-X (X= halogen) bonds that can couple and allow for the formation of a new C-C bond. These can exist on a single monomer to create a homopolymer or individually on two different monomers to create an alternating copolymer. A key experimental parameter that has been found to enhance the efficiency of these reactions is increased pressure during the polymerization, achieved by heating past the critical point of a given solvent system in a sealed vial. Under these conditions larger molecular weight polymers can be formed, resulting in enhanced delocalization and minimum bandgap energies. While the bulk of DArP studies have focused on reduced bandgap (E_g = 1.5-2.0 eV) materials, this presentation will present recent efforts to generate low bandgap (E_g < 1.5 eV) materials, with a focus on the types of polymeric systems that can be made via DArP, the variable experiment parameters, and results of successful implementation.

![Chemical reaction diagram]
Comparative study of hydrogen bond organization between hyperbranched polymers and dendrimers based on bis-MPA.

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The physical properties of hyperbranched polymers (HBPs) based on 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), have been widely studied, and are largely influenced by the presence of hydrogen bonds (H-bonds). However, similar studies and characterization have not yet been extended to bis-MPA based dendrimers which require considerable synthetic effort. Herein, hydrogen bond organization and interrelated structural order formation of a bis-MPA based dendrimers of the first through third generation (D1-3) were investigated as compared to their commercially available counterpart Boltorn H20, which is widely used in the coatings industry. Initial dielectric investigations show that both Boltorn H20 and D2 have high dielectric constants as compared to their linear analogs due to these H-bonded clusters. Molecular dynamics (MD) simulations were used to predict the WAXS spectra and reveal 'chain-like' clusters of H-bonds. The length distribution of these clusters over the three generations were compared and contributions of different proton acceptors were analyzed. Computational results agree well with experimental data previously obtained and show that D2 has the highest propensity of forming long H-bonded clusters. This indicates that not only are dendrimers more capable of forming long cluster associations but also that the second-generation dendrimer is a “sweet spot” for terminal hydroxyls to cluster length associations.

Left is an example of a simulated D2 unit cell
Right: resulting XRD data from simulated unit cells compared with experimental data
Microphase separation of oppositely charged polyelectrolytes brushes triggered by ion pairing

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This work applies a molecular theory to study the formation of lateral self-assembled aggregates in mixed brushes composed of polyanion and polycation chains. To overcome the well-known limitations of mean-field electrostatics to capture polyelectrolyte complexation, the formation of ion pairs between anionic and cationic groups in the polyelectrolytes is explicitly modeled in our theory as an association reaction. Polyanions and polycations mixed in solution are known to form interpolyelectrolyte complexes stabilized by ion pairs between the charged groups in the polyelectrolyte chains. The formation of these ion pairs results in the expulsion of small counterions that are condensed on the polyelectrolytes. This entropic process is now recognized to be a main driving force behind polyelectrolyte complexation. A mixture of polycations and polyanions end-grafted to a surface, is also expected to form interpolymer complexes on the surface, but it cannot macroscopically phase-separate because of the constraints introduced by grafting. Polyelectrolyte complexation is a key phenomenon for applications in different areas like nano/microencapsulation. We theoretically study whether the complexion of oppositely charged polyions in a mixed polyelectrolyte brush can lead to the formation of lateral aggregates via a microphase-separation process triggered by polyelectrolyte complexation. The effects of solution pH and ionic strength, surface coverage, and chain length on the morphology of the mixed brush are systematically explored. It is shown that increasing salt concentration leads to the rupture of polyelectrolyte complexes and the stabilization of the homogeneous, non-aggregated brush, providing that the formation of ion pairs between the polyelectrolytes and the salt ions in solution is explicitly accounted for by the theory. The inclusion of ion-pairing association reactions between oppositely charged polyelectrolytes within a mean-field description of electrostatics emerges from this work as a useful and simple theoretical approach to capture the formation of polyelectrolyte complexes and their responsiveness to solution ionic strength and pH.
Dynamic polyamides with tailored curing times for real time 3D printing application

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This work intends to develop a rapidly curable polymer network system for application as 3D printing materials. Polyamides are known for their superior mechanical properties, acid and base resistance and fire resistance properties. Therefore, products derived out of these class of polymers are suitable for a range of commodity as well as specialized applications. In this work, we are targeting to develop a tailor made system that can be cured with a pre-determined incubation time and recycled back to the monomers on demand. For 3D printing applications, at least three order increase in viscosity in fairly short period is desired before and after injection. This will allow to retain the shape of the product and help us in developing miniature designs. We have achieved a similar objective with our system so far as reflected from the rheological studies. Recently, we had reported a dynamic polyamide network system that readily cured under room temperature conditions with 5 h. The activated tetra ester (TPMD) promptly reacted with the oligoamine compounds under catalyst free conditions and tough networks with tensile strength above 20 MPa and modulus in the GPa were achieved suggesting the networks may be utilized for various load bearing applications. To utilize these for 3D applications, the curing time needed further optimization. For effective 3D printing, the curing is desired to be achieved in less than 5 mins. To further improve the rate of polymerization, we used a phase transfer catalyst, i.e. Tetrabutylammonium bromide, cyclodextrin or crown-ether as the catalyst. The fast curing time allows the material to be used for the development of degradable 3D printed products for different application. Few demonstrations are presented by creating different shapes as a proof of concept.
Arginine units as instigators of an UCST behavior in cationic polymers in pure water

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Some polymers can respond to changes in the environmental conditions in which they find themselves. These changes, also called "stimuli", include temperature, pH, ion concentration, and light, which are of increasing interest in the biomedical field (e.g. drug and gene delivery). Among the various stimuli studied, temperature allows an abrupt and discontinuous change in solubility properties of thermo-responsive polymers, which opens the way for the delivery of drugs. These are divided into two categories: 1) polymers with a Lower Critical Solution Temperature (LCST) and 2) polymers with an Upper Critical Solution Temperature (UCST). In the first case, the polymer is soluble below the phase transition temperature and insoluble above this temperature, while polymers with an UCST behavior exhibit the opposite phenomenon. Polymers belonging to the UCST category are much less common in the literature than those belonging to the LCST category. The UCST phase transition usually results from two types of interaction: hydrogen bond and Coulombic (or electrostatic) interactions. The latter property is essentially observed for zwitterionic polymers and polyelectrolytes in presence of salts. This presentation will describe the synthesis and thermal behavior of cationic comb polymers for which a thermo-responsivity (i.e. UCST behavior) in pure water was not expected.
Enhanced crystallinity and porosity of hydrazone linked covalent organic frameworks through supercritical carbon dioxide activation

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Covalent organic frameworks (COFs) are a class of crystalline, porous polymers which are synthesized from light weight elements under dynamic control. These materials have been employed for different applications including gas storage, gas separation, sensing, and energy storage. Among different COF activation methods supercritical carbon dioxide (scCO$_2$) activation provides milder conditions to process COFs without compromising their crystallinity and porosity. To this end, two hydrazone COFs (TFPB-DHz, TFPT-DHz) were synthesized with a hydrazide linker (DHz) without substituents. Synthesized COFs were characterized with FT-IR spectroscopy, powder X-ray diffraction (PXRD), and computer modeling. Surface area of COFs was determined using N$_2$ adsorption–desorption experiments. scCO$_2$ activated COFs were crystalline and porous. This study shows the significance of efficient, fast, mild scCO$_2$ activation towards porosity and crystallinity of COFs.
Exploring transient covalent crosslinking of dynamic polymer materials using a carbodiimide as a chemical fuel

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Acrylamide (Am) and acrylic acid (AA) was polymerized by RAFT to create dynamic copolymer networks with pendant carboxylic acids which were transiently crosslinked to form anhydrides via dehydration by carbodiimide. The gels formed as a result of covalent crosslinking hydrolyzed back to the liquid polymer and can be refueled multiple times to reproduce the anhydride crosslinked gel. Rheological experiments were performed on the transient gels and utilized to study the corresponding effects of temperature, carbodiimide concentration, chain length and varied ratio of Am/AA on the storage ($G'$) and loss ($G''$) moduli of the polymer materials and the time taken to decrosslink. Under same conditions, regardless of the temperature used, a $G'$ of $10^4$ Pa is observed. The decrosslinking time was also observed to decrease as room temperature is approached in experiments carried out at 10°C, 16°C and 22°C respectively. Varied concentrations of carbodiimide at constant temperature reveals a progressive decrease in $G'$ and the time taken for polymer materials to decrosslink.
New sunlight-degradable and even edible bio-plastics

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Recent advances in Green Materials Science should be of interest to Sustainability Science, in the form of providing cost-effective bio-sourced alternatives to artificial plastics. Indeed, traditional disposable plastics have now become a global environmental problem due to their overuse, non-degradability, and toxicity. The carbon-carbon backbones of polymers, like polyethylene, are just too strong for nature to easily disassemble these materials. Yet covalent bonds are not necessary for strong materials, as many biological examples make clear (seashell, tendon, cellulose, silk…) that are held together by reversible ‘weak’ or ‘soft’ interactions, such as hydrogen bonds. Thus, there has been an immense demand for materials made from bio-sourced and bio-degradable polymers.

The preparation of azo-cellulose layer-by-layer thin films is demonstrated for the first time. This type of layer-by-layer process is driven by hydrogen-bonding interactions between sodium cellulose sulfate (NaCS) and the bisazochromophore Bismarck Brown Y(BBY). UV-VIS spectroscopy, FTIR spectroscopy and Raman spectroscopy measurements confirm a high level of hydrogen bonding between the cellulose polymer and the azobenzene dye in the multilayer films. UV-VIS absorption spectral analysis of the multilayer films following exposure to visible light in an aqueous environment, confirms the successful disassembly of films due to the reversible trans-cis isomerization of the azobenzene moiety via photo-irradiation and thermal back relaxation.

Schematic of the disassembly of layer-by-layer azo-cellulose film
Predicting the biodegradation of monomers in soil and wastewater environments: Experiment and QSAR modeling

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Polymeric waste is accumulating in varying environments globally. This is a result of two main contributing factors - high mass production of polymers and the low degradability of polymers. There are multiple mechanisms for polymers to degrade including a biological way, with the use of microorganisms in the process of biodegradation. Polymer degradability is heavily influenced by the structure of the monomer unit, the building blocks of the polymer. This research focuses on biodegradation study, by investigating the monomer units’ molecular structure and its relationship with biodegradability. With the use of combined experimental and computational study, applying machine learning-based quantitative structure-activity relationship (QSAR) methodology, a predictive model has been developed for biodegradation of monomers assessment. Concurrently, further experimental data collection is underway for the development of a predictive model for polymers undergoing biodegradation.
Numerical simulation of extrusion-based additive manufacturing in order to predict flow instabilities of a single deposited polymer melt

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Fused filament fabrication (FFF) is one of the most widely used rapid prototyping or additive manufacturing (AM) technologies based on the extrusion deposition process. In this process, a semi-molten thermoplastic is extruded and deposited along a prescribed road onto a build platform. Later, the extruded thermoplastic bonds to neighboring materials as it solidifies to create a 3D-printed object. The FFF process is a complex, multi-step, and multi-physics phenomena.

This research aims to understand the flow instabilities that may arise during the deposition of a single road in a FFF process and to predict the shape of the printed strand, particularly where local acceleration around sharp turns may lead to high-stress concentration at the nozzle outlet. A 3-dimensional model based on the finite element method (FEM) is carried out using COMSOL Multiphysics. In this numerical model, the molten thermoplastic is considered an incompressible non-Newtonian fluid as a function of temperature and shear rate. Different transfer phenomena (energy and momentum equations) are incorporated with the generalized Maxwell equation to describe the viscoelastic behavior of the polymer melt. Our current model tracks the moving interfaces by using both level set and phase field methods. Simulations of this two-phase system suggest a relationship between velocity profile, residual stress evolution, and axial temperature profile leading to new insights into the melt flow behavior and geometry of the printed road as a function of printing parameters.

- The level set method in COMSOL: The color bar shows the function $\Phi$ describes the local average volume fraction of the dispersed phase (polymer melt) in the air
- Geometry and mesh created in COMSOL for our system
Developing black women into polymer scientists

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I always tell my students, “you are my greatest assets”. I am training them to take their Spelman Bachelors of Science education and endeavor to solve the worlds’ problems from their unique perspective as young Black women. Spelman College the top-ranked historically Black college for women, dedicated to developing its students into academically excellent change-agents for the future. As a polymer chemist and underrepresented minority, I know they need both the foundational scientific skills and the inner confidence in themselves to excel in their next career endeavor. I am also vested in enticing them to consider incorporating polymer science into their future academic research plans. I do so by managing a research group themed around exploring the impact that substrate deformability has on the interfacial chemistry of soft materials. This presentation will highlight student contributions made while working on the research topics described above. I will also explain how their participation in academic research has supported their future career goals.
Multi-responsive polymer micelles bearing metal-catechol crosslinks: A mussel-mimetic approach

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Amphiphilic diblock copolymers (BCP) containing dopamine were synthesized via the RAFT polymerization method which undergo temperature-mediated micellization in aqueous media. The presence of catechol moiety in dopamine was exploited to form pH-responsive crosslinks with ferric ions (Fe³⁺) at different pH values. Herein, a comprehensive account of the effect of pH as well as temperature on the size and solution behavior of these BCP micelles is presented.
NIR analyzer for emulsion polymerization monitoring

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Emulsion polymerization is the basis of multiple industrial products from specialized additives to make polymer processable to paints & coatings decorating and protecting interior and exterior surfaces. The technology behind emulsion polymerization is multi-component and multi-stage with initiators, surfactants, monomers and medium contributing to the resulting polymer structure and properties. Monitoring is generally performed via sampling and off-line analyses. Dynamic monitoring is desirable for immediate feedback, adjustment opportunities, as well as enhanced process safety. Among applicable methodologies are infrared and Raman based on vibrational spectroscopy. This paper presents results obtained with a ThermoFisher Scientific FT-NIR analyzer capable of supporting four probes simultaneously. Monomer consumption and polymer latex formation are monitored in multi-probe setup configurations. Examples are provided for one and two stage monomer addition.

