ACS Division of Polymer Chemistry

Graphical Abstracts

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

August 2023
The POLY Programming Team is here to create a well-rounded ACS National Meeting polymer program, provide guidance, and assist session organizers and presiders. Your input on future session topics and suggestions on improved programming techniques will help us reach this goal. Interested organizers are encouraged to complete the “PROPOSE A SYMPOSIUM” form online. https://polyacs.org/symposium-proposal-landing-page/

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POLY believes in the strength of diversity in all its forms because the inclusion of and respect for diverse people, experiences, and ideas leads to superior solutions to world challenges and advances polymer chemistry as a global, multidisciplinary science.
# 2023 Fall ACS National Meeting – POLY Sessions

POLY Sessions will be held in the San Francisco Marriott Marquis, San Francisco, CA. – Check the ACS app for the latest schedule and location!

## POLY SESSIONS ROOM LOCATOR - 2023 Fall ACS National Meeting

**Symposium Title & Dates**

### 6th CME NASA Symposium: Advancing Materials for Space Exploration: Monday & Tuesday, Nov 6-7, Moscone Center, Hall F 3rd Floor

<table>
<thead>
<tr>
<th>Location</th>
<th>Presentation</th>
<th>Date/Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mon Salon 7</td>
<td>ACS Award in Pure Chemistry in Honor of Julia Kafle</td>
<td>Wed Nov 8</td>
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<td>Wed Nov 8</td>
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<td>ACS Macro Letters/Biomacromolecules/Macromolecules Young Investigator Award</td>
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<td>Marc Milion, Saba Rezaei, Richard Majumder, Stuart Rowan</td>
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<td>Wed Nov 8</td>
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</tbody>
</table>
Table of Contents

6th CME NASA Symposium: Advancing Materials for Space Exploration ....................... Pg. 6
  George Rodriguez, Ksenia Takhistova, Shah Karim

ACS Award in Pure Chemistry in Honor of Julia Kalow................................................ Pg. 40
  AJ Boydston, Ellen Sletten, Bassil El-Zaatari

ACS Macro Letters/Biomacromolecules/Macromolecules Young Investigator Award.... Pg.48
  Marc Hillmyer, Sebastien Lecommandoux, Paulomi Majumder, Stuart Rowan

Big Data in Polymer Chemistry ..................................................................................... Pg. 57
  Kaoru Aou, Debra Audus, Adam Gormley, Abigail Knight, Bradley Olsen, Ardiana Osmani, Kenneth Kroenlein

Biorelated Polymers in Honor of Dr. Ray Ottenbrite...................................................... Pg. 79
  Joerg Kressler, Carmen Scholz, Stefanie Sydlik, Kathryn Uhrich

Charles G. Overberger International Prize for Excellence in Polymer Research in Honor
of Uli B. Wiesner ......................................................................................................... Pg. 116
  AJ Boydston, Ellen Sletten, Bassil El-Zaatari

Chemical Recycling and Upcycling of Polymers ......................................................... Pg. 123
  Mark Dadmun, Brett Helms, Brian Long, Tomonori Saito, Brent Sumerlin,
  Jessica Lamb

Circular Economy of Polymers...................................................................................... Pg. 199
  Dimitris I Collias, Martin James, Kat Knauer, Yujing Tan

General Topics: New Synthesis and Characterization of Polymers .............................. Pg. 223
  Alina Alb, Ferenc Horkay, Yongfu Li, Edwin Thomas, Julia Murphy

General Topics: New Concepts in Polymer Characterization....................................... Pg. 341
  Alina Alb, Ferenc Horkay, Yongfu Li, Edwin Thomas, Julia Murphy

General Topics: Ultrahigh Molecular Weight and Network Polymers........................ Pg. 365
  Alina Alb, Ferenc Horkay, Yongfu Li, Edwin Thomas, Julia Murphy

Henkel Award for Outstanding Graduate Research in Polymer Science and Engineering
Honoring Chris Delre................................................................................................... Pg. 395
  Jessica Kramer, Frank Leibfarth, Charles Paul, Ting Xu

Herman F. Mark Award in Honor of Robert Waymouth............................................... Pg. 402
  James Hedrick

Industrial Innovations in Polymer Science................................................................ Pg. 411
  Laura Murdock, Michael Petr, Shrut Venkatram, Rohini Gupta, Peter Boul

Natural Polymers - A Back to the Future Approach to Deal with the Plastics Issues .. Pg. 419
  Jun Wang, Wei Gao, Qiong Yuan

POLY Poster Session ................................................................................................. Pg. 443

POLY/PMSE Plenary & Awards .................................................................................. Pg. 614
  Danniebelle Haase, Robert Mathers, Levi Moore, Sara Orski, Allan Guymon
# Table of Contents

Polymers for Defense Applications: Advanced Polymeric Materials for Innovative Composites ................................................................................................................. Pg. 468  
  Alexander Lonnecker, Dawanne Poree, Timothy Pruyn, Alice Savage, Peter Zarras  
Polymer Mechanochemistry ........................................................................................................ Pg. 504  
  Robert Göstl, Andreas Herrmann, Harm Klok, Jeff Moore  
Simulation and Data Science Approaches to Design Biologically Relevant Polymers and their Applications ......................................................................................................... Pg. 562  
  Logan Bishop, Corinne Lipscomb  
Virtual Graduate Students Symposium in Asia-Pacific Region on Polymer Chemistry Pg. 575  
  Yanli Feng, Dahui Qu, Jia Tang, Chunxiao Zheng  
Young Industrial Polymer Scientist Award in Honor of Hayley Brown ......................... Pg. 605  
  Colin Li Pi Shan, Leslie Oleary
Luminescent coatings for aerodynamic applications - Schanze, Kirk (Oral – Hybrid)

3D printing polyimide aerogels for hierarchical porosity - Cipriani, Ciera (Oral–Hybrid)

Mechanism of porous Se@SiO2 nanospheres inducing cuproptosis in CRPC - Yang, Boyu (Oral – Hybrid)

AeroFusion: Data fusion and uncertainty quantification for entry vehicles - Snyder, Steven (Oral – Hybrid)

NASA’s SIBatt-3D: In-space and on-surface 3D printing sodium-ion batteries from ISRU materials - Sherrard, Cameroun (Oral – Hybrid)

Sorbents for CO2 capture from air - Gurkan, Burcu (Oral – Hybrid)

Development of additive manufacturing technologies for 3D printing of spacecraft heat shields - Boghozian, Tane (Oral – Hybrid)

Parts-per-billion detection of gases and volatiles with hybrid multifunctional nanosensor platform - Sultana, Mahmouda (Oral-Hybrid)

Dynamic networks as a route to access pluripotent materials - Rowan, Stuart (Oral-Hybrid)

Multifunctional structural materials for sustainable human exploration in extreme space environments - Park, Cheol (Oral-Hybrid)

Fast light-switchable polymeric carbon nitride and adsorptive membranes for tunable gas separation - Ashirov, Timur (Oral-Hybrid)

Design of macromolecular radicals for next generation energy storage - Easley, Alexandra (Oral-Hybrid)

Supramolecular sython approach for high capacity electrodes in lithium-ion batteries - Coskun, Ali (Oral-Hybrid)

Toward sustainable organic polymer batteries - Lutkenhaus, Jodie (Oral-Hybrid)

Click chemistry: New directions - Sharpless, Karl (Oral Hynrid)

Sustainable approach to carbon management to enable our energy and economic transition - Douglas, Anna (Oral-Hybrid)

Advanced recycling: Meeting the needs of plastic recycling today and tomorrow - Go, Tony (Oral-Hybrid)

Polymers and their roles in space astronomy - Arenberg, Jonathan (Oral-Hybrid)

Harnessing the power of data through QURIOSITY - Kundsen, Benjamin (Oral-Hybrid)
6th Annual CME Advancing Materials for Space Exploration

Accelerated development of advanced materials for diverse mission needs at Lawrence Livermore National Laboratory - Budil, Kim (Oral-Hybrid)

Panel on advanced technologies - Rodriguez, George (Oral-Hybrid)

CME STEM Leadership Awards Presentation - Rodriguez, George (Oral-Hybrid)

Chemistry beyond gravity: Unlocking the potential of space chemistry for exploration and industry - Batton, Chyree (Oral-Hybrid)

Bioelectronics applications of skin-inspired electronics - Bao, Zhenan (Oral-Hybrid)

Nurturing innovation in sustainability through early stage partnership development at NASA - Gustetic, Jennifer (Oral-Hybrid)

Using lessons learned to create a safer, more sustainable future in space - Barrios, Elizabeth (Oral-Hybrid)

Informatics-driven design of polymers for extreme conditions - Ramprasad, Rampi (Oral-Hybrid)

Plant molecular farming to support human life on the Moon, Mars, and beyond - McDonald, Karen (Oral-Hybrid)

Greenchem innovation: What is next? - Anastas, Paul (Oral-Hybrid)

Polymer structure property with machine learning models - Moebus, Joseph (Oral-Hybrid)

Panel discussion on sustainability - Rodriguez, George (Oral-Hybrid)

Hidden in plain slime: Finding inspiration in mucus for building synthetic biological interfaces - Godula, Kamil (Oral-Hybrid)
Luminescent coatings for aerodynamic applications

Kirk S. Schanze, Kirk.Schanze@utsa.edu. The University of Texas at San Antonio, San Antonio, Texas, United States

During the past several decades interdisciplinary work involving aerospace engineering, chemistry, and materials science has led to revolutionary new methods for flow visualization on aerodynamic surfaces. The methods that have been developed utilize luminescent materials and compounds that are dissolved or dispersed into binders. The luminescence from the coating responds to the environment, resulting in changes in the spectral properties, luminescence decay time, and/or luminescence quantum yield. These changes in luminescence can be imaged using high-resolution and large dynamic range (large bit depth) CCD imagers, giving rise to high-fidelity images of aerodynamic flow characteristics and pressure distributions on aerodynamic objects. This talk will overview the methods that rely on pressure-sensitive coatings, which operate by oxygen quenching of luminescence intensity and lifetime, and temperature-sensitive coatings, which can resolve differences in surface temperature resulting from differences in flow characteristics. The fundamental photochemistry and polymer science underlying the operation of these coatings is described.
3D printing polyimide aerogels for hierarchical porosity

Ciera E. Cipriani, cipriani@tamu.edu. Texas A&M University, College Station, Texas, United States

Polyimide aerogels are of interest for aerospace applications because they are ultralightweight, insulative, and strong. However, methods for producing parts from aerogels are limited, with molding being the most common. To address this, 3D printing is harnessed to create truly custom components. We report a technique for 3D printing polyimide aerogels by incorporating particles into the aerogel precursor sol to produce printable inks. The particles are removable, resulting in hierarchically porous prints with voids on the nano-, micro-, and macroscale.
Mechanism of porous Se@SiO2 nanospheres inducing cuproptosis in CRPC