![FT-NIR spectra as a function of time during emulsion polymerization](image)

FT-NIR spectra as a function of time during emulsion polymerization
Free-radical frontal polymerization initiated by charge transfer complexes

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Thermal frontal polymerization is a process in which a localized reaction zone propagates from the coupling of thermal diffusion and the Arrhenius dependence of reaction rate of an exothermic polymerization. This allows FP to make cure-on-demand materials such as coatings, adhesives, and composites. Like traditional free-radical polymerization, FP uses classic thermal initiators such as peroxides. The storage of these initiators is hazardous. Using Charge Transfer Complexes (CTCs) as thermal initiators is one way to overcome the issue of hazardous storage. A CTC is formed through the interaction of an electron acceptor with an electron donor. CTCs are easy to prepare and do not have the safety issue of storage. Despite this advantage, only a few studies have been done to explore their usage as thermal initiators for free radical polymerization. We report the first study done using charge transfer complexes as thermal initiators in frontal polymerization. An iodonium salt, 4-Octyloxydiphenyliodonium hexafluoroantimonate, was used as the electron acceptor while various amines were used as the electron donor. The front velocity was studied as a function of the stoichiometric ratio and total concentration.
Sustainable multi-functional nanocomposite material based on cellulose, its oligomers, and poly(styrene)

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Cellulose is increasingly utilized as reinforcing agent in nano-composites, due to its natural abundance, low cost and useful properties (low density, high specific surface area and elastic modulus, low coefficient of thermal expansion). Addition of cellulose nanocrystals or nanofibers to bulk polymers has been proven to enhance the mechanical and thermal properties of the resulting nanocomposites. However, the direct incorporation into thermoplastic matrixes has some negative effects on the mechanical properties due to the formation of strong agglomerates during the dispersion process. Chemical modification of the fiber surface alleviates the problem to a certain extent, but the limitation is not completely eliminated.

This presentation will describe a new approach aimed at the formation of poly(styrene) nanocomposites with homogeneous dispersion of cellulose nanocrystals and nanofibrils. The strategy is based on the radical bulk polymerization of styrene in the presence of cellulose oligomers modified with different amounts of styrene moieties. Under classical conditions (AIBN, 65°C) semi-interpenetrating networks are formed in high yields. The gels are hybrid materials, where the synthetic polymer chains are either crosslinked on the uniformly dispersed naturally-derived component or entangled through the network, see figure. The influence of the cellulose degree of substitution and polymerization conditions on the properties of the resulting poly(styrene)/cellulose nanocomposites will be discussed in detail.

Synthesized nanocomposite material, where poly(styrene) chains are crosslinked by modified cellulosic crosslink. There are present not crosslinked linear poly(styrene) chains in the material
Covalently cross-linked tetrafunctionalized m-THPC chitosan hydrogels as delivery platforms

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Photodynamic therapy (PDT) is an anti-cancer treatment method, which uses the combined effect of a photosensitizing drug, light, and oxygen to cause selective damage to target tissue. The second generation photosensitizer (PS) 5,10,15,20-tetrakis(m-hydroxyphenyl)chlorin (m-THPC) is a clinically tested and commercially available drug. In order to develop advanced treatment modalities there is a need for improved drug delivery platforms. Hydrogels, investigated as effective drug delivery systems, can prevent PS aggregation and have ability to swell in aqueous media. Chitosan (CS), a natural polysaccharide, is a suitable biodegradable material for hydrogel formulation and has been used in pharmaceutical applications on account of its lack of toxicity and good biocompatibility.

Herein, m-THPC was used as a starting point to obtain a library of compounds aimed at overcoming the PS’s limitations while maintaining its photophysical and clinical properties. Substitution, esterification and Sonogashira coupling reactions were employed to modify the m-THPC skeleton providing aldehyde and carboxylic acid moieties which served as a suitable synthetic handle for covalent cross-linking in the formation of CS hydrogels. Injectable, self-healing properties of hydrogels were confirmed by the rheological analysis. The tetrafunctionalized m-THPC derivatives, maintaining efficient singlet oxygen generation upon incorporation into hydrogels, are under ongoing in vitro evaluation against melanoma cancer cells (B16F10). Prepared hydrogel formulations are expected to allow for a local, injectable administration towards melanoma tumors, while preventing from systemic side effects related to the m-THPC treatment.
Synthesis and characterization of poly[N,N-(phenylamino) disulfide] derivatives: A sulfur rich set of polymers with adjustable color properties

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Polymerization of phenylamines with a disulfide transfer reagent to yield poly[N,N-(phenylamino) disulfides] were investigated due to their unique bonding structures which may lead to new reactivities and conjugation along the backbone. These polymers were synthesized from nine different anilines and sulfur monochloride with triethylamine in a step-growth polymerization. The polymers were characterized by NMR, SEC-MALS and UV-Vis spectroscopy. Spectroscopic methods were employed to confirm reaction through the amine and general structure of the polymers. These polymers possess a polymeric backbone solely consisting of nitrogen and sulfur [-N(R)SS-] which was conjugated and yielded polymers of moderate molecular weight. Most notably, these polymers were an array of colors ranging from pale yellow to a deep purple depending on the substitution of the aromatic ring. The more electron poor systems produced lighter yellow solutions, while the electron rich systems gave orange, red, and even purple solutions. These colors suggest extended conjugation through the polymer since the original monomers were white and clear in solution. This supports the possibility to tune the electron density in the conjugated system which may be useful for conductivity in developing a semiconducting organic polymer or tuning chemical sensitivity to react with the backbone. Although further exploration needs to be done, preliminary studies on the ladder application showed that these polymers reacted with thiols shown by their colors rapidly disappearing in the presence of excess 2-mercapto ethanol. This suggests potential chemosensitivity to nucleophilic groups which could allow these polymers to be used as chromophoric detectors.
Addition of highly reactive vinyl ethers in radical-induced cationic frontal polymerization

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Frontal polymerization (FP) is a phenomenon in polymer science where an input of energy initiates a reaction zone that propagates through a material, converting monomer to polymer as it travels. FP has advantages such as the ability to synthesize materials in a cure-on-demand, one-pot system. Thermal FP is initiated by thermal energy and relies on the kinetics of an exothermic reaction coupled with heat diffusion. Formulations containing vinyl ethers and an epoxy were successfully frontally polymerized thermally through a radical-induced cationic frontal polymerization mechanism, using an iodonium salt superacid generator with a peroxide thermal radical initiator. Fumed silica was added as a filler to suppress front-quenching buoyancy-driven convection. Once a propagating front reaches a steady state, the speed at which a front travels can be observed (front velocity), which is a result of the system’s reactivity. It was found that an increase of vinyl ether content resulted in much higher front velocities for vinyl ethers in formulations with an epoxy than systems containing epoxy alone. The kinetic effects of the acid generator and thermal radical initiator with varying vinyl ether content were also studied. It was observed that increasing concentrations of initiators increased the front velocity, with the vinyl ether system exhibiting higher sensitivity to the acid generator concentration. This work confirmed that vinyl ethers are frontally polymerizable through cationic mechanisms and the addition of vinyl ethers to systems will cause stark increases in front velocity.

![Reaction Mechanism Diagram](image_url)

![Graph](image_url)
3D printed pdms LEGO microfluidic device for drug delivery of anti-cancer therapeutics

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Microfluidic devices have become increasingly popular due to their small size and unlike other scientific developed instruments, their capability to recreate an in-vivo environment three-dimensionally. They can be relatively inexpensive to design and reduce the sample sizes needed, allowing for quicker analysis. A PDMS LEGO® based microfluidic device was created to allow for easy reconfiguration, its ability to house cultured cells, and any desired adaptability of channel flow-through. This gives the possibility for different substances to be tested simultaneously and then analyzed. The device was designed with an inlet hole on one side for fluids to be inserted, passing through a deep middle chamber and then exiting on the opposite side. This design will help minimize leakage and backflow pressure compared to a previous design in our group. Additionally, base prongs were added for easy removal of the top piece without disturbing the experiment and obtaining better results. As a way to quickly and initially verify the device is working properly, cultured Staphylococcus aureus will be placed in the middle chamber and different cleaning agents will be passed through the device allowing interaction with the cells. The cells will be analyzed for cytotoxicity effects of the cleaning agents. This experiment will mimic drug delivery to cancerous cells which will be the next study to test the efficacy of the device to capture how cancer cells react to anti-cancer therapeutics.
Investigation of structure-property relationships of de novo amyloid peptides and stereospecific glycopolymers for composite glycohydrogels

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Amyloid peptide fibrils have the potential to enhance the biocompatibility and mechanical properties of materials for biomaterials applications. Due to their binding affinity to proteins, glycopolymers show great promise for the design of peptide-polymer biomaterials such as hydrogels. In this work, two synthetic amyloid peptides (DP7 and DP8) with varying amino acid sequences were analyzed using atomic force microscopy (AFM) to investigate the effects of amino acid sequence on amyloid fibril morphology. DP7 exhibited an average height of 4.5 nm and average diameter of 59.9 nm. DP8 exhibited an average height of 2.5 nm and an average diameter of 68.6 nm. Two acrylamide-based glycopolymers with stereospecific pendent groups of either β-D-glucose or β-D-galactose (PGlcEAm and PGalEAm) were synthesized using RAFT polymerization and characterized using gel permeation chromatography with multi-angle laser light scattering (GPC-MALLS) and proton NMR. Dynamic light scattering (DLS) was performed on the glycopolymer solutions to understand the effect of concentration on polymer chain aggregation in solution. PGalEAm exhibited concentration-dependent aggregation whereas PGlcEAm did not. Furthermore, PGalEAm exhibited aggregates with overall larger hydrodynamic diameters compared to PGlcEAm.
Thermochemical analysis of polysulfone-nanodiamond mixed matrix membranes

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Idaho National Laboratory is developing polymer membranes designed to enrich oxygen from air to enable utilization of the nation’s coal supplies with controllable carbon emissions. Technology that will be aided by cheap membrane-derived enriched oxygen includes gasification systems. Polysulfone (PSF) is found to have suitable properties for gas separation membranes; however, their performance for oxygen separation would benefit from being increased. Within polymer science, applications of nanodiamonds (ND) are still considered reasonably novel. To improve PSF membrane performance, PSF-ND mixed-matrix membranes have been fabricated with the goal of enhancing oxygen permeability while maintaining selectivity. In this presentation, thermomechanical analysis, common behaviors, and observed trends in these PSF-ND mixed matrix membranes will be discussed.

Displayed is a phase inversion of 2% carboxylated ND/PSF showing nanodiamonds within the polymer using SEM.
Synthesis, polymerization, and characterization of self-healing thiol-ene networks

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Self-healing capabilities have been observed in byssal threads of ocean mussels. These self-healing properties arise from the covalent bond interactions between the molecule histidine and a transition metal creating a coordinated network. While this self-healing capability has been studied to better understand the coordination mechanism, it has not been applied to polymer chemistry yet. This project focuses on the synthesis of self-healing polymer networks using thiol-ene chemistry, and the effect that thiol-to-ene ratio and transition metals have on the properties of the overall network. Using ethane-1,2-dithiol, and vinyl imidazole in varying ratios two monomers were synthesized for the creation of self-healing networks: a fully modified imidazole monomer (FMIM) and single modified imidazole monomer (SMIM). Full conversions of both the FMIM and SMIM monomers were confirmed using proton NMR spectroscopy. Metallic salts were added to synthesize the coordinated self-healing networks, with a noticeable difference in viscosity between the resultant gels. The Gaussian 16 system was used to simulate one fragment of a SMIM metal coordinated network and run to collect computational data on the molecules. IR spectroscopy and bond relaxation simulations were used to further examine why the viscosities of the two synthesized gels differ and better understand the binding affinity of the individual metal salts within the network to gain insight into the fundamental self-healing properties.
Ruthenium mediated ring-opening metathesis polymerization using green solvents

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The use of green solvents is of great interest promoting not only green metrics but also an economic benefit. While a lot of studies on the green solvent application has been conducted in most of the synthetic areas but rarely on polymerization. In this study, green solvents were evaluated for ruthenium-initiated ring-opening metathesis polymerization (Ru-ROMP) with representative monomers of norbornene, oxa-norbornene and cyclooctadiene, where mostly toxic chlorinated or aromatic solvents have been used. The solvent effect was obtained by comparing the results of the reference solvent (THF, CHCl3) and the green solvent (2-methyl tetrahydrofuran, ethyl acetate, dimethyl carbonate, and acetone). The results of all green solvents are generally promising, but chain length control was very sensitive. Among the suggested green solvents, dimethyl carbonate exhibited positive results in general.

![Chemical structure of the green solvent](image)

**Green Solvent**

2-Me-THF, EA, DMC, Acetone
Interconnected macroporous polystyrene synthesized from deep eutectic systems-based emulsion templating and high-speed homogenizers

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The increasing environmental awareness has led to the search for more environmentally friendly solvents that help reduce the use of organic solvents for polymer synthesis. In this context, deep eutectic systems (DESs) have emerged as an environmental alternative to expand the conditions at which various types of polymerizations are carried out. Specifically, in biphasic high internal phase emulsions (HIPEs) systems, the use of DES as the internal phase improves their stability and allows polymerization at temperatures that are not possible in aqueous HIPEs. Herein, interconnected macroporous polystyrene was synthesized through free radical polymerization of styrene confined in the continuous phase of HIPEs, where various choline chloride based-DESs composed the internal phase. The effect of both, DESs' composition -amide, trifunctional alcohol, diol, and carboxylic acid as hydrogen bond donors- and the homogenization method used for HIPE preparation – high-speed homogenizer versus vortexing –were systematically studied. The stability and droplet size of styrene HIPE, as well as the interconnected macroporous structure and the mechanical properties of the synthesized polyHIPEs were investigated and found to depend upon the viscosity of the DES in the internal phase. Finally, it was corroborated that due to their high viscosity and polarity, DESs stands as an attractive alternative class of internal phase for the nonaqueous synthesis of styrene macroporous polystyrene. These macroporous polymers will serve as support for further immobilization of inorganic (e.g., magnetite, carbonaceous nanomaterials) and organic nanoparticles (e.g. cellulose nanocrystals) for applications in separation and filtration devices.
Thermal properties of polymers via molecular dynamics simulations and thermal analysis

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Differential scanning calorimetry (DSC) is a thermo-analytical method that enables the quantitative determination of the thermally induced physical changes occurring in the sample during the heating or cooling process over the glass transition and melting regions. On the other hand, molecular dynamics (MD) simulations is a computational tool that allows the studies of the thermal properties of materials remotely also outside the laboratory.

In this work, the thermal properties of traditional and biopolymer materials have been investigated via MD simulations using the GROMACS2020 suite of programs. The implementation of a computational tool such as a MD simulation package, within a six months’ Master of Science work, is a challenge by itself, but the implementation and correct usage of the MD simulations for tackling the thermal properties of materials is another. In this research, the responses of polymer materials, which are heated or cooled, are simulated by MD and the results compared to experimental findings. First, the behavior of the poly(oxyethylene) is studied over the glass transition region, similarly to the C. Wu’s work, to verify the correct application of the simulation method. The verified method is then adapted to other polymeric systems. Comparative experimental studies will be carried out with DSC.

Figure 1. Energy minimized poly(oxyethylene) trimers in a cube. Starting structure for the amorphous morphology.
Cationic polymers incorporating pyrrolidine and piperidine

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Cationic polymers are of broad interest in the biotechnology sector due to their potential use in drug conjugation, tissue engineering, gene delivery, water purification and chelation, and stimuli-responsive materials. Of particular interest in designing cationic polymers is control over their pKa—allowing for the presentation of a positive charge at specific pH, which is dependent on molecular weight, connectivity, and pendant group identity of the polymer. Most cationic polymers incorporate amine groups to produce this positive charge; for example, poly(ethylene imine), a commercially available polymer with a pKa of 7-8.6, will display a positive charge at or below physiological pH. Polymers of similar pKa can exhibit this same positive charge; however, at pH very close to the pKa, only a fraction of the polymer’s groups will be protonated according to the Henderson-Hasselbalch equation. Because of this reason, cationic polymers with amine groups can display a wide range of variation in their interactions with biological molecules. To address this issue, we designed and synthesized a series of monomers and polymers that should be constitutively protonated at or around physiological pH; these polymers are based on pyrrolidine and piperidine (pKa~11.2-11.3). Using free radical polymerization, the series of polymers were synthesized—varying charge density via copolymerization with vinyl pyridine (pKa~5.2) and neutral monomer hydroxyethylmethacrylate. Subsequent complexation of these polymers and copolymers with biological molecules was investigated by dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS)—showing notable differences in complex formation. Systematic manipulation of monomer identity and characteristics help to shape our understanding of the variation in resultant complex geometry.

Figure 1: Representation of Polymer Library.
Homopolymers and copolymers synthesized may or may not include PyrMA or PipMA monomers copolymerized with cationic, hydrophobic, and hydrophilic monomers.
(1) Poly(4-vinylpyridine);
(2) Poly(2-vinylpyridine);
(3) Poly(hydroxyethyl methacrylate);
(4) Poly(styrene);
(5) Poly(tert-butyl methacrylate);
(6) Poly(butyl acrylate).
Rh-catalyzed carbene insertions into Si–H Bonds for the synthesis of functionalized silsesquioxane nanomaterials

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Polyhedral Oligomeric Silsesquioxanes (POSS) are a class of molecules consisting of an inorganic siloxane core surrounded by organic functionality. Controlling the organic groups of the POSS is important for constructing nanomaterials with various applications in materials science and biomedical engineering. Currently, the synthetic methods to access functionalized POSS are limited. To increase the diversity of synthetic methods, we have demonstrated metal-catalyzed carbene insertion into POSS containing one, three and eight Si–H bonds using aryl/ester diazo compounds as carbene precursors. A screen of metal catalysts identified that dirhodium(II) carboxylates provide optimal reactivity to form POSS insertion products that can be isolated in good to excellent yields. A novel POSS-based silane was synthesized and utilized for single carbene insertions. The Rh-catalyzed carbene insertion is applicable for POSS containing up to eight Si–H bonds (up to gram-scale) by simply increasing the equivalents of the diazo compound. A series of diazo compounds have been evaluated to demonstrate the functional diversity that is capable of being installed on both the ester and aryl groups. Several further transformations of POSS-insertion products were completed using both functional handles. Hydrolysis of the POSS ester was achieved to afford carboxylic acid-functionalized POSS under mild conditions. For POSS insertion products containing an aryl bromide, a Suzuki-Miyura coupling was achieved to enable the formation of biphenyl-containing POSS.
Directed assembly of carbon nanofiber (CNF) and MXene nanoparticles on 3D printed polymer templates

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Self-assembly has attracted increasing attention as an effective strategy for the fabrication of functional micro/nanostructures. Capillary force is a significant driving force for self-assembly and has become a versatile and scalable approach to building complex geometries via micro and nanoscale patterning. Traditional patterning techniques of DNA-programming, liquid-air interfaces, and external fields are not scalable due to complex manufacturing requirements. Here, we will elaborate on 3D printing as a novel patterning technique for its rapid prototyping, cost-effectiveness, and design flexibility. This work has shown a combination of 3D printing techniques to fabricate patterns and directed-assembly for the site-specific placement of one (1D) and two (2D) dimensional nanoparticles. The microns size featured pattern substrate is 3D printed by resin curing based techniques (Stereolithographic and Continuous Liquid Projection). Then, 1D (i.e., Carbon nanofibers) and 2D (i.e., MXene) dispersion were deposited on the substrates via capillary and evaporation induced self-assembly techniques. During the evaporation-drying process, the solid-liquid-air contact line is molded by the gratings' shape, and the nanoparticle experiences various fluidic forces like drag force, capillary force, and Vader wall torque, which promotes the layer-by-layer deposition of nanoparticles. The anisotropic deposition of CNF/Epoxy and MXene/Epoxy showed direction-dependent electrical conduction and mechanical sensitivity. We will also demonstrate the assembled nanoparticle/polymer composites' application for sensing toward mechanical deformation and volatile organic compounds (VOC). Our hybrid manufacturing and the polymer template effects showed enormous potential toward composite structures for directional electrical conductivity, small tensile/flexural strain sensitivity, and a wide range of VOC sensitivity, making them suitable for a multifunctional sensor.
Glycopolypeptide nanoparticles by N-Carboxyanhydride polymerisation

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Biodegradable nanoparticles are viable carriers for active compounds in pharmaceutical as well as in personal care products. Moreover, it is known that glycans play essential roles such as cell signalling, lubrication and detection of disease. Consequently, glycosylated nanoparticles have received increased interest in the field.

We have recently developed a new class of glycosylated degradable nanoparticles with a polypeptide core and a glycopeptide shell. Herein, we describe the synthesis and analysis of a series of degradable glycosylated polypeptide nanoparticles (GlycoPep NPs) with potential applications as targeted drug delivery vehicles. GlycoPep NPs were synthesised by miniemulsion ring-opening polymerisation (ROP) of N-carboxyanhydrides (NCA) in aqueous conditions; during which varying glycopolypeptides were utilised as surfactants. The size of the GlycoPep NP’s could be tailored based on the core polypeptide composition and the concentration of surfactant used. DLS confirmed the highly stable and reproducible nature of the particles produced. The nanoparticles could be lyophilised and resuspended in water and buffer solutions, enhancing their bio-applicability. Furthermore, the suspension stability of the GlycoPep NPs could be improved through the utilisation and post-polymerisation photo-crosslinking of modified natural amino acids.

This methodology opens up a library of bio-inspired glycosylated polypeptide nanoparticles that can be highly tuned. These GlycoPep NP’s have significant potential for the delivery of therapeutic agents.
Antimicrobial photosensitizers and their formulations: A potential solution to current world scenario

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In order to provide a long-lasting solution to infections affecting the current world scenario, photodynamic therapy (PDT) offers a means to destroy pathogenic microbes via formation of reactive oxygen species, promoting the damage of microbial targets such as nucleic acids (DNA or RNA), proteins, lipids, protein complexes, or by impeding the biofilm matrix.

Thus, the main aim of the study is to design and synthesize photoactive moieties based on porphyrin and chlorin macrocycles and BODIPY dyes for antimicrobial photodynamic therapy (aPDT). Furthermore, incorporating these photo-moieties into biopolymeric hydrogels as shown in Figure 1 for a variety of biomedical applications are targeted. Porphyrin based cationic photosensitizers (PSs) were synthesized and a chlorin based PS was extracted from Spirulina maxima and modified to be included on a biopolymeric hyaluronic acid hydrogel platform. This platform was characterized spectroscopically and evaluated for antimicrobial photoactivity via microbial evaluation on different gram strains of bacterial species. Singlet oxygen production was determined as well to evaluate the photoactivity of this polymeric hydrogel platform.

Furthermore, BODIPY dye-based PS species have been synthesized and modified for their activity as aPDT agents. Several N-heterocyclic BODIPY-dyes have been positively charged or functionalized for incorporation into hydrogel platforms. These dyes exhibit good water solubility. A library of such N-heterocyclic BODIPY dyes was prepared and characterized and will be evaluated for photoactivity against microbes.

Figure 1. Photosensitizers incorporated in a hyaluronic acid hydrogel matrix for aPDT applications
Synthesis of thiolated-poly ethylene glycol via post-modification polymerization

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Poly(ethylene glycol) (PEG) is a hydrophilic polymer, commonly used in batteries, medicine, pharmacy, and various industry. To achieve what synthesizes high value PEG, the synthesis of functionalized PEG has been of interest. Usually, functionalized-PEG is synthesized from epoxide monomers. However, the scope of monomers is limited due to functional group incompatibility and uneven reactivity. To overcome these limitations, the synthesis of functionalized-PEG via post-modification polymerization is preferred. Using the C-H functionalization strategy, PEG was directly functionalized. The reactive radical intermediate was captured by disulfide, producing the corresponding thiolated-PEG without decreasing the molecular weight. In conclusion, we developed an efficient post-modification polymerization methodology as a new protocol to introduce various thiolate functional groups along the polymer backbone. The reaction development and scope of our development will be discussed.
Evaluation of dispersion conditions on the oxygen barrier properties of polyisobutylene-grafted graphene oxide nanocomposite films

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Oxidative degradation of asphalt mixtures is one of the major causes of roadway deterioration. Polyisobutylene modified graphene oxide (PIB-g-GO) nanoparticles have been shown to be effective in reducing oxygen permeation through model asphalt matrices. However, to achieve a reduction in oxygen permeation, the PIB-g-GO nanoparticles must be well dispersed in the matrix. Traditionally, sonication has been used; however, it is energy-intensive and can damage the nanoparticles. Dispersion via shear mixing may be a low energy alternative that will not damage the basal plane of the PIB-g-GO particles. To explore this, nanocomposite films were fabricated using styrene-butadiene-styrene (SBS) copolymer as a model matrix with 0.25 wt. % PIB-g-GO as a functional additive. Shear mixing times of 1 hour and 24 hours were chosen to explore the effect of shear mixing on particle dispersion and oxygen barrier properties. All films were tested in a MOCON instrument to determine oxygen barrier properties.
Synthesis and characterization of chitosan derivatives for biomedical applications

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Chitin and chitosan are naturally abundant and renewable polymers that have excellent properties such as biodegradability, biocompatibility, non-toxicity, and adsorption. Due to its favorable physical and chemical properties, chitosan is being used in a vast array of widely different products and applications ranging from biomedical and cosmetic products to water treatment and plant protection. However, chitosan is only soluble in acidic aqueous solutions. Previous studies have demonstrated that polymers containing cationic charge condense nucleic acids quite efficiently. In this work we have modified chitosan to make it water soluble which can then be used as an effective vector for the purpose of gene delivery. More specifically in this work, we have synthesized chitosan derivatives containing ammonium and phosphonium groups and have tested their potentials for effective condensation of biomolecules such as DNA. Additionally, the ammonium and phosphonium chitosan derivatives have been PEGylated to improve their cellular uptake and to reduce cytotoxicity. We have shown that, the percent quaternization of chitosan can be controlled by changing the concentrations of chitosan and other starting materials. The various chitosan derivatives made in this work have been characterized with NMR and IR spectroscopies. The chitosan derivatives made have also been characterized in terms of their solubility in various pH solutions, their abilities for complex formation with DNA and their corresponding particle size. Synthesis and characterization of the chitosan derivatives will be presented and discussed.