Boyu Yang, ljcuology@163.com, urology, Beijing, China

Though selenium nano-particles are reported to inhibit tumor growth, the mechanisms are still not clear. Based on our previous work, porous selenium nanocomposites (Se@SiO2) with high biosafety and tumor-targeting properties were synthesized. Se@SiO2 could reduce proliferation and autophagy level in CRPC cells. Furthermore, our results showed that Se@SiO2 could enhance the protein stability of intracellular prostate acid phosphatase (cPAP). As a tyrosine phosphatase, cPAP blocks the initiation of autophagy by promoting ATG14 dephosphorylation, thereby reducing the proliferation of CRPC cells. In addition, three possible tyrosine phosphorylation sites (Y279/Y357/Y488) were identified using site-directed mutagenesis. Accordingly, we hypothesized that Se@SiO2 can inhibit autophagy by activating cPAP-ATG14 signaling axis in CRPC treatment. This study will elucidate the molecular mechanism of Se@SiO2 regulating autophagy through cPAP. Our research provides a new therapeutic option and theoretical evidence for the treatment of CRPC.
AeroFusion: Data fusion and uncertainty quantification for entry vehicles

Steven M. Snyder, steven.m.snyder@nasa.gov. NASA, Washington, District of Columbia, United States

Data science is a hot research area with applications across many fields. AeroFusion is an initiative to leverage advances in data science for the aerodynamic modeling process to improve efficiency. Quicker operational tempos and the need for novel vehicle concepts require the collection of the right data and extracting the most information from it possible. This talk will introduce some of our efforts to connect data science techniques and uncertainty quantification with aerodynamic modeling.
Sustainable on-demand power solutions are an absolute necessity as humanity works to establish a permanent presence on the moon and make the journey to Mars. NASA’s SIBatt-3D project is developing shape-conformable Sodium-Ion batteries that can be 3D printed in-space as needed during extended space missions. SIBatt-3D seeks to utilize materials found in Lunar/Martian regolith as feedstocks to provide sustainable power for surface operations. SIBatt-3D’s batteries also have terrestrial implications such as improved battery safety and sustainability.
Sorbents for CO\textsubscript{2} capture from air

\textit{Burcu Gurkan, beg23@case.edu}. Case Western Reserve University, Cleveland, Ohio, United States

Highly selective materials that are stable under a range of temperature and humidity conditions, and regenerable with minimum energy input are needed for CO\textsubscript{2} capture from air. We developed functionalized ionic liquids and deep eutectic solvents with high CO\textsubscript{2} capacities, negligible volatility, and regenerability with various stimuli. This talk will present the utility of these solvents in new material designs such as capsules and facilitated transport membranes for air revitalization under microgravity. Absorption mechanism, transport, and stability will be discussed.
Development of additive manufacturing technologies for 3D printing of spacecraft heat shields

Tane Boghozian, tane.boghozian@nasa.gov, Adam T. Sidor. NASA, Washington, District of Columbia, United States

Ablative heat shields are an enabling technology for entry into planetary atmospheres. The Additive Manufacturing of Thermal Protection Systems (AMTPS) project, an Early Career Initiative (ECI) funded by NASA’s Space Technology Mission Directorate and led by NASA Johnson Space Center, seeks to develop materials and processes for 3D printing ablative heat shields for spacecraft. Current methods for producing ablative heat shields are extremely labor intensive and require extensive hands-on processes and quality control characterization. Additive manufacturing (AM) offers the possibility of reduced production times, improved reliability, and enhanced performance via graded compositions. Direct integration of the heat shield onto the structure during processing simplifies integration and reduces risk. AM technology will be leveraged to grade the material formulation and properties through the thickness of the heat shield. A partnership with Oak Ridge National Laboratory (ORNL) aims to enable full-scale fabrication of a 3D printed heat shield.

Figure 1: 3D printed coupons (a) before and (b) after arc jet exposure. Material shows excellent ablative performance.

Manufacturing Scale-Up
Parts-per-billion detection of gases and volatiles with hybrid multifunctional nanosensor platform

Mahmooda Sultana, mahmooda.sultana@nasa.gov. NASA, Washington, District of Columbia, United States

In situ measurements of trace gases are crucial for the understanding of atmospheric, geological, and possible biological processes in planetary environments. We have developed a highly miniaturized and compact multifunctional nanosensor platform for such measurements using hybrid manufacturing techniques of low dimensional materials. We have demonstrated parts-per-billion level sensitivity and selectivity of target species with this novel instrument. In this talk, I will discuss the development of multifunctional nanosensor platform for in situ planetary research and upcoming mission opportunities.
Dynamic networks as a route to access pluripotent materials

Stuart J. Rowan, stuartrowan@uchicago.edu. University of Chicago Pritzker School of Medicine, Chicago, Illinois, United States

The concept of a pluripotent material is best explained by analogy to stem cells, which are pluripotent as they can give rise to different cell types. Thus, a "stem plastic" has the capability of being converted into different classes of plastic material. Given weight limitations when traveling in space the concept of pluripotent plastics that can be converted into very different materials depending on need, is an attractive one. The question, therefore, is “how can we design pluripotent materials? We have been investigating dynamic covalent networks combined with tempering or training procedures as one route to such materials.
Multifunctional structural materials for sustainable human exploration in extreme space environments

Cheol Park, cheol.park-1@nasa.gov, Sang-Hyon Chu. NASA, Washington, District of Columbia, United States

Extreme space environments such as space vacuum, radiation, jagged lunar dust, microgravity, high thermal excursion, micrometeoroids, thrust plume ejecta, seismic events, and their synergistically-adverse effects make sustainable space exploration extremely challenging. More robust and sustainable advanced materials and structures are needed to protect crew and equipment to extend space missions longer and safer with minimum service and repair needs. Recent progress of NASA efforts on sustainable multifunctional structural materials will be introduced.
Fast light-switchable polymeric carbon nitride and adsorptive membranes for tunable gas separation

Timur Ashirov, timur.ashirov@unifr.ch, Ali Coskun. Universite de Fribourg, Fribourg, Fribourg, Switzerland

State-of-the-art of gas separation membranes suffer from permeability-selectivity trade-off, i.e. membranes with high flow rate (permeability) have low selectivity and vice versa. Breaking this trade-off requires control over the transport properties of a single gas in a binary or ternary gas mixtures. Accordingly, we developed two-dimensional adsorptive separation membranes based on graphene to selectively remove target gas from the mixture. Moreover, we also designed light-switchable membranes based on polymeric carbon nitride for separation of gases based on their polarizabilities.
Design of macromolecular radicals for next generation energy storage

Alexandra Easley, ade28@cornell.edu. Cornell University, Ithaca, New York, United States

To curb reliance on strategic elements in Lithium-ion batteries, organic-based redox-active materials have received considerable attention as alternative electrode materials. New active material chemistries seek to address the need for on-demand deconstruction and reconstruction of batteries. In this talk, I will present the use of Hansen solubility parameters to rationally design of polymeric with enhanced performance. Additionally, the design of degradable redox-active polypeptides and their performance in metal-free batteries will be discussed.
Supramolecular sython approach for high capacity electrodes in lithium-ion batteries

Ali Coskun, ali.coskun@unifr.ch. Universite de Fribourg, Fribourg, Fribourg, Switzerland

Three high-energy density electrode materials – namely, silicon anodes, lithium (Li) metal anodes, and sulfur cathodes operating by alloying, electroplating, and electrochemical reactions, respectively – have gained discernable interest owing to their unparalleled theoretical capacity. Supramolecular chemistry and/or mechanically interlocked polymers such as polyrotaxanes can play a pivotal role to address the challenges facing rechargeable batteries. In this presentation, the concepts of supramolecular chemistry and their working principles in high energy density electrode materials in Li-ion batteries will be discussed.
Toward sustainable organic polymer batteries

**Jodie L. Lutkenhaus, jodie.lutkenhaus@tamu.edu, Alexandra Easley.** Texas A&M University, College Station, Texas, United States

The future of Li-ion battery manufacturing is challenged by projected shortages of critical materials and a highly centralized supply chain. Organic polymer batteries- which depend on C, H, N, O, and S elements- may address these challenges by diversifying the availability of raw battery materials while also offering a pathway toward a circular life cycle. This talk will discuss our latest efforts in understanding how these polymers store charge, how to recycle these materials, and how to improve their performance.
Click chemistry was defined by Kolb, Finn, and Sharpless in a 2001 Angewandte Chemie article. It has evolved substantially since then, to the point of having applications in most all fields of pure and applied chemistry. Thanks to Craig Hawker and Charlie Hoyle [thiol ene click reaction] it got off to a very fast start in materials science where making serial connections with extraordinary reliability is often the central requirement. The azide-terminal alkyne à triazole synthesis, aka CuAAC, was discovered independently in 2002 by the Meldal and Sharpless groups in Copenhagen and La Jolla, respectively. CuAAC quickly emerged as the quintessential click reaction for its near perfect yields over multiple serial steps. Polymer creating reactions that tolerate the dioxygen and water of earth’s atmosphere are rare to non-existent. Both CuAAC processes and our newer 2014 discovered SuFEx catalysis to polysulfate linkages are exceptional in this regard. Today I highlight the properties of some SuFEx polysulfate polymers which have emerged in a collaboration between Scripps and the Molecular Foundry Lab at Berkeley. The phenomenon mediated by these polymers is to shield electric capacitors from the destructive effects of both high temperatures and high electric fields, more effectively than the existing materials for this purpose. The question is, how can a thin film of polymer, a condensed chemical phase, shield against the electromagnetic field force of physics. Our latest results and thoughts are presented.
Sustainable approach to carbon management to enable our energy and economic transition

Anna Douglas, anna.douglas@skynanotechnologies.com, David Wood. SkyNano, Knoxville, Tennessee, United States

Scientists and the broader society are now highly aligned on the imperative to reach net zero emissions goals by the end of this century, with many goals including significant emissions reductions in the next few decades. The last decade has seen a rise in a variety of carbon management solutions ranging from carbon capture, conversion, utilization, sequestration, transformation, etc. being developed at varying technology readiness levels, from academia to industry. This talk will cover the question: how can all these technologies work collaboratively to achieve our net zero goals which enable our transition to the new green economy?
Advanced recycling: Meeting the needs of plastic recycling today and tomorrow

Tony Go, Tony.Go@exxonmobil.com. ExxonMobil Production Co, Houston, Texas, United States