General reaction of chitosan modification.
Successful application of bifunctional catalysts based on squaramides in ring-opening polymerization

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Bifunctional organocatalysts can provide a good compromise between activity and selectivity in ring-opening polymerizations (ROPs). It comprises both an H-bond donor (monomer activator) and an H-bond acceptor (hydroxyl activator) and functions through a synergetic activating-controlling effect. There were a few types of bifunctional organocatalysts reported, and most of them were derived from (thio)ureas. This paper aims to give a new catalyst obtained from squaramides (Sq), it can be deprotonated by a suitable Brønsted base to render a bifunctional anion catalyst for fast and selective ROPs of cyclic monomers. The combinations of aryl-substituted and alkyl-substituted squaramides (Sq1-8) with different Brønsted organic bases were evaluated in the ROP of l-lactide (l-LA). The influence of the substitution of ortho-, meta- and para- phenolic hydroxyl on the catalytic activity of squaramides was discussed as well. The partner of 3-(benzylamino)-4-((4-hydroxybenzyl)amino)cyclobut-3-ene-1,2-dione (Sq8) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in terms of reactivity and selectivity. It afforded the metal-free poly(l-lactide)s with precise molar masses ($M_n, GPC = 4.1 \text{ kg mol}^{-1}$) and narrow dispersity (1.10) in 15 min. The controlled/living nature of the ROPs was supported by kinetics experiments, chain extension experiments, and MALDI-ToF-MS characterizations. The deprotonation of squaramides and synergetic activation mechanism was proposed and validated by NMR titrations. Higher relative cell viability (> 66 %) of the untreated PLLA samples containing Sq8/DBU compared with the control phenol (20%) was tested by MTT assay on L929 cells ensured the desirable biosafety and biocompatibility.
Multifunctional polymer synthesis: Sequential postpolymerization modification of aldehyde polymers

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PostPolymerization Modification (PPM) is an important way to elaborating polymer performance, and PPM of polymer is one of the options for diversifying functional groups. However, finding conditions for polymerizing two or more reactive monomers, not touching other groups, and proceeding the selective modification bring on synthetic complications. In addition, the distribution of functional groups is uneven when structurally other monomers are polymerized. Synthesis and PPM of the multifunction homopolymers have emerged th detail the precision. However, the number of functional groups available is very limited. we conducted the study presented here to add the aldehyde group to the list of single functional groups to accommodate multiple chemical units. aldehydes, which easy to obtain and highly reactive to converted various functional groups, play important role in synthetic chemistry. here are the two step sequential operations: 1) the Rhodium catalyzed C-H activation of the aldehyde pendant through the PPM forms ketone polymers, 2) functional group condensed between ketones and amines is synthesized and discussed as a new tool for synthetic complex polymers.
Super-stable suspension based on thermo-responsive polymers

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From the perspective of their widespread use in daily life, stable suspensions are particularly useful, such as foods (batters, puddings, sauces), pharmaceuticals (pharmaceutical formulations ensuring uniform dosing), household products (paints and inks), and the petroleum industry (drilling fluids, cementing slurries). In order to obtain a reasonably stable suspension, a cumbersome dispersion method is needed, and some stabilizing electrolyte or surfactant must be present as well. In this work, a stable suspension was obtained by simply increasing the temperature of an aqueous polymer solution. The polymer has three major components: polyethylene glycol (PEG), polyphenylene oxide (PPO), and hyperbranched polyglycerol (HPG). When the solution temperature is lower than the lower critical solution temperature (LCST), the polymer is completely dissolved in water. When the temperature of the solution is higher than the LCST, the polymer becomes insoluble in water and self-assembles into microparticles. By adjusting the polymer composition, the suspension containing microparticles can be stable for over 6 months without particle precipitation. The LCST of the polymer can be adjusted from 15°C to 45°C. The polymer is synthesized from commonly used monomers through a one-pot synthesis procedure. Therefore, the price will be relatively low. In addition, all polymer components have excellent biocompatibility and will not cause human and environmental toxicity. All these features make the suspension suitable for applications in pharmaceuticals, household products, and other products.
Imidazolium-containing thiol-yne ionene networks: thermal, mechanical and conductive properties

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A series of imidazolium-based bis(trifluoromethylsulfonyl)imide \([\text{NTf}_2]\) ionene networks were prepared by using thiol-yne ‘click’ photopolymerization to crosslink bisalkynylimidazolium \([\text{NTf}_2]\) monomers with pentaerythritol tetrakis(3-mercaptopropionate) (PTMP). The thiol:yne molar ratio was varied in order to examine changes in the thermal, mechanical and conductive properties of the resulting polymer networks. Photorheology was utilized to determine the approximate gel points for each of the polymer networks prepared. Both crosslink density, determined from dynamic mechanical analyses, and ionic liquid (IL) concentration were factors in changing the ionic conductivity of the networks. Overall, the polymer that combined a relatively low crosslink density with high IL concentration exhibited the highest conductivity (~10\(^{-6}\) S/cm at 20 °C).
Modulating artificial membraneless organelle via phosphorylation of oligopeptide

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Liquid-liquid phase separation (LLPS) was recently revealed as a facile, efficacious and ubiquitous tool of intracellular biomolecule organization. Driven by LLPS, membraneless organelles (MOs) largely host intrinsically disordered proteins (IDPs) and RNAs, representing a novel paradigm of compartmentalization spanning over a wide range of cellular metabolism. From a minimalist biomimetic chemical synthetic method, IDP-mimicking polymer-oligopeptide hybrid (IPH) was constructed via click chemistry between vinylsulfone-modified dextran and cysteine-terminated peptide, namely, cysteine-terminated low complexity domain-like peptide (CLCDP) and cysteine-terminated RRASL-containing peptide (CRP), which underwent LLPS (coacervation) into micron-sized compartmentalized droplets under physiology-mimicking conditions, driven by molecular interactions provided by CLCDP and CRP. In addition, model RNAs could be preferentially recruited into droplets to form RNA-enriched artificial MOs (AMOs), presumably owing to aromatic packing between tyrosine residues (of CLCDP) and nucleobases (of RNA), as well as charge attractions between arginine residues (of CRP) and phosphate group (of RNA). Harboring Kemptide-like (RRASL) motif, a model synthetic substrate for protein kinase A, the phosphorylation state of CRP will be tuned by virtue of kinase/phosphatase enzyme pair, thereby generating alteration of charged state of CRP. The cognate phase behavior of IPH will be characterized by turbidimetry assay and optical microscopic imaging. The RNA partitioning behavior will be investigated by fluorescence microscopic imaging in the presence of methylene blue as the imaging agent. In conclusion, an AMO was synthesized via click chemistry chemical synthetic route, wherein phase behavior and RNA partitioning effect will be modulated via enzymatic control leveraging kinase/phosphatase pair.
Interpolymer complexes of poly(sulfonic acid)s and poly(ethylene oxide): An unexpected association

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The formation of novel interpolymer complexes (IPCs) between poly(sulfonic acid)s and poly(ethylene oxide) (PEO) is reported. The complexes were precipitated from polymer mixtures in aqueous solution and depositated on surfaces as LBL films. The interpolymer association in poly(sulfonic acid)/PEO is ascribed to hydrogen bonding between the sulfonic acid and the ether of PEO, this characterization was confirmed from infrared spectroscopy evidence. Sulfonic acids are very strong acids, they are fully dissociated. However, we show in this work that some poly(sulfonic acid)s can form IPCs with PEO both in solution and on surfaces, these complexes were precipitated from aqueous solutions and depositated on surfaces in a LBL procedure. The experimental evidence supporting the formation of IPCs of poly(sulfonic acid)s and PEO is: (i) polymer precipitation is maximized for a 1:1 monomer stoichiometry and (ii) the two polymers can be sequentially deposited as LBL films, which require a complexation mechanism for assembly. Furthermore, IRRAS experiments demonstrate the presence of both PEO and the Poly(acid)s in the films. The formation of IPCs with PEO was successful for poly(styrene sulfonic acid) PSSA and Nafion, but not for PVSA. We explain this result as the combination of two effects: PSSA and Nafion are expected to be more hydrophobic than PVSA because hydrophobic interactions are known to stabilize IPCs and hydrogen bonds in ether/aromatic-sulfonic acid complexes are predicted to be stronger than those in ether/aliphatic sulfonic-acid complexes. The interpolymer bonding in PSSA/PEO and Nafion/PEO was tentatively proposed to result from hydrogen bonding between the non-dissociated sulfonic acid groups (SO$_3$H) and the ether in PEO because in spectra of Poly(sulfonic acid)/PEO IPCs have an IR band at 3060 cm$^{-1}$ that is absent in the spectra of the pure polymers. We explained the unexpected formation of PSSA/PEO and Nafion/PEO IPCs in terms of the strength of the ether/sulfonic hydrogen bond and the fact that its formation displaces the sulfonic-acid/sulfonate acid-base equilibrium toward the protonated SO$_3$H species.
Sulfur containing high refractive index polymers for better light outcoupling from OLED

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Development of opto-electronic devices is one of the key points of focus in modern day research for new functional materials. High refractive index organic materials play a crucial role in the field of light extraction from OLEDs. This study focuses on the synthesis of a series of linear and branched novel sulfur containing poly(arylene thioether)s and poly(arylene ether)s from sulfur containing bifunctional and trifunctional monomers. The synthesis of the polymers takes place via nucleophilic displacement of activated fluorine atoms of the bis-fluoro monomer (1) resulting in linear polymers (Fig. 1) and the nucleophilic displacement of activated fluorine atoms of the trifunctional monomer results in branched polymers. The structures of the polymers have been established by NMR characterization. The polymers prepared have very good film forming ability indicating high mechanical strength. The polymers have varied sulfur content depending on the structure of monomers. It has been found that as the sulfur content increases, the refractive index (RI) of the polymer films also increases (Fig. 2), because of higher polarizability of sulfur as compared to carbon. As a result, the effectiveness of the material in OLED application also increases. The outcomes from this study will provide a pathway for achieving new and better substitutes for enhancing outcoupling efficiency of OLED.

![Reaction scheme and structures of poly(arylene thioether)s and poly(arylene ether)s.](image)

**Fig. 1.** Reaction scheme and structures of poly(arylene thioether)s and poly(arylene ether)s.

![Plot of refractive index measured at 589 nm versus sulfur content of polymers 3a – 3f.](image)

**Fig. 2.** Plot of refractive index measured at 589 nm versus sulfur content of polymers 3a – 3f.
Mesoscale modeling of nanogel degradation: Effect of crosslink density and particle size

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Controlled degradation of micro and nanogels can be utilized in numerous applications, ranging from drug delivery applications to facilitating tissue engineering. As drug or biomolecules release from the hydrogels can be regulated via controlled degradation, further advancements in these applications would benefit from a clearer understanding of the hydrogel network degradation process. To this end, we have developed a Dissipative Particle Dynamic (DPD) method utilizing a stochastic approach to simulate the degradation of tetra-arm polyethylene glycol based nanogels. During degradation, clusters break off from the nanogel particle. We measure the cluster sizes in terms of the number of DPD beads in each cluster and track the distribution of these sizes along with the radius of gyration of the nanogel particle. We also track weight average degree of polymerization in these degrading systems. Our simulation approach allows us to probe the effects of degradation rate constant, polymer-solvent affinity, crosslink density, and initial nanogel size on the dynamics of the degradation process. Our results indicate that an increase in the particle size results in greater variance in the size of the clusters, provided that initial crosslink density remains constant. Further, we show that at the initial stages of the degradation process an increase in the radius of gyration of the nanogel is observed due to the decrease of a number of elastically active polymer strands resulting in gel swelling; we quantify this increase as a function of initial crosslink density. Specifically, we show that this effect is more pronounced for the loosely crosslinked gels. At late times, nanogels undergo reverse gelation and then complete disintegration to tetra-arm precursors.

Periodic snapshots from a nanogel simulation at various stages of degradation; beads representing solvent are hidden for visual clarity.
Cellulose-based, 1,2,3-triazolium-functionalized polymerized ionic liquids: thermal properties, ionic conductivities and morphological analysis

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Several 1,2,3-triazolium-functionalized cellulose derivatives were prepared using an azide-alkyne ‘click’ cyclization strategy, followed by quaternization. As cellulose represents a cheap, sustainable biomacromolecule, the ability to generate conductive materials through simple functionalization of the backbone with an ionic liquid is of great interest. Three different counteranions ([Br], [OTf] and [NTf₂]) were employed in order to explore the interplay between thermal, conductive, and morphological properties. Functionalization of native cellulose resulted in the observation of a T_g, the values of which were inversely related to the size of the counteranion. Morphological analysis of the derivatives indicated that the materials were amorphous in nature, showing a clear nanophase separation dependent on the type of anion. By simply quaternizing the 1,2,3-triazole ring to produce the corresponding ionic moiety, the ionic conductivity of the material was increased by ~ 6-orders of magnitude at higher temperatures as compared to the native samples. Ionic conductivity was observed to have an Arrhenius (linear) behavior and was enhanced up to 4-orders of magnitude upon exposure to humidity. The results provided evidence to suggest that the thermal and ionic conductivity properties are dependent on anion basicity and hydration. Furthermore, this rather simple functionalization technique to modify cellulose opens the door to a vast array of possible ion-conducting side structures and properties.
Enhancing the through space interactions in insulated π-conjugated polymers

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Understanding the structure property relationship of π-conjugated polymers at the molecular level is important for the design and development of conjugated materials with desirable properties. Insulating the π-conjugated polymer backbone is known to enhance the polymer properties such as solubility, chemical stability and photostability, and optoelectronic properties such as fluorescence quantum yield, electroluminescence, and interchain charge transport. However, this sheathing or insulation will significantly hamper the conjugated polymer fluorescence quenching by acceptor molecules as the π-surface is insulated. This limits the applicability of insulated conjugated polymers in organic solar cells and amplified fluorescence quenching sensors in which the photoluminescence quenching of donor polymer by an acceptor is one of the key steps in charge generation. Therefore, the development of insulated conjugated polymers that combine the advantages of insulation while retaining the photoinduced electron transfer through the polymer backbone is highly desirable. We hypothesized that incorporating dithia[3.3]paracyclophanes into the insulated polymer backbone will enhance the polymer fluorescence quenching via through space π-π interactions known as transannular π-π interactions. In this poster, I will discuss the synthesis of a series of different insulated copolymers with different percentage incorporation of dithia[3.3]paracyclophanes and the impact of dithia[3.3]paracyclophane on the optical properties of copolymers. As the percentage incorporation of the dithia[3.3]paracyclophane monomer increases, we observed an increased absorption in the red-region of the spectrum, a reduction in photoluminescence quantum yield and a significant enhancement of the Stern-Volmer quenching constant (ca. 4.5 times) as compared to the corresponding insulated homopolymer. The results indicated that our hypothesis is true, and the through space conjugated phenyl rings play a significant role in determining the optical properties of copolymers.
Assessing the physicochemical properties of nano- and microparticles produced with chemically modified gliadin

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Food-grade protein-based nano- and microparticles are attracting more attention given their potential application in the formulation of novel nutrient delivery systems. Gliadin is currently under-utilized in the food industry, as its application is hampered by its low solubility in water at neutral pH. Deamidation is an effective way to modify the solubility of wheat gliadin as it leads to the conversion of uncharged amide groups (glutamine residues of gliadin) to charged acidic residues (glutamate). Deamidation is, hence, a suitable technique to increase electrostatic repulsion between the protein molecules and dissociate protein-polymer clusters. In this project, only moderate levels of deamidation are focused upon as it is important that gliadin molecules will still aggregate in nano- and microparticles. As such, the effect of deamidation on particle formation kinetics will be explored. Particle formation in this project is done through liquid antisolvent precipitation. The ζ-potential of the untreated and deamidated gliadin over the pH range of 2-9 was monitored. A sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) test on the native and deamidated gliadin was conducted to monitor the molecular weight upon deamidation. The isoelectric point (IEP) of gliadin was shifted from pH 6.5 in native gliadin to pH 4.5 in deamidated gliadin. This IEP shift to more acidic pH conditions could improve the stability of gliadin-based nanoparticles at neutral pH conditions. The results of SDS-PAGE show an increase in molecular weight of the protein in function of deamidation degree. This can be indicative of crosslinking in deamidated gliadin and requires further study. This project will yield a better understanding of the interactions and structures underlying particle formation in function of deamidation degree. This will boost the rational development of highly customizable protein-based nano- and microparticles for nutrient-delivery and food structuring applications.
Photo controlled polymerization of amphiphilic block copolymer in aqueous solution

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Block copolymers are versatile materials with a wide variety of chemical applications. Typical synthesis of these materials employs a controlled polymerization of one monomer with a subsequent chain extension using another monomer sometimes under extreme reaction conditions. Here, a facile polymerization induced self-assembly (PISA) method for block copolymer synthesis is reported using a poly(ethylene glycol) based chain transfer agent and 2-hydroxypropyl methacrylate monomer in aqueous solution using blue light. Reaction times can easily be varied to produce block copolymer micelles of different sizes and morphologies. Five separate PEG-PHPMA samples were isolated after 24, 18, 12, 6, and 3 hours of PISA and then analyzed with NMR to elucidate the structural differences in the samples based on the time length of photo-PISA. The prepared PEG-PHPMA block copolymers have many potential applications including being used as templates for the synthesis nanoporous materials.
Blending of conductive and electrochromic polymers for ITO-free smart labels

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Electrically conducting conjugated polymers undergo reversible changes in electrical properties as a function of oxidation state and are also electrochromic by nature, meaning that their color and optical properties change reversibly in response to electrochemical oxidation and reduction. Over the years, a significant focus of electrochromic polymer (ECP) research has been designing materials that switch reversibly between a colored and colorless state, as they are promising candidates for smart displays because of their ability to switch color with a low voltage input (< 2 V). Typically, electrochromic devices and displays use expensive transparent conductive substrates such as indium tin oxide (ITO), but the high cost of ITO is prohibitive for mass producing low-ticket items like printed smart labels, where it accounts for up to 80% of the cost. It has been shown that ECPs with conductivities > 1 S/cm can switch between different colored states in seconds over several millimeters without an underlying ITO layer. This demonstrates that even relatively poorly conducting ECPs can potentially replace the ITO while still serving as the color changing element in EC labels. Expanding the color palette of ECPs that can fulfill both roles could potentially be achieved using ECP blends. This means a less conductive ECP (< 1 S/cm) with a desirable color may be suitable for ITO-free labels if the color-changing properties (speed and contrast) are improved by blending the ECP with small quantities of a highly conductive ECP (100+ S/cm). We will show how the quantity of conducting ECP in each blend influences the electrical, electrochemical, and color changing properties of these materials and how this straightforward blending approach can be used to expand the color space of smart EC labels.

Schematic of ECP blending and its use with an ITO-free smart label
Synthesis of co-oligomers containing 1,1-dialkyl-3,4-diphenyl-2,5-silolene and aromatic-diolene and their electrochemical characteristics

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Dialkyl(iso-propyl or n-hexyl)-bis(phenylethynyl)-silanes were reacted with lithium naphthalene, anhydrous ZnCl$_2$, and N-bromosuccinimide (NBS), and then the crude materials were purified to obtain 1,1-dialkyl(iso-propyl or n-hexyl)-2,5-dibromo-3,4-diphenyl-siloles, respectively. Nucleophilic substitution reactions of aromatic diols (e.g. 4,4'-biphenol or bisphenol A or 4,4'-(hexafluoroisopropylidene)diphenol) with two bromine groups of the prepared 2,5-dibromo-siloles as co-monomers in the presence of potassium carbonate under the co-solvent of N-methyl-2-pyrrolidinone (NMP) or N,N-dimethylacetamide (DMAC) and toluene with Dean-Stark trap were used to synthesize co-oligomers containing 1,1-dialkyl(iso-propyl or n-hexyl)-3,4-diphenyl-2,5-silolene and 4,4'-biphenolene or bisphenolene A or 4,4'-(hexafluoroisopropylidene)diphenolene. The crude products were purified by decantation using deionized water and then furthermore purified by extraction with chloroform. The product materials were characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR as well as GPC. We also studied the photoelectronic properties by UV-vis absorption, excitation, and fluorescence emission spectroscopic methods, particularly, along with electrochemical properties.
Density functional study of the reactions of OH radicals with sPEEK fuel cell membranes

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Sulfonated polyether (ether) ketone (sPEEK) membranes (repeating unit displayed) are an environmentally friendly candidate for membranes for polymer electrolyte membrane fuel cells. Radical OH molecules are present in the process of a fuel cell’s operation and may react with sPEEK to degrade the membrane. It has been suggested that the main decomposition reaction is addition of OH radical to sPEEK, followed by acid-catalyzed water elimination to leave an unstable cation, which then degrades. Our recent computational work investigates this mechanism as well as another addition-elimination mechanism, suggested by a recent density functional study of the reaction of sPEEK with H radicals, in which OH adds add to sPEEK and bond-breaking degradation reactions immediately follow. Results suggest that both reactions are exothermic and thermodynamically favorable with comparable barriers, and that it is likely that both mechanisms occur in fuel cells and contribute to its degradation.
Disulfide cross-linked poly(acrylamide-co-acrylonitrile) microgels: Synthesis, properties, and de-cross-linking kinetics

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Targeted drug delivery along with controlled drug release mechanisms have been of tremendous interest concerning the battle against cancer. Lipobeads – spherical bipartite nanoparticles consisting of a hydrogel core coated by a lipid bilayer – exhibit properties of mechanical stability and environmental responsiveness attractive for the drug delivery systems. This work is devoted to the synthesis and properties of the degradable under presence of reducing agents microgels, which could be used as the hydrogel core within lipobeads. Using the inverse suspension polymerization (ISP) method, “thermophilic” spherical microgels (~Ø10–300 µm), which swell upon heating, have been prepared via thermal polymerization of acrylamide and acrylonitrile as co-monomers along with either N,N’-bis(acryloyl)cystamine as a cross-linker with disulfide bridges or N,N’-methylenbis(acrylamide) without disulfide cross-links. In both cases, microgels were fluorescently labeled in order to characterize them under confocal microscope. Direct observations by confocal microscopy revealed the following properties of thus prepared microgels: (i) microgels without disulfide cross-links do not exhibit degradation, whereas microgels with disulfide cross-links exhibit degradation under presence of a reducing agent (dithiothreitol or glutathione); (ii) two steps of degradation are distinguished: microgel expands due to the reduction in cross-linking density and degrades due to outward diffusion of the cleaved polymer chains; (iii) kinetics of swelling and degradation was measured to conclude that the swelling is slower than the degradation; (iv) the extent and rates of degradation depend on pH and amount of a reductant added. These findings propose an avenue towards drug delivery systems that encapsulated drug molecules to release with the maximal rate within specified microenvironment of cancerous cells.
Optimizing the synthesis of single-ion conducting polymer electrolytes using graft through and graft to techniques via ring opening metathesis polymerization and click chemistry

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Lithium ion batteries with small molecule organic electrolytes continue to be limited by safety issues related to their volatility and flammability as well as potential dendrite formation. This work focuses on the synthesis of single-ion solid polymer electrolytes through the use of ring-opening metathesis polymerization and click chemistry where the anion is covalently bound to the polymer so that ion conductivity is dominated by lithium ion motion. Graft through and graft to approaches are studied to build in the single ion content into homopolymers and copolymers. The two monomers have a consistent oxanorbornene dicarboximide backbone where one has a trifluoromethane sulfonimide side group attached via click chemistry and the other has an oligomeric ethylene oxide (OEO) side chain. The OEO content in the copolymer and length of the side chain allows for the tailoring of the glass transition temperature which may improve ion conductivity balanced with a reduction in the lithium content.
Using RAFT polymerization to purify water using metal-binding polymers

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Water is one of the most precious resources on our planet, making up roughly two thirds of the earth’s surface. Despite the abundance of water, access to clean water has become increasingly difficult. Decades of industrial activities and neglect for the environment have contributed to water pollution. Common pollutants include heavy metals, which are toxic and carcinogenic not only to humans but also to aquatic life. Removal of heavy metal contaminants is a critical part of water purification. While several methods exist, the use of polymers to bind heavy metals offers many advantages over comparable methods, such as improved efficiency and elimination of harmful byproducts. The goal of this project is to synthesize a series of metal chelating polymers to determine which type of polymer results in the most efficient binding to a series of metals. By altering the structure of the polymers and the identity of the chelating group, this research will help elucidate the importance of polymer structure and functionality on metal binding efficiency. The polymers will be synthesized via a “modular” approach, which enables the study many different metal-chelating groups while minimizing the synthetic complexity. A single polymer can be functionalized with a variety of metal binding groups, creating a “library” of metal binding polymer for detailed binding studies. Metals of interest include common heavy metal water contaminants, such as Zn, Ni, Pb, V, Cu, Cr, and Cd. While the ability to remove metal ions from solution is the primary goal of the project, evaluating the recovery of the bound metal from the polymers is also of interest. Many of the heavy metals that contaminate water are valuable resources, so the recovered metal could be sold after isolation. This would help offset the cost of the water-purification process and present a more sustainable approach in the long run. At the conclusion of this project we will have identified a polymer structure and functionality that is most effective in binding metal-contaminants and demonstrates the highest percent recovery of the bound metal.
Estimation of reactivity ratios for an amino-containing monomers/PEGMAs copolymerization mini-library

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Amino-containing monomers (TAMMs), such as 2-(N,N-diethylamino)ethyl methacrylate (DEAEMA) and 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA), have frequently been used in the copolymerization with PEGMAs macromonomers in order to lead to biocompatibility and a pH/temperature-sensibility character in the final polymer. However, the reports on their kinetic behaviors has been so limited in the literature.