Materials Recycling is critical to our world and also to ventures which are limited on virgin resources (such as long space travel). Advanced Recycling is an important technology which enables the recycling of polymers back to their original monomers, enabling full circularity back to the polymer without loss of mechanical or molecular properties. This talk will discuss the importance of Advanced Recycling and the innovations in this space by ExxonMobil.
Polymers play a wide variety of roles in space-based observatories. These roles range from their ubiquitous roles in insulation to seminal to new technologies and architectures. This talk will introduce and discuss roles polymers have played in previous generations of space observatories, with an emphasis on the recently launched James Webb Space Telescope. We will also discuss the role that polymers play in future observatories, such as the Habitable Worlds Observer and SALTUS a mission based on inflatable technologies.
Harnessing the power of data through QURIOSITY

Benjamin Kundsen, benjamin.knudsen@basf.com. BASF Corporation, San Diego, California, United States

With global revenues of 87 billion Euros in 2022, BASF continues to drive economic success with environmental protection and social responsibility. As the power of data plays an ever-larger role, BASF has deployed the most powerful computer in the chemical industry. This talk gives an overview on how at 1.75 quadrillion calculations per second, QURIOSITY – the new BASF supercomputer – accelerates discovery, makes manufacturing processes more efficient, optimizes logistics faster than ever before and supports completely new digital business models.
Accelerated development of advanced materials for diverse mission needs at Lawrence Livermore National Laboratory

Kim Budil, limtiaco2@llnl.gov, Glenn A. Fox, Anthony Van Buuren, Mayalibo J. Matthews. Lawrence Livermore National Laboratory, Livermore, California, United States

The convergence of machine learning and high-performance computing, advanced manufacturing, and automation promises to accelerate the development of advanced materials from concept to demonstration. LLNL has developed an ecosystem of facilities and capabilities in these areas that can work in a holistic manner to accelerate materials development and scale up. In this presentation, we detail how this ecosystem has been used on materials systems for a diverse set of applications ranging from national security to clean energy and beyond.
Panel on advanced technologies

George L. Rodriguez, cmewebcast@gmail.com, Ksenia Takhistova. CME, Morristown, New Jersey, United States

This session involves a panel discussion on cutting-edge advances in technologies for advanced materials featuring experts from academia, industry and government. This will be part of the Sixth Annual CME NASA Symposium to be held on 8/14-15 featuring Barry Sharpless who will cover the follow on to his ground-breaking research "Click Chemistry: New Directions." Sharpless is the 2001 and 2022 Nobel Laureate. The list of over 30 eminent speakers includes Kimberly Budil (13th Director of the Lawrence Livermore National Laboratory), Jon Arenberg (Chief Engineer at Northrop Grumman), Benjamin Knudsen (BASF Vice President of Research NA), Zhenan Bao (Stanford), Stuart Rowan (UChicago), Kirk Schanze (UTSA), the CME PMSE Student & Mentor Award winners from Texas A&M and University of Friburg in Switzerland, and thought leaders at NASA Goddard, Ames, DC, and NASA Early-Stage Innovation & Partnerships, among others. The event brings together top leaders in industry, academia and government to advance science and accelerate diverse STEM talent for sustainable innovation and translate the cutting-edge research into practical applications for the benefit of Earth and its people. To keep up with the speakers and schedules, please see www.cme-stem.org
CME STEM Leadership Awards Presentation

George L. Rodriguez, cmewebcast@gmail.com. CME, Morristown, New Jersey, United States

This pre-CME Lectures session is about the STEM leadership award presentation to Barry Sharpless, Kim Budil, and another distinguished figure to be announced. This will be part of the Sixth Annual CME NASA Symposium to be held on 8/14-15 featuring Barry Sharpless who will cover the follow on to his ground-breaking research "Click Chemistry: New Directions." Sharpless is the 2001 and 2022 Nobel Laureate. The list of over 30 eminent speakers includes Kimberly Budil (13th Director of the Lawrence Livermore National Laboratory), Jon Arenberg (Chief Engineer at Northrop Grumman), Benjamin Knudsen (BASF Vice President of Research NA), Zhenan Bao (Stanford), Stuart Rowan (UChicago), Kirk Schanze (UTSA), the CME PMSE Student & Mentor Award winners from Texas A&M and University of Friburg in Switzerland, and thought leaders at NASA Goddard, Ames, DC, and NASA Early-Stage Innovation & Partnerships, among others. The event brings together top leaders in industry, academia and government to advance science and accelerate diverse STEM talent for sustainable innovation and translate the cutting-edge research into practical applications for the benefit of Earth and its people. To keep up with the speakers and schedules, please see www.cme-stem.org
Chemistry beyond gravity: Unlocking the potential of space chemistry for exploration and industry

Chyree S. Batton, Chyree.Batton@gmail.com, Jana Stoudemire. Axiom Space, Houston, Texas, United States

This session provides an overview of progress toward creating a comprehensive Space Chemistry Roadmap, which will support both NASA exploration programs and the emerging commercial space economy. By focusing on approaches that simultaneously advance exploration, commercialization, and fundamental research in space chemistry, the roadmap seeks to accelerate the growth of a robust commercial space economy and further NASA’s exploration objectives. Utilizing the ISS and future commercial LEO destinations, the roadmap development process will emphasize the unique opportunities provided by microgravity and space environments for innovative chemical reactions, processes, and manufacturing technologies. The culmination of this collaborative effort will be a presentation of the Space Chemistry Roadmap at the CME NASA Sustainability conference in August 2023.
Skin-inspired electronics is emerging as a new generation of soft electronics that may allow intimate contact with biological systems with minimal mechanical damage. Furthermore, they allow sensing information with higher signal-to-noise ratio due to the lower impedance at electrode-tissue interface. In this talk, I will discuss several projects related to engineering conductive materials and developing fabrication methods to allow electronics with effective electrical interfaces with biological systems, through tuning their electrical as well as mechanical properties. The end-result is a soft electrical interface that has both low interfacial impedance as well as match mechanical properties with biological tissue. Several applications of such electronics will be presented.
Nurturing innovation in sustainability through early stage partnership development at NASA

Jennifer Gustetic, jennifer.l.gustetic@nasa.gov. NASA, Washington, District of Columbia, United States

NASA STMD’s Early Stage Innovation and Partnerships portfolio seeks to empower a community of innovators spearheading aerospace research and transformative technology ventures through 700+ awards each year that impact not only in the space industry, but also consumer goods, health and medicine, public safety and other spinoffs. This session will discuss how NASA early-stage investments in numerous technology areas, such as materials, in-situ resource utilization, energy and more, are making an impact on sustainability in space and here on earth.
Failure analysis is critical to the aerospace industry – we cannot improve on our safety and efficiency in space exploration without it. NASA’s MSFC is home to world-renown experts in failure analysis, with a specialty in the avionics systems used for the aerospace and defense industries. This presentation will highlight the criticality of a robust failure analysis program, while exploring the unique challenges that come with incorporating advanced electronic materials into our space systems.
Energy-efficient vehicular electrification requires polymeric dielectrics that can withstand large electric fields and high temperatures. Chief among the barriers to new materials discovery is the staggering size of the chemical space to be sifted through, and lack of reliable and rapid property prediction models. In this lecture, I will discuss how such barriers may be overcome using emerging computational and machine learning methodologies, synergistic with experiments. I will highlight a recently discovered new class of polymer dielectrics tolerant to extremes.
Plant molecular farming to support human life on the Moon, Mars, and beyond

Karen McDonald, kamcdonald@ucdavis.edu, Somen Nandi. University of California Davis, Davis, California, United States

Plants are important resources for space exploration life support – they are capable of harnessing light, producing food and oxygen, purifying water, recycling waste streams, and buoying the mental health of crew members. But plants can also be used as living molecular foundries, engineered to produce a broad range of mission-critical compounds including biomaterials, nutraceuticals, food additives, enzymes, diagnostic reagents, and biopharmaceuticals. This presentation will provide an overview of the technologies involved and potential space applications of plant molecular farming.
Greenchem innovation: What is next?

Paul T. Anastas, paul.anastas@yale.edu. Yale University, New Haven, Connecticut, United States

This talk will discuss the advances made in the period from 1998 in which Green Chemistry was defined as the “design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances” until now. It will include the best practices to engineer the molecules and production methods that help make the world sustainable through research and global networking in collaboration with industry, government and academia taking into account the social, economic, and environmental challenges.
Improving polymer properties provides opportunities in developing new applications. However, trial and error methods cannot meet the current need for new materials. We demonstrate the utility of Machine Learning (ML) in creating structure property models. We will present the integration of polymer characterization data sets and the application of ML to exemplify an approach to polymer development. This approach afforded us the ability to generate predictive capability for performance attributes which we expect to become the basis of an improved unified framework.
Panel discussion on sustainability

George L. Rodriguez, cmewebcast@gmail.com, Ksenia Takhistova, Shah Karim. CME, Morristown, New Jersey, United States

This session involves a panel discussion on cutting-edge advances in sustainability featuring experts from academia, industry and government. This will be part of the Sixth Annual CME NASA Symposium to be held on 8/14-15 featuring Barry Sharpless who will cover the follow on to his ground-breaking research "Click Chemistry: New Directions." Sharpless is the 2001 and 2022 Nobel Laureate. The list of over 30 eminent speakers includes Kimberly Budil (13th Director of the Lawrence Livermore National Laboratory), Jon Arenberg (Chief Engineer at Northrop Grumman), Benjamin Knudsen (BASF Vice President of Research NA), Zhenan Bao (Stanford), Stuart Rowan (UChicago), Kirk Schanze (UTSA), the CME PMSE Student & Mentor Award winners from Texas A&M and University of Friburg in Switzerland, and thought leaders at NASA Goddard, Ames, DC, and NASA Early-Stage Innovation & Partnerships, among others. The event brings together top leaders in industry, academia and government to advance science and accelerate diverse STEM talent for sustainable innovation and translate the cutting-edge research into practical applications for the benefit of Earth and its people. To keep up with the speakers and schedules, please see www.cme-stem.org
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Hidden in plain slime: Finding inspiration in mucus for building synthetic biological interfaces

Kamil Godula, kgodula@ucsd.edu. University of California San Diego, La Jolla, California, United States

The mucosal glycocalyx is as a biological barrier that mediates cellular functions ranging from protection, to exchange of gases and nutrients, to transfer of biological information. It encodes molecular signatures of “self” recognized by the immune system and constantly evolves to prevent attack by pathogens, which exploit its components to enter cells. The glycocalyx has inspired novel nanomaterials that recapitulate its molecular complexity, nanoscale architecture, and functions for applications as protective coatings and responsive biomimetic interfaces in foreign and hostile environments.
ACS Award in Pure Chemistry in Honor of Julia Kalow (Invited)

Iridescence from total internal reflection in polymer microstructures - Zarzar, Lauren (Oral Only)