In this work, a series of three poly (ethylglycol)(PEG)-containing monomers (n = 1, 9 and 23) and TAMMs (such as DEAEMA and DMAEMA) were synthetized by free radical polymerization in a high polarity solvent, such as EtOH, at 70 °C. Estimations of the reactivity ratios by using ¹H-NMR spectroscopy were carried out in experiments at low conversion and short times to avoid the transesterification. The estimated reactivity ratios (r's) were r₁≤1 and r₂≤1, therefore random copolymers were predicted for all cases. Furthermore, both r's were dependent on the most basic character of the DEAEMA than that presented in the DMAEMA, giving rise to the formation of the cycle adduct. It was concluded that the steric hindrance of the amino group affects the reactivity ratios, which is higher when the amine is less available and that decreases as the PEG-side chains are extended. The values of the r(DEAEMA) decreased slightly when a solvent with high relative polarity was used, possibly due to the intramolecular interaction of the protonated amine with the carbonyl oxygen in the methacrylate. Besides, both r(DEAEMA) and r(PEGMAs) were similar regardless of the relative polarity of the solvent. Furthermore, the effect of the size of the PEG-side chains on the copolymer composition and the PEG-containing monomer consumption did not show a statistical difference.
Co-nonsolvency induced collapse transition in thin PMMA-b-PNIPMAM films

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Stimuli responsive thin films combine the advantages of polymers in bulk, i.e. their increased stability, and of polymer solutions, i.e. their fast response. Therefore, they are attractive for a wide range of applications. To extend it even further, we investigate the not yet well-understood phenomenon of co-nonsolvency. We prepared thin films of the thermoresponsive diblock copolymer PMMA-b-PNIPMAM, which exhibits a co-nonsolvency induced collapse transition when organic cosolvents, like acetone or methanol, are introduced in a certain ratio into the surrounding vapor atmosphere. The macroscopic changes during the swelling in aqueous vapor and the collapse transition in cosolvent vapor mixtures were investigated by spectral reflectance (SR) and verified through time-of-flight neutron reflectometry (ToF-NR) measurements. On the molecular level we further elucidate the underlying mechanism by in situ Fourier-transform infrared spectroscopy (FTIR) measurements to gain further insight into the origin of the co-nonsolvency effect.

Molecular structure of PMMA-b-PNIPMAM with relevant IR signal positions (left) and time resolved FTIR spectra of PMMA-b-PNIPMAM in varying D₂O/acetone vapor mixtures (right).
Understanding the incorporation of transition metals into imidazole modified thiol-ene networks for improved self-healing and other functional advancements

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The imidazole functionality, notably present in histidine, has been used to impart stimuli-responsiveness to polymeric materials, e.g. enabling self-healing through metal coordination bonds, drawing inspiration from byssal mussel threads. Self-healing increases lifetime, efficiency, and environmental safety of materials. Most reports on imidazole-containing polymers discuss the microencapsulation of imidazoles or their use as side chains. Here, we aim to research networks with only coordination crosslinking points to better understand the physical properties. Due to its high functional group tolerance, we used thiol-ene chemistry to incorporate imidazoles into addressable networks. Linear dithiols were modified with vinyl imidazole to yield mono and disubstituted monomers. The monomers were then reacted with various metal salts to form crosslinked networks. In the case of the mono substituted thiol-enes, a secondary linear ene was introduced to form the complete network. Differential scanning calorimetry and rheologic measurements were taken to understand the effect of different metals on the network properties. Positron annihilation lifetime spectroscopy was used to probe the free hole volume changes due to the different crosslinks, while dynamic mechanical analysis probed the self-healing properties of the various networks. This research opens up perspectives for polymeric membranes increased use lifetime, thereby decreasing polymeric waste.

Reaction schematic showing metal coordination with difunctionalized imidazole monomer to form complexed network.
Analysis of print parameter effects on interlayer adhesion of semi-crystalline polymers processed using fused-filament-fabricated parts

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Parts manufactured via Fused Filament Fabrication (FFF) are subject to particular mechanical vulnerability in the z-axis. Enhanced diffusion of polymer chains between layers shortly after extrusion dictates the extent of interlayer adhesion for which controllable parameters such as print speed and temperature significantly affect. Elucidating patterns in interlayer adhesion and macroscopic characteristics such as overall crystallinity with respect to print parameters will allow for optimization of FFF manufactured parts. Specifically, there is a lack of available research focusing on print parameter effects on interlayer adhesion of semi-crystalline polymers which provides the impetus for our research.

Annular rectangles with single-extrusion-walls were printed at different print speed and temperature combinations using polylactic acid (PLA) (low degree of crystallinity) and polypropylene (PP) (a higher degree of crystallinity). Samples were subjected to trouser tear testing to directly measure interlayer adhesion force and energy and differential scanning calorimetry (DSC) to measure degree of crystallinity. Multiple replicates at a specific treatment were printed to evaluate the precision of the applied trouser tear tests and DSC.

PLA samples printed at a constant speed showed an increase in adhesion energy as the temperature increased from 190 to 210°C. Furthermore, adhesion energy was found to decrease marginally as the print temperature increased from 210 to 230°C. The increase in adhesion energy with respect to print temperature is consistent with the notion that existing layers remaining above the glass transition contributes to better interlayer diffusion. The data suggest that interlayer adhesion of PLA has little dependence on print speed. Degree of crystallinity data was found to fluctuate over a wide range for samples of the same treatment. This high variability would suggest that print conditions have minimal effect on the overall crystallinity of the FFF printed part of polymers having a low degree of crystallinity.

Simplified depiction of FFF, left, and adhesion energy as a function of print temperature at constant print speed, right.
Study of ideally dispersed carbon based nanofiller effects on nylon 6 polymer material properties using molecular dynamics

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The enhancement of polymer properties through the addition of carbon nanofillers is an effective method to improving polymer performance. The addition of carbon nanotubes (CNTs), graphene, and carbon nanofibres (CNFs) to polymers have been shown to reinforce the material properties of some polymers, resulting in potential applications for ballistic resistance. Further, research has shown that CNT can form complexes with graphene, improving the material properties of the final complex and enhancing interactions with a polymer matrix. However, these carbon nanofillers agglomerate within polymer matrices, limiting the effectiveness of the nanofiller, and are further limited by weak interactions with most polymers. This research uses molecular dynamics (MD) to examine the effects of ideally dispersed carbon nanofillers within nylon 6 polymer, a lightweight, common material, on the material properties of the resulting nanocomposite to isolate the potential of carbon nanofillers as enhancers of polymer matrices independent of agglomeration limitations. Weight percentages of carbon nanofillers from 0-5% are studied and the potential of the nanofillers is examined when under ideally dispersed conditions. Results indicate that interactions are an equally significant factor in optimal reinforcement of a polymer matrix as improvements plateau at higher weight percentages of nanofiller.
Synthesis of sterically hindered pyridine containing semi-fluorinated polyelectrolyte membranes with high peroxide resistance

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A novel array of copolytriazoles PYFTSH-XX, with semifluorinted structure in both hydrophilic and hydrophobic unit, were synthesized exploiting a novel trifluromethyl (-CF₃) functionalized diazide monomer with flexible aromatic ether moiety in order to get enhancement simultaneously in both peroxide resistance and proton exchange property. These polytriazoles were synthesized by azide-alkyne cycloaddition polymerization of a novel per-fluro dialkyne monomer mixing with a newly synthesized trifluromethylated ortho-blocked pyridine containing diazide; with or without a sulfonated diazide monomer. NMR (¹H, ¹³C, and ¹⁹F) with FTIR studies approved the synthesis of polytriazoles with a quantitatively controlled variation in percentage of sulfonation. The membranes proved to possess high chemical, thermal durability and high tensile properties. Addition of -CF₃ and sterically hindered pyridine units in polymer structure, with both ortho positions blocked, proved to play an important part in raising peroxide resistance by selective quenching of radicals, which was established by FTIR and pulsed EPR spectroscopy. The existence of pyridine unit in polymer structure also boosted proton conductivity owed to weak basicity of pyridine. HR-TEM and AFM micrographs of the specimens proved the creation of phase separation in morphology and that appeared extra prominent with the upsurge in the percentage of sulfonation. The membrane prepared from PYFTSH-90 displayed 139 mS cm⁻¹ as proton conductivity at 80 °C (fully hydrated condition), which is comparable to Nafion®-117 under similar testing condition.

Figure: (a) HR-TEM image of PYFTSH-80; (b) FTIR spectra of PYFTSH-80 and O-PYFYS-80 (after half oxidation life in Fenton’s solution).
Transient modeling of PEDOT:PSS based organic electrochemical transistors

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Understanding the working principles of artificial synaptic devices is crucial for neuromorphic computing and the hardware of artificial neural networks. As an emerging class of synaptic devices, organic electrochemical transistors (OECTs) have attracted significant interest due to ultra-low voltage operation, analog conductance tuning, flexibility, and biocompatibility. However, little work has been focused on the first-principle modeling of OECTs' synaptic behaviors. The simulation study on OECTs synaptic behavior is of great importance to understanding OECT working principles as neuromorphic devices and optimizing ultra-low power consumption neuromorphic computing devices. We developed a 2D transient drift-diffusion model based on phase separation in PEDOT:PSS and qualitatively reproduced OECTs' typical transistor characteristics. More importantly, typical synaptic phenomena, such as excitatory/inhibitory postsynaptic current (EPSC/IPSC), paired-pulse facilitation/depression (PPF/PPD), short-term plasticity (STP) are demonstrated. This work is crucial in guiding experimental exploration on neuromorphic computing devices and has the potential to serve as a platform for future OECT device simulation for a wide range of semiconductor materials.

Schematic representation of the synaptic OECT in analogy to a biological synapse.

EPSC respond to a train of 1k Hz presynaptic pulses, representing synaptic behavior of an OECT
Amphiphilic star polypeptoides as nanomeric vectors in mucosal drug delivery

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Mucosal delivery across the gastrointestinal tract, airway, and buccal epithelium is an attractive mode of therapeutic administration, but the challenge is to overcome mucus- and epithelial barriers. Degradable star polypept(o)ides can permeate both barriers and they are promising biomaterials for mucosal delivery. Star polypept(o)ides were obtained by initiation of benzyl-L-glutamate N-carboxyanhydride (NCA) from an 8-arm polypropylene dendrimer, with subsequent chain extension with sarcosine NCA. The hydrophobic poly(benzyl-L-glutamate) block length was maintained at 20 monomers, while the length of the hydrophilic poly(sarcosine) block ranged from 20 - 640 monomers to produce star polypept(o)ides with increasing hydrophilic : hydrophobic ratios. Transmission Electron Microscopy (TEM) images revealed elongated particles of ~120 nm length, while Dynamic Light Scattering (DLS) provides evidence of a decrease in the size of polymer aggregates in water with increasing poly(sarcosine) block length, with the smallest size obtained for the star PBLG\textsubscript{20}-b-PSar\textsubscript{640}. Fluorescein isothiocyanate (FITC)-conjugated PBLG\textsubscript{20}-b-PSar\textsubscript{640} permeated artificial mucus and isolated rat mucus, as well as rat intestinal jejunal tissue mounted in Franz diffusion cells. A permeability coefficient ($P_{\text{app}}$) of 15.4 ± 3.1 x 10\textsuperscript{-6} cm/sec for FITC-PBLG\textsubscript{20}-b-PSar\textsubscript{640} was calculated from the flux obtained with apical-side addition of 7.5 mg polypept(o)ide to jejunal tissue. The $P_{\text{app}}$ could not be accounted for by flux of unconjugated FITC. Exposure to trypsin demonstrated enzymatic stability of FITC labeled polypept(o)ide over 2 h, but enzymatic degradation at the mucus-epithelial interface or during flux cannot be ruled out as contributing to the increased $P_{\text{app}}$. The absence of any histological damage to the jejunal tissue during the 2 h exposure suggests that flux was not associated with toxicity.
Modification of inverse vulcanized polymers

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As a byproduct of the refinement of crude oil, millions of tons of sulfur are created each year. With sulfur in relatively low demand, large stores of sulfur are available and inexpensive. A method has recently been developed called inverse vulcanization that uses sulfur to initiate polymerization by breaking open the sulfur ring to form radicals at high temperatures. Here the polysulfide was made by combining sulfur and divinylbenzene (DVB) for 30 minutes at 185°C. However, inverse vulcanization does have drawbacks including high temperature synthesis, monomers must be miscible with sulfur, and low polymer solubility. These polysulfides can be reduced to form polythiols using sodium borohydride and can then be used in thiol click reactions in order to alter the polymer structure and introduce new properties. In prior studies, a protecting group was needed to form polythiols due to the reactivity of thiols, but with poly(S-DVB) the synthesis is relatively simple and does not require the use of a protecting group. Studies were done on the formation of polythiols from poly(S-DVB) with of 30 to 70% sulfur. Poly(S-DVB) was reduced using 1:2, 1:4, 1:8, and 1:16 ratio of NaBH₄: polymer. All polymers were characterized using NMR and IR to look for the presence of thiols as well as GPC to determine the effects of the reduction on polymer molecular weight. The reduced polythiols were modified by thiol-click reactions with small molecules. Successful product formation was confirmed with IR and NMR. The ability to easily modify these polymers will increase their utility of use in future applications.
High grafting density polymer brush growth from a switchable inimer coating for SI-ATRP and SI-RAFT