Award Address (ACS Award in Pure Chemistry sponsored by the Alpha Chi Sigma Fraternity and the Alpha Chi Sigma Educational Foundation) - From mechanism to materials in photocontrolled polymer networks - Kalow, Julia (Oral Only)

Exploring the use of room temperature dynamic bonds in materials - Rowan, Stuart (Oral Only)

Usnic acid linked bioinspired polymers - El-Zaatari, Bassil (Oral Only)

Photon-driven strategies for challenging bond activations - Stache, Erin (Oral Only)

Synthesis and single molecule mechanics of silicon-rich polymers – Klausen, Rebekka (Oral Only)

Metal-free ring-opening metathesis polymerization - Boydston, AJ (Oral Only)
Iridescence from total internal reflection in polymer microstructures

Lauren D. Zarzar, ldz4@psu.edu. The Pennsylvania State University, University Park, Pennsylvania, United States

I will describe the experimental investigation and optical modeling of the structural coloration produced from total internal reflection interference within 3D microstructures. Ray tracing simulations coupled with color visualization and spectral analysis techniques are used to model, examine, and rationalize the iridescence generated for a range of micro-geometries, including hemicylinders and truncated hemispheres, under varying illumination conditions. An approach to deconstruct the observed iridescence and complex far-field spectral features into its elementary components and systematically link them to ray trajectories that emanate from the illuminated microstructures is demonstrated. The results are compared with experiments, wherein microstructures are fabricated with methods such as chemical etching, multiphoton lithography, and greyscale lithography. Microstructure arrays patterned on surfaces with varying orientation and size lead to unique color-traveling optical effects and highlight opportunities for how total internal reflection interference can be used to create customizable reflective iridescence. The findings herein provide a robust conceptual framework for rationalizing this multibounce interference mechanism and establish approaches for characterizing and tailoring the optical and iridescent properties of microstructured surfaces.
Award Address (ACS Award in Pure Chemistry sponsored by the Alpha Chi Sigma Fraternity and the Alpha Chi Sigma Educational Foundation). From mechanism to materials in photocontrolled polymer networks

Julia A. Kalow, jkalow@northwestern.edu. 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. 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 the molecular mechanisms underlying these macroscopic changes, as well as the design of photoswitches to enable applications in 3D cell culture.
Exploring the use of room temperature dynamic bonds in materials

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

The dynamic bond can be defined as any class of bond that selectively undergoes reversible breaking and reformation, usually under equilibrium conditions. The incorporation of dynamic bonds allows access to structurally dynamic polymers and composites. Such materials can exhibit macroscopic responses upon exposure to an environmental stimulus, on account of a rearrangement of the polymeric architecture. In such systems, the nature of the dynamic bond not only dictates which stimulus the material will be responsive to but also plays a role in the response itself. Thus, such a design concept represents a molecular level approach to the development of new stimuli-responsive/adaptive materials. A class of dynamic bond that has perhaps received less attention are those bonds that are dynamic at room temperature. The addition of thiols to benzalcyanoacetate or benzalcyanoamide Michael acceptors results in room temperature dynamic thia-Michael bonds and we have been exploring this class of dynamic bonds to make mechanically robust films, pressure sensitive adhesives and access stress-adaptive dense colloidal suspensions. Our latest work in this area will be discussed.
Usnic acid linked bioinspired polymers

Bassil El-Zaatari, baelzaatari@davidson.edu. Department of Chemistry, Davidson College, Davidson, North Carolina, United States

Since its discovery in the mid 1800s as a secondary metabolite of naturally occurring various lichens (e.g. Usnea, Lecanora, and Evernia), usnic acid has emerged as one most important biologically active lichen compounds. Usnic acid has demonstrated antimicrobial potential where it exhibits a wide array of resistance against new microbial strains, including those resistant to traditional antibiotics. Usnic acid has furthermore been utilized as a photoprotective agent due to its UV absorbing properties. While many studies have taken advantage of polymer matrices as a method to physically encapsulate usnic acid, the synthesis of usnic acid based and chemically linked polymer materials remains understudied. In this talk, efforts to chemically react usnic acid into various polymer structures will be highlighted through the synthesis and polymerization of usnic-acid derivatives. The ability to polymerize usnic acid into thermoplastics and thermosets through polyester linkages is moreover featured. Finally, relevant thermomechanical properties and antimicrobial activities of these materials are discussed.
Photon-driven strategies for challenging bond activations

Erin Stache, ees234@cornell.edu. Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States

Photon-driven processes have emerged as a powerful tool for achieving challenging bond cleavages and bond formations. Photocatalysis offers the benefit of temporal and spatial control with low-energy light, which has been widely advantageous in polymers and materials to access sequence control or 3D structure. The judicious choice of photocatalyst enables a precision of reactivity not amenable to other strategies. I will discuss our efforts towards photon-enabled temporal heating for generating and confining highly reactive intermediates for selective C–C bond cleavages and other high activation barrier reactions.
Synthesis and single molecule mechanics of silicon-rich polymers

Rebekka S. Klausen, klausen@jhu.edu. Johns Hopkins University, Baltimore, Maryland, United States

Polysilanes, polymers comprised of SiR₂ repeat units, possess distinctive optical properties relative to all-carbon congeners arising from the interaction of Si-Si sigma bonds. While the unique conformational profiles of molecular and polymeric Si-Si chains relative to C-C chains have long been appreciated to impact sigma-delocalization in polysilanes, comparably little investigation has focused on the impact of macromolecular conformation on single molecule elasticity. Herein, the synthesis of novel silicon-based monomers for metathesis polymerization will be described. This novel suite of polymeric structures can be readily compared to all-carbon chains by single molecule force spectroscopy, revealing increased single molecule plasticity in Si-rich macromolecules.
Metal-free ring-opening metathesis polymerization

AJ Boydston, aboydston@wisc.edu. University of Wisconsin-Madison, Madison, Wisconsin, United States

Our group integrates fundamental and applied research within the scope of soft materials. In this seminar, we will discuss a new mechanism for ring-opening metathesis polymerization that is now a centerpiece of our program. The approach leverages photoredox catalysis to allow for organic initiators, in contrast to widely used metal-alkylidene initiators. Studies on our mechanistic hypothesis have yielded an exciting interplay of challenges and opportunities, often with one disguised as the other. We will share our findings that include methods for stereocontrol, chain transfer, and functional group compatibility, as well as our adventures into the applied and commercial sectors.
Regeneration of activators in ATRP - Matyjaszewski, Krzysztof (Oral Only)

Modern approaches for controlled radical polymerization and depolymerization - Anastasiaki, Athina (Oral Only)

Discrete and well-defined materials - allure and application - Hawker, Craig (Oral Only)

Polymer nanoplexes: Linking *in vitro* experiments to *in vivo* outcomes - Epps, Thomas (Oral Only)

Controlling reaction timescales towards responsive materials: A synergy of polymer kinetics and architecture - Konkolewicz, Dominik (Oral Only)

Synthesis and application of biologically active and responsive polymers - Maynard, Heather (Oral Only)

Sequence-controlled peptoid polymers - Tran, Helen (Oral Only)

Spatiotemporal control for integrated catalysis - Diaconescu, Paula (Oral Only)
Regeneration of activators in ATRP

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

Atom transfer radical polymerization (ATRP) carried out with ppm amounts of Cu catalysts requires regeneration of activators lost due to radical termination. Principles of the regenerations will be presented together with new regeneration/reducing mechanisms applied to synthesis of well-defined polymers.
In this talk I will present recent approaches developed by our lab in the areas of controlled radical polymerization and depolymerization. Oxygen is typically regarded as an undesirable component resulting in terminated polymer chains, deactivated catalysts, and subsequent cessation of the polymerization. Our group recently developed an unusual atom transfer radical polymerization whereby oxygen favors the polymerization by triggering the in situ transformation of CuBr/L to reactive superoxido species at room temperature. Through a superoxido ARGET-ATRP mechanism, an order of magnitude faster polymerization rate and a rapid and complete initiator consumption can be achieved as opposed to when unoxidized CuBr/L was instead employed. In the depolymerization arena, I will introduce thermal and light depolymerization approaches as a chemical recycling strategy to regenerate the starting monomer. The retrieved monomers can then be utilized for subsequent polymerization cycles or to synthesize completely new materials. The possibility to depolymerize materials in bulk will also be presented.
Discrete and well-defined materials - allure and application

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

Multiple polymeric families, such as poly(ethylene glycol) (PEG) play an important role in material and pharmaceutical applications. However, commercial samples are polydisperse, which hampers detailed studies on chain length-dependent properties and potentially increases antibody responses in pharmaceutical applications and undesirable performance in material applications. Here, we report a practical and scalable method to prepare libraries of discrete homo, random and block copolymer structures. By enabling the scalable synthesis of a broad library of copolymers, fundamental self-assembly properties can be understood and shown to directly correlate with the total number of repeat units, nature of the chain ends, and overall backbone length/structure. These results illustrate the advantages of discrete macromolecules when compared to traditional disperse materials.

Strategy for scalable preparation of well-defined macromolecules
Polymer nanoplexes: Linking *in vitro* experiments to *in vivo* outcomes

**Thomas H. Epps**¹,², *thepps@udel.edu*, Millicent O. Sullivan¹,³, Esther H. Roh¹. (1) Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware, United States (2) Materials Science & Engineering, University of Delaware, Newark, Delaware, United States (3) Biomedical Engineering, University of Delaware, Newark, Delaware, United States

One key challenge in drug delivery and gene therapy is the lack of convergence between in vitro experiments and in vivo results. To probe this convergence issue, we synthesized novel diblock polymers to deliver nucleic acid therapeutics capable of promoting wound 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. 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. The complete knockdown of both genes, in combination, resulted in significant attenuation of TGF-β1-triggered fibroblast proliferation and differentiation into myofibroblasts. 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. Finally, we have recently expanded our kinetic modeling to predict *in vivo* delivery results from *in vitro* experiments as confirmed via retrospective analyses, unlocking a potentially streamlined pathway to *de novo* design for polymer nanoplexes and lipid nanoparticles.
Controlling reaction timescales towards responsive materials: A synergy of polymer kinetics and architecture

Dominik Konkolewicz, d.konkolewicz@miamioh.edu. Miami University, Oxford, Ohio, United States

Control over the timescale of a reaction has unique impacts on both the efficiency of a polymerization to the properties of the resulting structure. Here, the impact of kinetics in polymerization is explored including an interplay between the rate of RAFT polymerizations and the control over the structure resulting polymer. Additionally, the impact of polymer kinetics on the performance of responsive materials, including chemically fueled and dynamic networks. The dynamic materials involve a synergy of fast exchanging hydrogen bonded linkers and slow exchanging, responsive dynamic covalent systems. A particular focus on chemically fueled, systems, specifically the carbodiimide fueled generation of anhydride bonds is explored. The control over the timescales of the processes, and the impact of network structure on the properties of the materials including their reprocessability and their performance in complex functions such as tunable adhesives and rewritable patterns. In all highlighted systems, the performance of a responsive material is tied to both the underlying polymer’s structure and the underlying kinetics.
Synthesis and application of biologically active and responsive polymers

Heather D. Maynard, maynard@chem.ucla.edu. Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California, United States

Polymers with inherent biological activity or biological responsiveness are useful in medicine. This talk will focus on different recent studies in our group. For example, polymers with antimicrobial activity will be discussed. These polymers have caffeine as the hydrophobic side chain and various cationic side chains. We identified caffeine-cationic copolymers that are biocompatible and also active against *S. aureus* including methicillin-resistant clinical isolates. In another example, responsive polymers that have been utilized to prepare abuse-deterrent delivery systems will be disclosed. The materials were studied for efficacy and also for biocompatibility in vivo. Synthesis, characterization, and potential application of these and other polymeric materials will be discussed.