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We expand the monomer scope of our universal approach to grow high grafting density polymer brushes from a variety of substrates by switching atom transfer radical polymerization (ATRP) initiating sites to chain transfer agent (CTA) sites for surface-initiated reversible addition-fragmentation chain-transfer (SI-RAFT) polymerization. We previously developed an ultrathin, single-component inimer coating made of a copolymer of ATRP inimer and glycidyl methacrylate (GMA). The copolymer is spin-coated and thermally crosslinked into a 5 nm inimer coating. This coating is then used for SI-ATRP of high-density polymer brushes. In this work we demonstrate that the ATRP initiator can be efficiently switched to RAFT initiator after crosslinking of the film to enable SI-RAFT, while maintaining density of the brushes, uniformity of grafting sites, and predictable chain length. Hence, monomers such as vinyl pyridines that cannot be easily grown by SI-ATRP can now be grown by SI-RAFT, vastly expanding the monomer scope. We further exploit this chemistry to grow A/B mixed polymer brushes via SI-NMP and SI-RAFT, from a coating composed of a copolymer of ATRP inimer, NMP inimer and GMA. Unlike growth of polymer brushes via self-assembled monolayer of initiators, the inimer coating results in a high grafting density of >0.7 chains/nm². We study the resulting morphology in a high chi A/B mixed brush system.
PANI/MWNTs thermoelectric generator for energy generation applications

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The conjugated polymers possess electrical conductivity, lightweight, accessibility, non-toxicity, and low thermal conductivity. Therefore, they can potentially serve as thermoelectric materials, where thermal energy is directly converted into electricity. Carbon nanotubes are often used to form thermoelectric composites with conjugated polymers due to the synergistic effect, i.e., π-π stacking, between them. Herein, we report polyaniline (PANI) and multiwalled carbon nanotubes (MWNTs) as inexpensive thermoelectric materials. The in-situ polymerization took advantage of the π-π interaction between PANi and MWNTs and optimized their interface with locally aligned molecular chains (Figure 1a.) to reach a high power-factor and improved mechanical robustness. We optimized the processing parameters such as the mixing ratios, the thermodynamics, the pressing weight percentage during device making, and the number of gills for one thermoelectric generator. We also measured the thermoelectric efficiency for powering wearable sensors. This study sheds light on mitigating the energy crisis with waste energy recovery and promotes health monitoring, wearable electronics, and Internet-of-things with body temperature harvesting and its wide adaptability.
Design of tartaric acid-based amphiphilic macromolecules as neurodegenerative nanotherapeutics

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Tartaric acid is a naturally occurring sugar-like molecule that has been utilized to make biocompatible and bioactive materials. Tartaric acid-based amphiphilic macromolecules (AMs) can be synthesized by incorporating hydrophobic side chains and hydrophilic polymer tails, and used as shell molecules for nanoparticle (NP) fabrication. Such AM NPs can reduce α-synuclein (ASYN) oligomer formation in microglia via a receptor-mediated pathway, making them potential therapeutics against neurodegenerative diseases such as Parkinson’s and Alzheimer’s.

In this work, a new class of tartaric acid-based AMs are presented and discussed. We modify the tartaric acid backbone with different aliphatic side chains and hydrophilic polyethylene glycol tail lengths. NPs made using different AM shell structures are screened for their bioactivity in binding CD36 receptors and therefore modulating ASYN-induced microglial activation. Hydrophobic cores are also encapsulated in the NPs to enable formation of NPs and strengthen NPs’ bioactivity. Studies of the structure-property relationships of the NPs will offer insights to further guide the design of enhanced therapeutics against neurodegenerative diseases.
Design and synthesis of functional star-shaped polypeptides as (nano)medical devices for therapeutics delivery

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There is an emerging need for the development of new biomaterials that will be used as platforms in the delivery of therapeutic cargoes. For this purpose, different types of polymers have been developed as biodegradable and biocompatible materials. One such class of materials are the synthetic polypeptides. They are built from amino acids, which makes them bio-derived, biodegradable and biocompatible. Synthetic polypeptides contain the structural motifs of natural proteins such as α-helical, β-sheet, as well as random coil elements. These polymers are capable of self-assembly, which ensures their stability. Synthetic polypeptide structures are synthesized via Ring Opening Polymerisation (ROP) of amino acid N-carboxyanhydrides (NCA). ROP permits obtaining high yield polypeptides with improved properties and with well-defined structures.

The objective of this study was to synthesize and characterize star-shaped polypeptides consisting of different generations 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) dendritic cores and linear polypeptide chains attached to the core. A series of well-defined star-shaped polypeptides were successfully obtained by ring-opening polymerisation of ε-carboxbenzyloxy-L-lysine(ZLL) NCA, initiated by ammonium salts groups of bisMPA dendrimers. Polypeptides with different numbers of arms, in which the number of amino units per arm were 5 and 10, were synthesized by varying dendrimer generation and adjusting the monomer feed ratio of ZLL NCA. The reactions were monitored by FT-IR spectroscopy, until completion. The structure and composition of synthesized polypeptides were examined by \textsuperscript{1}H and \textsuperscript{13}C NMR analyses, while their molar mass and molecular weight distribution were determined by gel-permeation chromatography (GPC).
Synthesis of alternating degradable metathesis polymers with ruthenium Fischer carbenes

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Ring-opening metathesis polymerization (ROMP) has become one of the most efficient methods to construct olefinic polymers carrying an impressive range of functionalities, but the obtained materials are usually persistent in the environment due to all-carbon backbone. In this poster, the ability of Fischer-type carbenes to participate in cascade alternating metathesis polymerization is leveraged to generate poly(enol ether)s. These ruthenium complexes have rarely been demonstrated as active species in metathesis reactions and are frequently regarded as inert species in ring-opening metathesis polymerization. When enyne monomers are combined with low-strain cyclic vinyl ethers, a chain-growth copolymerization occurs that exhibits high degrees of alternation (>90% alternating diads) and produces degradable polymers decorated by hydrolytically labile enol ether backbones with low dispersity and targetable molecular weights. Also, this methodology is amenable to the synthesis of alternating diblock polymers that can be degraded into small-molecule fragments under aqueous acidic conditions. This work furthers the potential of Fischer-type ruthenium alkylidenes in polymerization strategies and presents new avenues for the generation of functional metathesis materials.

facile Fischer carbene addition to alkyne

living polymerization • >90% alternating diads • degradable
Synthesis and applications of unique $\pi$-conjugated polymers containing $\pi$-extended fused metallacycle units

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For the synthesis of $\pi$-conjugated polymers containing heteroatoms, reactive organometallic polymers may serve as useful synthetic precursors. We have been working on the synthesis of titanacyclopentadiene-containing polymers by the reaction of aromatic diynes and a low-valent titanium complex. Considering the advantages of fused ring systems such as more effective $\pi$-conjugation and narrower HOMO-LUMO gaps, here we describe the synthesis of titanacycles with fused ring systems and polymers containing the corresponding units.

A titanafuorene derivative (i.e., dibenzotitanacyclopentadiene) was obtained as orange crystals by the lithiation of 2,2'-diiodobiphenyl using n-BuLi followed by the reaction with titanocene dichloride. Likewise, a dithienotitanacyclopentadiene, in which two thiophene rings are fused with the titanacyclopentadiene unit, was obtained as green crystals from 3,3'-dibromothiophene. Arylene dihalide monomers possessing the corresponding units were also obtained with modifications and were subjected to the Sonogashira-Hagihara coupling polycondensation with 1,4-di(octyloxy)-2,5-diethynylbenzene in the presence of a palladium catalyst to give the objective poly(arylene ethynylene)s containing titanafuorene and dithienotitanacyclopentadiene units in the $\pi$-conjugated main chain. Unlike titanacyclopentadiene-containing, the fused tianacycle-polymers relative proved to be stable under air at ambient temperature that provided us a chance to explore functions and applications of the polymers. The unique optical and electronic properties of the resulting polymers will also be described.

Synthesis of Polymers Containing Fused-Heteroles Titanacyle Units
Effect of regioisomer ratios on physical properties of poly(bicyclohexyldimethylene) terephthalate

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Melt polymerization facilitated the synthesis of a series of novel polyesters composed of dimethyl terephthalate (DMT) and various ratios of two bicyclohexyldimethanol (BCD) regioisomers, 3,4′-BCD and 4,4′-BCD. Proton nuclear magnetic resonance spectroscopy (¹H NMR) confirmed successful incorporation of all monomers into the polymer backbone. The materials exhibited high thermal stabilities as evidenced by a consistent T_d,5% around 390 °C. Further thermal studies using differential scanning calorimetry (DSC) revealed a close correlation between regioisomer content and polymer morphology. Polymers comprising 80% or higher 4,4′-BCD content were semi-crystalline with melting temperatures ranging from 142 to 216 °C, while materials with less 4,4-BCD were amorphous. Density studies showed a direct correlation between amorphous density and 3,4-BCD content, which also corresponded to young’s moduli. Dynamic mechanical analysis (DMA) revealed sub-T_g β-relaxations with similar intensities for all polymer compositions, suggesting that energy absorption at low temperatures is influenced by the unsaturated rings in the BCD diol. Tensile mechanical testing indicated the longest elongation at break (34%) for the 50% composition of both regioisomers, while considerably less elasticity was observed for the homopolymers of either regioisomers with elongations at break <5%.
Glycosylated nanoparticle by SET-LRP PISA

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Once introduced into a biological environment such as blood, nanoparticles (NPs) tend to adsorb proteins onto their surface creating a layer known as the protein corona, this ultimately changes their surface identity. Furthermore, it is well known that carbohydrates are overexpressed on the surface of cells, and are involved in many biological processes such as cell-cell recognition.

Glycopolymers are synthetic polymers bearing carbohydrate units which maintain their binding efficiency with glycan binding proteins, such as lectins, thus they gained attention in recent decades as promising candidates to study carbohydrate-protein interactions. This work aims in the preparation of mannosylated nanoparticles for the evaluation of targeted protein affinity. Polymerization-induced self-assembly (PISA) in disperse media was employed as polymerization technique allowing the in situ self-assembly of a glycosylated macroinitiator.

Herein, we describe the novel synthesis and analysis of glycosylated NPs utilizing single electron transfer living radical polymerization induced self-assembly (SET-LRP-PISA). Poly(ethylene glycol methacrylate)-statistical-poly(propargyl methacrylate) (PEGMA-s-PPgMA) was obtained by conventional atom-transfer copolymerization (ATRP), and was subsequently glycosylated via copper catalysed alkyne-azide cycloaddition (CuAAC), utilising two different azo-mannosides derivatives with differing linker lengths. The glycosylated macroinitiator was then chain extended with 2-hydroxypropyl methacrylate (HPMA) via SET-LRP, which induced self-assembly, yielding mannosylated NPs. Manosylated NPs were analysed by dynamic light scattering (DLS) and transmission electron microscopy (TEM) in order to determine their size and morphologies.
Bacterial production of polyhydroxyalkanoates using horse manure hydrolysate as carbon source

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The excessive usage of petroleum-based plastics has left a detrimental impact on the environment, jeopardizing the future of our planet. In this regard, an eco-friendly substitution of such plastics is of high demand for consumers, industry, and regulators. Biopolymers, which are produced by living organisms, can offer advantages over commercial plastics by their biodegradability and biocompatibility. Among the list of biopolymers, polyhydroxyalkanoates (PHAs) have emerged as potential candidates for this purpose owing to their superior physiochemical properties. However, sustainable production of PHAs is limited due to the high production costs, especially fermentation process. To address this issue, researchers have been focused on utilization of abundant and cost-effective nutrition and carbon sources from agricultural to food and biodiesel industry wastes. Here in, we demonstrated the possibility of using horse manure hydrolysate (HMH) as a carbon source for sustainable bioproduction of polyhydroxybutyrate (PHB) using an engineered strain of E. coli harboring necessary genes—that is—phaCAB. Our studies demonstrate no significant growth inhibition of HMH in culture medium indicating successful elimination of toxic compounds (e.g., furfural). The composition of HMH was studied and Xylose was found as the dominant sugar. In addition, the amount of PHB isolated from bacteria using HMH as the carbon source was similar to that of control, in which glucose was used.