Example antimicrobial polymer that will be discussed in this talk. Image created by Dr. Pedro Salas (UCLA).
Sequence-controlled peptoid polymers

Helen Tran, tran@utoronto.ca. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

The presentation of bioactive moieties in terms of multivalency, ligand density, and architecture plays a central role in biological recognition processes, including cellular adhesion and pathogen binding. Polypeptoids that self-assemble into two-dimensional (2D) nanosheets have potential to recapitulate these precise molecular recognition motifs onto a flexible platform for biosensing. The traditional solid-phase method for the synthesis of peptoids allows for precise control over the placement of potential recognition sites in the sequence, yet generates molecules on a small scale (~100 mg). Recent solution-phase synthetic methods have enabled gram-scale synthesis, but lack sequence-specificity needed for self-assembly and precise incorporation of molecular recognition motifs. Herein, we present our motivations and efforts in bridging this divide. Moreover, we share our progress in replacing solvents traditionally used in the synthesis of peptoids with greener alternatives.

Solid phase: absolute sequence control, small scale

IEG: absolute sequence control, higher chain length, bulk scale
Spatiotemporal control for integrated catalysis

Paula Diaconescu, pld@chem.ucla.edu. Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California, United States

Integrated catalysis is an emerging methodology that can streamline the multistep synthesis of complicated products in a single reaction vessel, achieving a high degree of control and reducing the waste and cost of an overall chemical process. Integrated catalysis can be defined by the use of spatial and temporal control to couple different catalytic cycles in one pot. As an example, a strategy for coupling electrochemical and organometallic catalysts that enables polyketone synthesis from CO2 and ethylene in a single multicompartment reactor will be discussed. Polyketone materials that are up to 50% derived from CO2 can be prepared in this way. Potentiostatic control over the CO-producing catalyst enables the controlled generation of low-pressure CO, which in conjunction with a palladium phosphine sulfonate organometallic catalyst enables copolymerization to nonalternating polyketones with the CO content tuned based on the applied current density.
Big Data in Polymer Chemistry

Harnessing machine learning for the design of advanced drug formulations - Allen, Christine (Oral Only)

Bayesian-optimization-assisted discovery of stereoselective catalysts for ring-opening polymerization of racemic lactide - Tong, Rong (Oral Only)

Autonomous exploration of block copolymer thin films - Yager, Kevin (Oral Only)

Digital transformation in the coatings industry: Paving the way for a big data future - Kim, Sun Hye (Oral Only)

Self-driving Lab (Polybot) for electronic polymer discovery - Xu, Jie (Oral Only)

Elucidating chemical design principles in biomimetic synthetic polymers using high-throughput measurement - Chittari, Supraja (Oral Only)

Enhancing machine learning with theory for improved polymer solution phase behavior predictions - Audus, Debra (Oral Only)

Stochastic simulation of RAFT heteropolymerization kinetics and sequences - Jayapurna, Ivan (Oral Only)

Polymer design via SHAP and Bayesian machine learning optimizes pDNA and CRISPR ribonucleoprotein delivery - Reineke, Theresa (Oral Only)

Early prediction of ion transport properties in solid polymer electrolytes using machine learning and system behavior-based descriptors of molecular dynamics simulations - Khajeh, Arash (Oral Only)

Domain-specific languages as a tool for knowledge representation in polymer chemistry - Park, Nathan (Oral Only)

Quantifying pairwise chemical similarity of polymers - Shi, Jiale (Oral Only)

Open macromolecular genome: Generative design of synthetically accessible polymers - Kim, Seonghwan (Oral Only)

Automating data collection workflows for the creation of electronic polymers databases - Vriza, Aikaterini (Oral Only)

Linking fibrillar structure and chain packing in methylcellulose solutions to extent of methylation using machine learning, genetic algorithm, and multiscale simulations - Jayaraman, Arthi (Oral Only)

Open source web-based data platform to support the sustainable development of plastic recycling - Toraman, Hilal Ezgi (Oral Only)

Enabling Interoperability through FAIR Vocabulary Models - Kroenlein, Kenneth (Oral Only)
Big Data in Polymer Chemistry

Materials mine: Curation, ontology, and knowledge graph for discovery in polymer nanocomposites - Brinson, Catherine (Oral Only)

Modular synthesis of end-functional polymers for high-throughput supramolecular block copolymer preparation - Wang, Yunfei (Poster Only)

Predicting polymer solubility through machine learning: towards solvent recycling of plastics - Stubbs, Christopher (Poster Only)
Harnessing machine learning for the design of advanced drug formulations

Christine Allen, cj.allen@utoronto.ca, Pauric Bannigan, Riley Hickman, Zeqing Bao, Alan Aspuru-Guzik. University of Toronto, Toronto, Ontario, Canada

The formulation of therapeutic agents in advanced drug delivery systems such as nanoparticles and microparticles can significantly improve their safety and efficacy. However, the design and development of advanced formulations remains expensive, labour-intensive and time consuming with a heavy reliance on the expertise of the formulation development team and composition of formulations that have been clinically approved to date. In the design of these systems, there are a plethora of parameters that must be considered in relation to the drug, material(s) or excipient(s) as well as processing variables. Experimental evaluation of every combination is intractable and at this time it is not possible to predict the performance of specific formulations \textit{a priori}. As a result, it is likely that some of the formulation candidates that have moved forward to clinical development are not optimal but rather the best that could be achieved with the time and resources available.

Machine learning (ML) has led to significant advances in various fields, such as drug discovery and materials science. In recent years, the Allen lab has explored integration of ML to discern the relationships between composition, property and performance with a goal towards fast-tracking innovative drug formulation development. In this work, we have identified a lack of robust datasets in the published literature to apply data-driven methods. This has led us to consider strategies such as experimental automation, and more recently to the concept of a materials acceleration platform (MAP), or self-driving laboratory (SDL), that combines automated experimentation with ML-guided experiment planning for the design of advanced drug formulations. The integration of such technological advancements in the pharmaceutical sciences has the potential to fast-track preclinical research, improve efficiency in drug development pipelines and thus improve patient access to effective medicines.
Bayesian-optimization-assisted discovery of stereoselective catalysts for ring-opening polymerization of racemic lactide

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High-performance homogeneous single-site catalysts for polymer synthesis are required for economically producing environmentally friendly degradable polymers. Trial-and-error-based discovery and optimization of polymerization catalysts can be both time-consuming and expensive because this method relies on polymer chemists’ experience and empirical knowledge, and on serendipity. Recently, a complementary approach has emerged in the chemistry community that applies data-driven machine learning methods to capture multidimensional structure–activity relationships for catalysts. Machine learning approaches can accept numerous reagent features and reaction conditions as inputs without recourse to a specific mechanistic hypothesis, and can recognize hidden patterns in a multidimensional chemical space. This approach has been successfully used to develop enantioselective catalysts and to predict reaction yields in organic chemistry. However, to the best of our knowledge, Bayesian optimization has never been used to discover stereoselective polymer catalysts. Moreover, no efficient implementable strategy based on data science has been developed for use as a mechanistic tool for understanding nonintuitive trends in catalyst performance in polymer science. Herein, we describe a workflow and analysis framework to achieve these goals (Figure 1). We focused on Al-mediated stereoselective ring-opening polymerization (ROP) of racemic lactide, which affords stereoregular poly(lactic acid). Starting from literature data points for tetradeionate salen-type Al complexes, we showed that our Bayesian optimization model can guide the discovery of multiple high-performance isoselective and heteroselective Al complexes for the ROP of rac-LA. Analysis of the machine-learned results revealed important albeit nonintuitive descriptors that can be used for mechanistic studies. Ultimately, our framework serves as an important quantitative tool for both iterative catalyst discovery and mechanism rationalization in polymerization chemistry.

Figure 1. Overview of Bayesian optimization for discovery stereoselective catalysts.
Autonomous exploration of block copolymer thin films

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Autonomous experimentation (AE) holds enormous promise for accelerating scientific discovery. This paradigm leverages machine-learning methods to construct experimental loops where the machine selects and conducts experiments, liberating the human scientist to focus on high-level goals and understanding. This talk will discuss progress in the development of autonomous x-ray scattering, and application to study of block copolymer (BCP) thin films. We apply these methods to study the complexity of blended and layered BCP systems, which form transient structures and non-native morphologies. Judicious choice of initial state, boundary conditions, and processing history can be used to select among competing structures.
Digital transformation in the coatings industry: Paving the way for a big data future

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While the concept and usage of big data is widely accepted in social media, streaming services, and e-commerce platforms, the materials industry is still in its early stage with respect to digital data and faces unique challenges to overcome. These challenges are especially onerous when dealing with complex macromolecular materials and mixtures, such as polymeric resins or rheology modifiers used in coatings formulations. Furthermore, collecting relevant experimental data to describe materials and formulations is an exhaustive, time-consuming process, and even after the collection of large amounts of data, a deficient data infrastructure will hinder data analysis and subsequent insights.

This talk will provide an overview of Dow Coating Materials' digital transformation journey towards an updated infrastructure capable of handling and storing data more efficiently. Specific data engineering efforts, including data digitization, automation, and centralization will be addressed. This transformation has allowed seamless integration of data with various machine learning techniques to accommodate the development and launch of new digital applications tailored to the needs of the modern researcher. Additionally, as a successful digital transformation involves more than just technological changes, this talk will address the thoughtful change management required at multiple levels of the organization and how organizational culture change is an essential element to the lasting success of digital transformation initiatives.
Self-driving Lab (Polybot) for electronic polymer discovery

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Owing to the optoelectronic property, chemical pluripotency and viscoelastic nature of electronic polymers, polymer electronics have shown unique advances in many emerging applications such as skin-like electronics, large-area printed energy devices, and neuromorphic computing devices, but their development period is years-long. Recent advancements in automation, robotics, and learning algorithms have led to a growing number of self-driving (autonomous) laboratories that have begun to revolutionize the development and accelerated discovery of materials. In this talk, I first introduce our efforts in building an autonomous laboratory, namely Polybot, that combines the strengths of rapid and robust experiment acquisition from robotic technologies and fast analysis of complex datasets using machine learning (ML) for autonomous electronic polymers discovery. Then, I will talk about our recent research examples on closed-loop electronic thin film manufacturing and autonomous electrochromic polymer discovery. This new experimental framework is a user facility and amenable to continuous improvement, such that sophistication can be added over years to continually redefine the cutting-edge of electronic polymer discovery.
Elucidating chemical design principles in biomimetic synthetic polymers using high-throughput measurement

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The modularity and scope inherent in synthetic polymers make them attractive candidates as functional materials for target applications. However, this extraordinary synthetic flexibility has also made the de novo design of these materials challenging. Machine learning models are powerful tools capable of optimizing this high-dimensional space, but they require large datasets with detailed feature information to result in high predictive power. For example, the details of sample preparation are critical for elucidating meaningful design principles. In our recent work, we described how the phase behavior in lower critical solution temperature (LCST) polymers depends not only on the chemical composition but also on the features of the temperature protocol, such as the rate of stimulus change and chosen temperature windows. Furthermore, ongoing work in our group includes the development of high-throughput colorimetric measurements and rapid library synthesis to enable the construction of interpretable regression models. These findings provide important insights into how the generation of large, well-defined data provides the foundation for data-driven discovery of fundamental structure-function relationships.
Enhancing machine learning with theory for improved polymer solution phase behavior predictions

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Flory-Huggins theory is foundational to macrophase separation of polymer solutions. Despite its widespread use and ability to capture qualitative trends such as molecular weight, it often quantitively disagrees with experiment. In contrast, machine learning (ML) methods are able to predict phase behavior across a broad range of chemistries and state variables within experimental uncertainty, but they lack interpretability. Here, we combine Flory-Huggins theory and ML with the dual goals of providing interpretability of the ML model and further improving interpolation and extrapolation with less experimental data. Specifically, we consider three different ways of using theory to inform the choice of input features for a neural network, as well as an ML model where the predictions are constrained by theory. Using the well-studied system of polystyrene in cyclohexane as a case study, we compare the various methods in the context of interpolation, extrapolation, data scarcity and interpretability. We find that the optimal model is highly dependent on the amount and type of data. One of the simplest theory-informed models performs best when data is extremely scarce, but a more sophisticated theory-informed model performs best when there is more data. Finally, we discuss implications of all methods on explainability.

Coexistence curve for polystyrene in cyclohexane as predicted by a theory-informed neural network
Stochastic simulation of RAFT heteropolymerization kinetics and sequences

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Random heteropolymers (RHPs) are a class of materials with a growing repertoire of demonstrated functionality inclusive of organic solvent biocatalysis, biodegradable plastics, and membrane protein and biological fluid mimicry. RHPs are only statistically defined and cannot be sequenced. Thus, prior works have used a simple Mayo-Lewis inspired stochastic algorithm to simulate RHP sequences for bioinformatics-inspired analysis, structural simulation with molecular dynamics and as inputs for training deep learning models. Growing RHP functionality will demand for more complex RHPs. However, increasing complexity in heteropolymer design and analysis paradigms will be bottlenecked by simulation accuracy. In this work we present the first general, open-sourced, reversible addition-fragmentation chain-transfer (RAFT) polymerization kinetic simulator for heteropolymers. Incorporating kinetics into heteropolymerization simulation results in more accurate molecular weight distributions, more accurate sequence patterns, living versus dead chain distribution differentiation, and can assist in experimental planning by mapping percent conversion to reaction time. To democratize access to polymer chemists who do not have access to or experience with high-performance computing resources, our simulation library was written in Julia to run on most CPUs with low memory requirement. This simulator can be easily incorporated as a modular upgrade to our previously published, open-sourced RHPapp. Together, the two macromolecular cheminformatics libraries can be used to design heteropolymers as protein mimics and beyond.
Polymer design via SHAP and Bayesian machine learning optimizes pDNA and CRISPR ribonucleoprotein delivery

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Nucleic acids are important therapeutics yet issues with delivery efficiency continue to hinder widespread advancement in the clinic. Delivery systems are crucial to encapsulate and protect these large and highly sensitive payloads and improve tissue internalization ensuring efficacy. However, we are limited by the vast chemical space and prediction of formulation chemistries indicating discrete selection and optimization of next generation systems. Indeed, new machine learning models aimed at selecting and predicting discrete parameters influencing biological efficacy are needed to advance the next frontier of personalized medicine. We present the facile synthesis of a clickable polymer library with systematic variations in length, binary composition, pK\textsubscript{a}, and hydrophobicity (clogP) to optimize intracellular pDNA and CRISPR-Cas9 ribonucleoprotein (RNP) performance. We couple physiochemical characterization and machine learning to interpret quantitative structure-property relationships within the combinatorial design space. For the first time, we reveal unexpected disparate design parameters for nucleic acid carriers; via explainable machine learning on 432 formulations, we discover that lower polymer pK\textsubscript{a} and higher percentages of benzimidazole ethanethiol enhance pDNA delivery, yet polymer length and captamine cation identity improve RNP delivery. Closed-loop Bayesian optimization of 552 formulation ratios further enhances in vitro performance. The top three polymers yield higher signal and stable transgene expression over 20-days in vivo, and a 1.7-fold enhancement over controls. Our facile coupling of synthesis, characterization, and machine analysis provide powerful tools to quantitate performance parameters accelerating next generation vehicles for nucleic acid medicines.
Early prediction of ion transport properties in solid polymer electrolytes using machine learning and system behavior-based descriptors of molecular dynamics simulations

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Molecular dynamics simulations are useful tools to screen solid polymer electrolytes with suitable properties applicable in Li-ion batteries. However, due to the vast design space of polymers, it is highly desirable to accelerate the screening by reducing the computational time of ion transport properties from simulations. In this study, we show that with a judicious choice of descriptors, we are able to predict the equilibrium ion transport properties in LiTFSI-homopolymer systems within the first 0.5 ns of the production run of simulations. The set of descriptors used in the current study includes the configuration of ion clusters and early time evolution of transport properties. Specifically, we find that descriptors that include information about the behavior of the system, such as ion clustering and dynamics of ion transport in the polymer environment outperform features extracted from only the molecular structure of the polymers. We show that these behavior-based descriptors have several advantages over polymer structure-based descriptors, as they encode system (polymer and salt) behavior rather than just the class of polymer and can be computed at any time point during the simulations. These characteristics increase the applicability of our descriptors to a wide range of polymer systems (e.g., co-polymers, blend of polymers, salt concentrations, and temperatures) and can be impactful in significantly shortening the discovery pipeline for solid polymer electrolytes.
Domain-specific languages (DSLs) are used for specific domain areas for where their custom syntax and narrowed scope allow for concise, interpretable expression of the programming tasks. Despite the extensive use of DSLs for a variety of domains, they are relatively underexplored for knowledge representation and translation tasks within experimental science. Here, using a DSL termed Chemical Markdown Language (CMDL), we demonstrate its flexibility and expressiveness enables effective representation of experimental data in polymer chemistry. We will discuss how the inherent extensibility of DSLs such as CMDL allows for straightforward support and use of a variety of polymer structural representation systems and accommodation of a multitude of experimental data types. Experimental data represented using CMDL has been seamlessly utilized to develop ML-models for materials and catalyst design, which in turn have been validated experimentally. The interoperability of CMDL enabled platforms and data representations with broader open-source data initiatives within polymer chemistry will also be discussed.
Quantifying pairwise chemical similarity of polymers

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Defining the similarity between chemical entities is an essential task in polymer informatics for enabling ranking, clustering, and classification. In contrast to small molecules and sequence-defined biomacromolecules, the vast majority of synthetic polymers lack well-defined deterministic structures and instead are represented as molecular ensembles or distributions. Since the existing similarity methods used for small molecules and sequence-defined biomacromolecules require well-defined deterministic structures, they cannot be directly utilized for polymer similarity calculations. Therefore, despite its importance, pairwise chemical similarity for polymers remains an open problem.

Here, a similarity function for polymers with well-defined backbones is designed based on polymers’ stochastic graph representations generated from canonical BigSMILES, a structurally-based line notation for describing macromolecules. The stochastic graph representations are separated into three parts: repeat units, end groups, and polymer topology. The earth mover’s distance is utilized to calculate the similarity of the repeat units ($S_{RU}$) and the similarity of end groups ($S_{EG}$). The graph edit distance is used to calculate the similarity of the topology ($S_{TOP}$). These three values can be linearly or nonlinearly combined to yield an overall pairwise chemical similarity score ($S_{OA}$) for polymers that is largely consistent with the chemical intuition of expert users and is adjustable based on the relative importance of different chemical features for a given similarity problem. The similarity metric gives a solution to calculate the chemical pairwise similarity score, which enables the sorting of retrieved database entries based on a query polymer and anomaly detection for polymer data validation. Therefore, this method is an essential and significant contribution to polymer informatics.
A grand challenge in polymer science lies in the predictive design of new polymeric materials with targeted functionality. However, de novo design of functional polymers is challenging due to the vast chemical space and an incomplete understanding of structure-property relations. Recent advances in deep generative modeling have facilitated the efficient exploration of molecular design space, but data sparsity in polymer science is a major obstacle hindering progress. In this work, we introduce a vast polymer database known as the Open Macromolecular Genome (OMG), which contains synthesizable polymer chemistries compatible with known polymerization reactions and commercially available reactants selected for synthetic feasibility. The OMG is used in concert with a synthetically aware generative model known as Molecule Chef to identify property-optimized constitutional repeating units, constituent reactants, and reaction pathways of polymers, thereby advancing polymer design into the realm of synthetic relevance. As a proof-of-principle demonstration, we show that polymers with targeted octanol-water solubilities are readily generated together with monomer reactant building blocks and associated polymerization reactions. Suggested reactants are further integrated with Reaxys® polymerization data to provide hypothetical reaction conditions (e.g., temperature, catalysts, and solvents). Broadly, the OMG is a polymer design approach capable of enabling data intensive generative models for synthetic polymer design. Overall, this work represents a significant advance enabling the property targeted design of synthetic polymers subject to practical synthetic constraints.
There are notable endeavours to accelerate polymer materials discovery using machine learning (ML) and materials databases. However, data collection and processing from literature resources is still manual and time-consuming. The current ML workflows focus on correlating polymer structures to their properties, which is not suitable for driving high-throughput experiments where the polymer structure/chain architecture is unknown. Therefore, experimental data is necessary to guide the experimentation, such as types of starting monomer building blocks and stoichiometric ratios.