Schematic representation of Redox-responsive drug release in cancer cell
Structural investigation of modified and unmodified polyethyleneimine polyplexes

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Due to high cytotoxicity, endosomal degradation, and aggregation on cell surfaces encountered with gene delivery particles condensed by unmodified branched PEI, chemical modification has been a common strategy to enhance performance. In this work, we have synthesized a series of succinylated (zPEI, 2-35%) and acetylated (acPEI, 10-50%) branched polyethyleneimine (bPEI) polymers to better understand how modulating PEI charge affects both the DNA packaging inside the polyplexes as well as the gene delivery efficacy in vitro. Acetylation decreases the number of protonated amines on the bPEI reducing the PEI charge density, while succinylation introduces COO⁻ groups to produce zwitterion-like PEI (zPEI). Both acPEI/DNA and zPEI/DNA are capable of condensing DNA and form similar colloidal nanoparticles that are observed to have comparable polyplex diameters as measured by nanoparticle tracking analysis (NTA) and ζ-potential for all but the highest degrees of modification studied. While acPEI and zPEI have been shown improvement under serum-free conditions, we show that only zPEI shows greatly enhanced transfection efficacy in vitro in the presence of serum. Using small-angle X-ray scattering (SAXS), we also investigated the internal structure of DNA condensed with zPEI and acPEI polymers and compared to unmodified bPEI/DNA. As the degree of acetylation increases, the packaging density decreases in a linear fashion. Succinylated PEI is also observed to decrease packaging density at low degrees of modification, but, surprisingly, leads to increased packaging density at higher degrees of modification. Polyplexes in cells have been shown to experience a decrease in pH as particles are transported along the endosomal-lysosomal pathway. The interior of lysosomes (pH ~4.5-5.0) is considerably more acidic than the cytosol (pH~7.2). To mimic these cellular conditions, we also examined the DNA packaging of our polyplexes as a function of pH. For all three systems, tighter DNA packaging results when samples are condensed at pH 4 compared to pH 7.5. Both PEI modifications result in higher pH sensitivity with zPEI/DNA having the largest difference in packaging density as a function of pH. Lastly, we show that condensing DNA at pH 7.5 and then moving to pH 4 also results in tighter DNA packaging over the course of several hours. Together, our results give insight into how modifying PEI alters polymer-DNA interactions and its connection to enhanced gene delivery in vitro.
Capsules of ionic liquid prepared from pickering emulsion templates stabilized by graphene oxide and its derivative

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This research focuses on fabricating capsules of ionic liquid (IL) stabilized by graphene oxide (GO) and its derivative through interfacial polymerization at the fluid-fluid interface in Pickering emulsions. GO nanosheets and primary alkyl amine functionalized GO nanosheets were used as surfactants to prepare different types of IL-containing Pickering emulsion templates. Capsules with GO/polyurea hybrid shell were successfully prepared in which IL was wrapped. We explored the impact of monomer identity on the formation of capsule shells and vary the kind of IL used and thereby produce capsules with varied compositions. Optical microscopy, scanning electron microscopy, FTIR spectroscopy, and NMR were used to evaluate morphology and gain structural information. These tailored IL capsules showed great contaminant removal efficiency.
Amphiphilic block copolymers with DASA junctions

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Introduction of preselected functional units at the junction of block copolymers, while relatively unexplored in comparison to other polymer functionalisation methods, has been a valuable and efficient method for designing novel polymer architectures and stimuli-responsive systems. This is especially pertinent in the case of amphiphilic systems, where phase separation and self-assembly can create molecular thin layers of the stimuli-responsive unit, allowing for any physical/chemical alteration of the functional unit to have a profound effect on the entire polymeric system. Block copolymers with functional junctions have been applied to generate complex polymer architectures, as cleavable units for controlled release in supramolecular assemblies, improved electronic cascades in conductive polymers, and to alter diffusion properties of nanoassembly membranes. Our work involves the development, and study of, Donor-Acceptor Stenhouse Adducts (DASAs) at the junction of amphiphilic block copolymers. DASAs are a new class of photoswitches that DASAs undergo a reversible, coloured to colourless, linear to cyclic isomerisation under irradiation with visible light which is accompanied by a polarity switch from hydrophobic to hydrophilic. By establishing a modular synthesis strategy, we can incorporate DASAs into various block copolymer systems. Alternatively, employing hexafluoroisopropanol as a catalytic cosolvent allows us to form block copolymers through the DASA reaction itself. Future aims involve exploiting the tunable wavelength of absorption, polarity and conformational switching of DASAs in the junction of amphiphilic block copolymers in nanoscale assemblies such as polymersomes to afford novel controlled release systems and light-responsive nanoreactors/bioreactors, as well as to and probe the mechanophore potential of DASAs.
Waste fish oil for the production of greener polyurethane materials

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Polyurethanes are oil-based synthetic polymers frequently used in the manufacture of various materials such as synthetic fibres or hard plastics. Traditionally, polyurethanes are synthesized by reacting polyols with isocyanates, both derived from crude oil, to form the urethane linkage. Along with depleting our natural resources, this process can be toxic to both humans and the environment. Phosgene, a toxic gas, is used to make the required isocyanates and can cause negative health effects. Isocyanates themselves are also considered toxic, and therefore the production of polyurethanes requires high levels of safety measures. Even with low levels of biodegradability, small amounts of polymer degradation can lead to the formation of carcinogenic aromatic amines released into the environment. These safety, toxicity, and biodegradability issues have led to the need for safer and greener alternatives to polymer synthesis.

In this presentation, we will discuss greener methods to produce polyurethane materials. Previous synthetic routes have avoided the use of isocyanates by incorporating plant-based oils into the process. However, using these oils for polymer synthesis can compete with food production. Our research incorporates fish oil derived from aquaculture waste, a biomass-derived material that does not compete for land space. It was found that capelin-herring fish oil or fish oil extracted from salmon offal can be epoxidized and reacted with CO₂ to form carbonated fish oil, which can then form a non-isocyanate polyurethane material (NIPU) from a reaction with a diamine. Biodegradability studies were performed on the resulting films under enzymatic conditions to determine the level of degradation the polymer would undergo, and Scanning Electron Micrographs suggest high levels of degradation. Further improvement of the synthetic process was then attempted by screening the reactivity of biocompatible amino acids in the crosslinking process. L-histidine, L-glutamine, and L-asparagine were chosen and tested for a reaction with the carbonated fish oil via Differential Scanning Calorimetry. Results show an exothermic reaction between the carbonated fish oil and the L-histidine, showing the potential of a crosslinking reaction to form a NIPU.
Mechanochemical living anionic polymerization with solid state initiator using ball mill

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Living anionic polymerization is a one of powerful and practical tool for synthesizing polymers. This polymerization is well established for many monomers without chain transfer or termination. Thus, living anionic polymerization systems were developed for precise and complex architecture polymers synthesis. However, most studies were conducted under the solution and bulk systems. Usually, anionic polymerization is difficult to handle because it is a highly reactive species (carboanion) under solution or bulk conditions. Therefore, anionic polymerization requires the purification of solvent, inert conditions, and low temperatures. For this reason, our interests are developing living anionic polymerization under ball-milling conditions for simple methods and without solvent.

In this presentation, we will discuss the development of anionic polymerization using mechanochemical transformation under ball-milling conditions. Recently, We have been conducting anionic polymerization using a solid-state initiator for the vinyl derivative (styrene, methyl methacrylate) under ball-milling conditions at room temperature without solvent. As a result, We have obtained a polymer through anionic polymerization using a ball mill. In particular, this method has the advantages of simple experimental operation and without solvent compared to solution reaction. The details of the experiment will be discussed in the poster presentation.
Sustainable approaches to ring-opening polymerizations and post-polymerization modification
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Plastic has become an essential part of modern society, but due to the indisputable environmental drawbacks of petroleum products, it has become increasingly pertinent to shift to renewable plastic feedstocks. Although recent advances in organic synthesis have successfully produced elastomers from monomers deriving from mint, tulips, and vegetable oils, these feedstocks provide limitations in consideration for consumer demand due to their variations from petroleum counterparts both in lifespan and durability. An experimental response to this is post-polymerization modification which allows for the synthesis of polymers with greater characteristic control and property diversity through chemical crosslinking. This research focuses on a model study with the compound limonene, derived from citrus peels, for designing a more efficient process of polymer chain modification via photolysis and a ruthenium catalyst. The findings detailed in this research elucidated the effective and consistent modification of limonene with functionalized thiols utilizing a blue LED light source. NMR characterization revealed that the modification of limonene produced effective and consistent results within a 12 hour stir period.
Universal coating strategy for controllable functionalized polymer surfaces

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Development of a universal and stable surface coating, irrespective of surface chemistry or material characteristics, is highly desirable but has proved to be extremely challenging. Conventional coating strategies including the commonly used catechol surface coating are limited to either a certain type of substrates or weak and unreliable surface bonding. Here, we proposed and demonstrated a simple, robust, and universal surface coating method capable for attaching any stimuli-responsive glycidyl methacrylate (GMA)-based copolymer, consisting of one surface-adhesive moiety of epoxy groups and one stimuli-responsive moiety, to any type of hydrophobic and hydrophilic surfaces via a one-step ring-opening reaction. The resultant GMA-based copolymers not only strongly adhered on different substrates (e.g., silicon, polypropylene, polyvinyl chloride, ITO, polyethylene terephthalate, aluminum, glass, polydimethylsiloxane, and even polyvinylidene fluoride with low surface energy), but also possessed distinct thermal-, pH-, and salt-responsive functions of bacterial killing, bacterial releasing, tunable multicolor fluorescence emission, and heavy metal detection. This coating method is also compatible with the directional quaternization of GMA-based copolymers for further improving surface adhesion and functionality. This study provides a simple yet universal coating method to solve the long-standing challenge of robust integration of stimuli-responsive polymers with strong adhesion between various polymers and substrates.
Understanding viscosity-scaling relationships of highly charged, anhydrous ionic polymers

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The viscosity and diffusion coefficient of polymers are two of the most important parameters for applications and processing. Scaling relationships as a function of degree of polymerization (N) are well-characterized in neutral polymers, but many current and emerging applications in polymer science involve ionic charges including electrolytes, coacervates, and membranes. We have synthesized fluorescently-labeled polymerized ionic liquids (f-PILs) with a broad range of molecular weights to understand scaling relationships in dry, ionic polymers with a charge on every repeat unit. Fluorescence recovery after photobleaching (FRAP) is used to measure polymer self-diffusion coefficients (D) using the post-bleached fluorescence images and fitting the intensity to a Gaussian profile over time. The zero-shear viscosity was measured via rheology. In the shortest f-PILs, the ionic interactions between imidazolium and bis(trifluoromethane sulfonamide) have little effect on extending the terminal regime. However, the terminal region did extend to lower frequencies as N increased. Interestingly, the wide-angle x-ray scattering shows an amorphous halo and anion-anion peak, but no longer range ionic aggregate peak which we assign as the origin of the rheological behavior. Scaling relationships show the same dependence, 1/N, as in neutral polymers in contrast to some literature reports. Diffusion coefficient scaling will also be discussed.
Design considerations for a graft-through copolymerization

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Precise control of branching in synthetic polymers represents an essential tool for manipulating material properties. Of the branched polymer structures that can be readily synthesized, a graft molecular architecture is one of the simplest to produce yet offers a rich design space through the control of grafting density, side-chain molecular weight, and backbone molecular weight. The ability to precisely tune these parameters has attracted much interest in the polymer synthesis community in recent years. The work reported here expands on the current understandings of a graft-through synthetic approach. Specifically, we investigate how the chemical structure and initial feedstock composition in Ring Opening Metathesis Polymerization (ROMP) affects the copolymerization kinetics of a macromonomer and small molecule comonomer and, therefore, the statistical distribution of side-chains along a polymer backbone. To characterize the copolymerization kinetics, terminal and non-terminal models were applied to monomer conversion data collected via nuclear magnetic resonance spectroscopy. Our findings point to a complex correlation between macromonomer molecular weight, monomer chemistry, and the initial feedstock composition, regarding the effects that these parameters have on the statistical distribution of side chains along a graft polymer backbone. These findings elucidate fundamental design principles that must be considered when using a graft-through copolymerization.

Figure. Macromonomer reactivity ratios as a function of molecular weight and initial feedstock composition (i.e., grafting density). Results shown are from non-terminal model fits.
Ring-opening polymerizations of cyclic esters by a genuine H-bond donor and Lewis base amine cocatalyst

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Hydrogen bond donor (HBD) and organic base binary cocatalyst established a gold standard in organocatalytic ring-opening polymerizations (ROPs). In depth probe of the mechanisms revealed that proton abstraction of the acidic H on the HBDs by the bases do occur frequently. However, a truly simple HBD and Lewis base (LB) cocatalysis was elusive. We proposed a genuine HBD/LB cocatalyst for ROPs by introducing 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) as a bidentate H-bond donor and triethylamine (TEA) as a mild Lewis base. ROPs of lactide (LA) and trimethylene carbonate (TMC) in solutions at room temperature were success. The mild ROPs produced polylactide (PLA) of predictable molecular weights (from 1.6 to 26.7 kg mol\(^{-1}\)) and extremely narrow dispersities (from 1.01 to 1.06). The controlled and 'living' nature of the ROP was supported by \(^1\)H NMR, \(^{13}\)C NMR, and MALDI-ToF MS, kinetic studies and chain extension experiments. Well-defined diblock copolymers, PTMC-b-PLA, were synthesized successfully with predictable molecular weight and extremely narrow dispersity. Furthermore, NMR titration experiments verified exclusive H-bond donor activation of the monomer and TEA activation of the hydroxyl chain end without trace of proton abstraction. ABTD/TEA binary catalytic system has paved a mild, cheap, and effective avenue to ring-opening polymerization through genuine HBD/base catalysis as original designed.