In this work we showcase an automated workflow for scrapping optical spectra from literature using image extraction algorithms and large natural language models, converting the graphs to data tables and building an electronic polymers database that relates the building blocks and ratios to desired properties. This database serves as the baseline for training ML models, building simulation workflows and guiding autonomous experiments. We designed an ML workflow that leverages the collected information and is using a transformer model architecture to predict polymer properties associated with their color. We will discuss the challenges faced during this process, applicable ML algorithms and future steps for automating the creation of large polymer databases.
Linking fibrillar structure and chain packing in methylcellulose solutions to extent of methylation using machine learning, genetic algorithm, and multiscale simulations

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Methylcellulose (MC), a cellulose derivative polymer, exhibits unique phase behavior wherein it is soluble in aqueous solutions at room temperature and at elevated temperatures self-assembles to form fibrils that can in turn form gels and networks. For targeted design of MC based materials for applications (e.g., food additive, drug delivery, tissue engineering, etc.), there is a need to understand this phase behavior, especially the hierarchical structure - assembled networks of fibrils, multiple MC chains packing into a fibril, and individual MC chain conformation - as a function of extent of methylation in the MC chains. In this talk, we present a comprehensive study of the hierarchical structure in MC solutions using a combination of machine learning and genetic algorithm-based analyses of experimental scattering measurements and physics-driven multiscale modeling and simulations. We first use machine learning (ML) enhanced Computational Reverse-Engineering Analysis of Scattering Experiments (CREASE) method to interpret published small-angle scattering (SAS) profiles of commercially available MC chains forming fibrils in aqueous solutions. (Z. Wu, A. Jayaraman, Macromolecules, 2022, 55, 24, 11076-11091). This ML-CREASE approach provides a quantitative characterization of MC fibril dimensions (i.e., fibril diameter distribution and fibril stiffness). We complement the ML-CREASE interpretation with structural information about chain packing within the fibrils and behavior of water around MC chains obtained through coarse-grained and atomistic molecular dynamics simulations. Together, this top down (ML-CREASE) and bottom up (multiscale modeling and simulation) computational approach provides explanation as to why commercial MC chains assemble into fibrils with consistent diameters regardless of concentration and molecular weight, and how and why the MC chains pack in parallel configuration in the fibril. We also go beyond commercial MC chains and describe how and why the extent of methylation in the MC chains affect their packing and assembly into fibrils.
Open source web-based data platform to support the sustainable development of plastic recycling

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One of the important aspects in the emerging field of solid waste recycling that is often overlooked is the extraction of data available in the literature, storage, analysis and dissemination of the existing or new data. This is crucial not only for the development of solid waste conversion processes but also for the techno-economic analysis (TEA) and life cycle assessment (LCA). In this presentation, I will focus on giving an overview of our research efforts to develop an open source web-based data platform focusing on plastics recycling data relevant for the development of chemical recycling of plastics through pyrolysis as a case study. In the first part of my presentation, I will focus on optical character recognition (OCR) models that we developed to extract data from literature. In the second part, I will focus on showcasing our initial efforts towards building a plastic recycling database. In collaboration between researchers at Penn State University and Community Resource for Innovation in Polymer Technology (CRIPT) team, the database is hosted as part of the CRIPT platform. Finally, I will discuss future insights for open source databases to support the sustainable development of plastic recycling.
Enabling Interoperability through FAIR Vocabulary Models

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Scientifically relevant datasets are often highly specialized explorations of subtle phenomena that require careful control over environmental conditions and sample preparation. While individual investigations can identify prior experimental design that informed a given experiment, the global relationship between experiments is a tangled, high-dimensional web. While it may be trivial to feed a table published in an individual study into a machine learning model, mapping this complexity into the required rigid vectors incautiously will result in the loss of essential metadata and confounding variables that communicate whether the experiments are truly comparable for the sake of the immediate model. In order to generate a large dataset relevant to polymer physics, one must reconcile discrepancies in jargon across time and specialization, including many concepts that would be irrelevant to more general chemical studies.

In information science, such challenges are often addressed with taxonomies, ontologies and controlled vocabularies. These tools for modeling language allow computers to aid humans in gathering relevant resources from a collection, determining utility through both qualitative and quantitative similarities in experimental design. They also provide an opportunity to augment immediately relevant data by identifying tangentially related physical tabulations, such as using thermophysical properties of small molecules as input features to inform repeat unit dynamics. Accumulation of truly large data, and all the diversity that comes with such a corpus, will require community members to use standardized language and knowledge graphs to distinguish subtleties of meaning. Here, we will discuss community efforts to generate the Open tooling to provide bench practitioners with software like pipelines and transformers that require minimal programming effort to interface with larger collections. Interoperability is where efforts to create FAIR (Findable, Accessible, Interoperable, Reusable) data resources most often fall short, and so such community tooling dramatically improves the likelihood of the collection of consistent and well formed metadata.
MaterialsMine: Curation, ontology, and knowledge graph for discovery in polymer nanocomposites

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With the advent of the materials genome initiative (MGI) in the United States and a similar focus on materials data around the world, numerous materials data resources and associated vocabularies, tools, and repositories have been developed. While the majority of these systems focus on slices of computational data with an emphasis on crystallographic materials, platforms for organic materials and their composites, especially those incorporating experimental data, have been quite limited. We will discuss the unique aspects of tackling data assembly and informatics associated with experimental organic materials data, with focus on our experiences creating an open-source data resource, NanoMine, part of MaterialsMine. Our goal has been to curate, annotate and store widely varying experimental data on polymer nanocomposites (polymers doped with nanofiller) and providing access to characterization and analysis tools with the long-term objective of promoting facile nanocomposite design. To accelerate this process, we have utilized natural language processing (NLP) techniques to identify entities and links between them in the literature on polymer nanocomposites. We are working on Lange Language Models (LLMs), which are a recent addition to the materials science domain and have shown promising results for extracting structured information from unstructured text. The challenges and promises associated with data curation, ontology and vocabulary development, standardization and interoperability, and data visualization and analysis tools will be discussed. Several case studies will be presented, including use of NLP for archival data curation, coupling of experimental and computational data for materials design, and development of machine learning tools for rapid property screening and inference. Overall, we focus on the promise of this new approach to tackle materials design principles for the complex, high dimensional problems inherent in the multi-phase polymer space.
Modular synthesis of end-functional polymers for high-throughput supramolecular block copolymer preparation

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Block copolymers (BCPs), with two or more homopolymer blocks, represent extraordinary materials applied in various fields, including ultrafiltration membranes, sensors, solar cells, etc. However, traditional block copolymer development requires a laborious process of synthesis, processing, and quantifying new material, which limits the throughput of the materials discovery rate. Supramolecular block copolymers (SBPs) are BCPs assembled with non-covalent end-functional group pairs (i.e., DAT/Thy for H-bonding). Synthesis of SBPs with different architectures, chain lengths, and chain length ratios can be simply achieved by physically blending two polymers, which shows great potential for rapid and high-throughput synthesis. To accomplish the high-throughput synthesis of SBPs, a large number of end-functional polymer blocks are required, which is still complicated. Inspired by the concept of 'LEGO', in this work, we developed a modular synthesis method that successfully achieved mass production of end-group functional polymers. We separated the synthesis into two parts, including functional polymers (Polymer-A) and functional H-bonding groups (HGroup-B). The Polymer-A were first polymerized via various controlled polymerization methods. Then click reaction was utilized to connect the HGroup-B to all kinds of Polymer-As via the 'grafting to' method. The HGroup-B was also clicked to initiator to initiate the polymerization to achieve the 'grafting from' process. Such synthetic method is flexible, universal, and adaptable to various kinds of polymers. Therefore, it shows numerous potentials to prepare functional polymers for the high-throughput synthesis of SBPs.
Predicting polymer solubility through machine learning: towards solvent recycling of plastics

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Polymer solubility is one of the most important physical properties for synthesis and processing, with microprocessor fabrication, paint formulation, and drug delivery applications. Despite this importance, it has remained relatively understudied. This can largely be attributed to many theoretical and experimental challenges specific to macromolecule solubility, which makes theoretical formulations challenging and invalidates common solubility measures used in small molecules. By utilizing a data-driven machine learning approach, one can avoid many challenges while quickly and accurately predicting polymer solubility over a diverse chemical space. Motivated by the effectiveness of machine learning and by the current plastics crisis, in this presentation we discuss our work to predict selective solvents for the solvent recycling of waste thermoplastics. Specifically, we will highlight our recent research on predicting binary solubility labels for polymers via message-passing neural networks alongside non-deep models such as random forests. We consider both homopolymers and copolymers in our model input, which were represented as both graphs and text strings. Our physics-informed approach to model construction results in an accurate and extensible model and demonstrates practical applications of the resultant machine learning models.
Biorelated Polymers (in honor and memory of Dr. Ray Ottenbrite)

Toward minimizing adverse events for silicone medical devices - Wynne, Kenneth (Oral Only)
Poly(amino acid)s: From nutrition to the biomedical arena - Scholz, Carmen (Oral Only)
Biodegradable balloons for tissue separation - Domb, Avi (Oral Only)
Polymeric nanomedicine targets brain cancer - Quader, Sabina (Oral Preferred)
Non-fouling surface modifications of "real-world" biomaterials with grafted surface brushes - Ratner, Buddy (Oral Only)
Honoring Ray Ottenbrite's "agnostic" philosophy of advancement: An expansive view of tissue engineering - Coury, Arthur (Oral Only)
Polymeric bioactives: Polymers from bioactives and as bioactives - Uhrich, Kathryn (Oral Only)
Towards translation of superhigh-capacity polymeric micelles for chemo/immunotherapy of cancer - Kabanov, Alexander (Oral Only)
Using charge patterning to modulate the solution self-assembly and structure of sequence-defined peptoid polymers - Zhang, Donghui (Oral Only)
Diblock polypeptide hydrogels as bioinks for 3D printing in tissue engineering - Cosgrave, Muireann (Oral Only)
Water-soluble polymer-collagen hybridizing peptide conjugates for targeting tumor extracellular matrix - Ghandehari, Hamid (Oral Only)
Orally administered polymer micelle-type antioxidants that scavenge the intestinal ROS lead to health - Nagasaki, Yukio (Oral Only)
Responsive amphiphilic block copolymers for selective sensing at liquid-liquid interfaces - Savagatrup, Suchol (Oral Only)
Nature-inspired synthetic polymers for customized biomedical applications - Lim, Soon-Mi (Oral Only)
Polypept(o)ides: From defined polymer architectures to better therapies - Barz, Matthias (Oral Only)
Synthesis and characterization of erythropoietin-polyester conjugates - Kressler, Joerg (Oral Only)
NCA polymerization for preparation of functional polyprolines and polypeptoids - Kramer, Jessica (Oral Only)
Minimally invasive biomaterial based approaches to manage osteoarthritic pain - Nair, Lakshmi (Oral Only)
Near-field electrospinning of polydioxanone to fabricate tissue-specific in situ regeneration templates - Bowlin, Gary (Oral Preferred)

Facile end-group diversification of poly(2-oxazoline)s towards applications in nanomedicine - Van Guyse, Joachim (Oral Preferred)

Poly(2-oxazoline): Based double network hydrogels as artificial cartilage - Tiller, Joerg (Oral Only)

Programmable synthesis and supramolecular self-assembly of stable DNA nanoparticles - Zauscher, Stefan (Oral Only)

Programming bacterial surface behavior with biosurfactant-mimetic polyurethanes - Chen, Zixi | Joy, Abraham (Oral Only)

Delivering polymer nanomedicines using living cells - Klok, Harm (Oral Only)

Poly(2-oxazoline)s: From fundamental research to biomedical applications - Hoogenboom, Richard (Oral Only)

Enhancing PDNA delivery with hydroquinine polymers by modulating structure and composition - Reineke, Theresa (Oral Only)

Exogenous application of salicylic acid-based poly(anhydride ester) in micro-tom for controlled release of salicylic acid against drought stress - Reis Nogueira de Lima, Mariana (Oral Preferred)

Sustainable polymers based on acrylic monomers from wide range of plant oils - Voronov, Andriy (Oral Only)

Polysaccharide-based macromolecules as safer chelation therapy for treating heavy metal poisoning - Sydlik, Stefanie (Oral Only)

Biobased and bioinspired polymers with controlled biodegradation conditions: From acetalated cellulose to polyphosphoesters – recent developments in molecular stability control - Wurm, Frederik (Oral Only)

Novel cyclodextrin-based nanoparticles delivering alpha-mangostin for the treatment of brain ischemia - Sakurai, Kazuo (Oral Only)

Controlled accelerated degradation of phosphoester (Co-)polymers - Rheinberger, Timo (Oral Only)

Negatively charged dendritic polyelectrolytes in biomedical applications - Braatz, Daniel (Oral Preferred)

Novel hydrolytically degradable salicylic acid-based poly(anhydride-esters) for triggered release of retinol - Nguyen, Nhien (Oral Only)

Biodegradable and biocompatible polymers for electronic applications - Cao, Yue (Oral Only)
Biomedical grade silicone, especially platinum cured poly(dimethylsiloxane), PDMS, is used in a broad range of medical devices because of ease of processing, biocompatibility and biodurability. Examples of devices comprised of “implantable” grade silicone elastomers range from urinary catheters and urethral stents to Ear/Nose/Throat (ENT) devices such as airway stents and ventricular shunts. PDMS has a hydrophobic surface that elicits a foreign body reaction. It is susceptible to adhesion of bacteria and/or fungi, the growth of biofilms, and other forms of biofouling. Consequently, a range of Adverse Events (AEs) can occur depending on the duration of implantation, the location in the body, and the disease state of the patient. In this presentation, surface modification is described aimed at mitigation of Catheter Associated Urinary Tract Infections (CAUTI). These infections are common in hospitals and health care facilities. A list of those susceptible to CAUTIs includes those who are disabled and the elderly and infirm with longer catheter indwelling times. Research is described for surface modification designated WG-1 silicone, which affects contact kill of bacteria. *In vitro* tests have been developed to provide an understanding of antimicrobial effectiveness and suitability of WG-1 for a device designation by FDA Office of Combination Products.
Poly(amino acid)s, PAAs, are built from amino acid monomers, but they lack the sequence specificity that is characteristic for proteins and peptides, as they usually consist of only one or two different amino acids. Poly(amino acid)s occur naturally; e.g. poly(g-glutamic acid) is the main component of natto, a Japanese staple food or they can be synthesized from the respective amino acids to form linear polymers, copolymers, block copolymers, dendrimers, dendrigrafts or hyperbranched polymers. An exceptional control over molecular weight and polydispersity of PAAs can be achieved, since amino acid N-carboxyanhydride monomers lend themselves to living ring-opening polymerizations, which also enable the formation of block copolymers. PAA copolymers and block copolymers have been studied by our group for (i) the modification of implants making use of the affinity of the thiol group in cysteine for gold, (ii) the modification of ceramic monolith making use of the ability of amino acids with reactive side groups to bind enzyme-specific ligands for protein purification, (iii) delivery vehicles for nucleic acids making use of the ability of poly(L-Lysine) to condense DNA, and (iv) delivery vehicles for imaging agents making use of the ability of hydrophobic PAAs to “cradle” and separate hydrophobically coated magnetite nanoparticles.
Biodegradable balloons for tissue separation

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Biodegradable inflatable balloon implants were developed for treating rotor-cuff injuries and tissue separation for reducing irradiation side effects. The balloons, prepared from poly(lactide-caprolactone), are folded into a rod shape that is inserted into the space between the prostate and rectum or within the rotor cuff and inflated to form a space of about 10 mm between tissues. This balloon separation allows healing of rotor cuff injury and reduces damaging irradiation of the rectum while irradiation of tumorous prostate. These balloons remain inflated for about 8 weeks before rupturing and eliminating from the implant site. Novel compositions of biodegradable polymers and oils have been developed to increase flexibility and retain inflated balloons for a longer time will be discussed.
Polymeric nanomedicine targets brain cancer

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Recent decades have seen unprecedented progress in understanding, preventing, and treating cancer. Despite significant breakthroughs, millions of people worldwide remain affected by cancer. Notably, the overall improvement in cancer therapy has not been uniform among different cancer types, and certain types of cancer, like brain tumors, remain intractable. A challenge in treating these cancers is delivering drugs to the brain tumor site in therapeutic concentration, bypassing the blood-brain (tumor) barrier (BBB/BBTB). In this direction, nanomedicines (NMs) are increasingly demonstrating noteworthy prospects for addressing these challenges utilizing their unique characteristics, such as improving the bioavailability of the payloads via controlled pharmacokinetics and pharmacodynamics, BBB/BBTB crossing functions, superior distribution in the brain tumor site, and tumor-specific drug activation profiles. However, the effective translation of these novel approaches remains sluggish. We aim to bridge innovation and translation efficiently in our laboratory at the Innovation Center of NanoMedicine (iCONM). Our nanomedicine platform is based on polymeric micelles that are constructed from poly(ethylene glycol)-b-poly(amino acids) (PEG-PAA) copolymers and have already demonstrated significant promise through their clinical translation potential. The PEG-PAA copolymers are highly biocompatible and have the unique ability to engineer versatile, dynamic covalent chemistry-based approaches to link the cargo with the carriers; this feature ultimately improves spatiotemporal control over drug release kinetics, which is one of the critical properties of drug-loaded nanocarriers, along with size and surface properties. This presentation will highlight a few specific examples of NM-based brain tumor targeting approaches.

With the ability to engineer a variety of dynamic covalent chemistry approaches, PEG-PAA copolymers offer an ideal means of linking cargo with carriers; this allows for spatiotemporal control of drug release kinetics, a critical property of drug-loaded nanocarriers along with size and surface properties enabling effective therapeutic outcomes against brain cancer.
Non-fouling surface modifications of “real-world” biomaterials with grafted surface brushes

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Brushes of zwitterionic poly(sulfobetaine methacrylate) (pSBMA) were surface-grafted to various biomaterial substrates to lower nonspecific protein adsorption using a highly-reactive bromoester. Methyl 3-bromopropionate (M3BP) was deposited using a radio frequency glow discharge plasma to functionalize polytetrafluoroethylene (PTFE), a reinforced polyurethane, silicon, and titanium with robust, uniform, and delamination-resistant initiator coatings. Activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) was used to synthesize the nonfouling pSBMA coatings. Surface-initiated grafting often utilizes processing steps that would be challenging for implantable biomedical devices, whereas the method reported here employing plasma-deposited initiator allows for nonfouling coatings on a variety of materials and geometries. X-ray photoelectron spectroscopy was used to characterize the M3BP and pSBMA coatings, demonstrating successful and uniform grafting. Coating thicknesses were measured to be 43 ± 5.9 nm after the M3BP deposition and 77 ± 6.3 nm after pSBMA grafting. The contact angle of titanium reduced from 84 ± 2.5 degrees for the pristine surface to 13 ± 1.9 degrees after pSBMA grafting demonstrating high wettability. Coating stability was assessed after a multi-solvent soak at each step. Finally, the nonfouling ability of the pSBMA coatings were measured using I-125 radiolabeled human serum albumin. An 84% reduction in protein adsorption was measured for pSBMA grafted on different polyurethanes and 77% reduction on PTFE, as compared to bare substrates. Low albumin adsorption (17.5 ± 2.9 ng/cm²) was measured for pSBMA on reinforced polyurethane. Thus, using a plasma-deposited ATRP initiator to grow non-fouling brushes is a viable option to reduce nonspecific protein adsorption for “real-world” applications.
Honoring Ray Ottenbrite's "agnostic" philosophy of advancement: An expansive view of tissue engineering

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Although I met Professor Ray Ottenbrite in person at a "Frontiers in Biomadical Polymers Symposium" in Ischia, Italy, in 2003, I had followed his work as Founding Editor of the "Journal of Bioactive and Compatible Polymers" for a long time. But it required meeting him in person to appreciate the many attributes of Ray that provided so much value to our Biomaterials field. I wrote the preface to a 2013 ACS Symposium Series book: "Tailored Polymer Architectures for Pharmaceutical and Biomedical Applications" co-edited by our current Symposium Co-Chair, Professor Carmen Scholz and dedicated to Ray. My preface stated: "This book is a perfectly appropriate way to honor Ray, since, as long as I have known him, he has exemplified and promoted the commendable "agnostic" premise that all scientific tools should be applied appropriately to the solution of unmet medical and other societal needs through his own research, the publications, conferences and symposia that he has sponsored and the professional service he has rendered.

I spoke at Ray's ACS Polymer Division Symposia numerous times, He never specified what I should speak about, indulging my controversial biomaterial topics without criticism, even with encouragement. Honoring Ray's expansive spirit, i herein define tissue engineering as effecting systematic control of the body's cells, matrices, molecules and fluids for beneficial purpose, and its breadth is far-reaching. I will provide supporting examples of this premise. My pronouncements about the definition and scope of Tissue Engineering defy "conventional wisdom" in the magnitude of their scope.
Polymeric bioactives: Polymers from bioactives and as bioactives

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Our research centers on polymeric bioactives; specifically, the design of biocompatible, biodegradable polymers. While polymeric bioactives were initially designed for delivering pharmaceuticals, the concept has been expanded to improve the lubricity of engine oils, to prevent plaque buildup on tooth enamel and to improve skin appearance. To design biocompatible and biodegradable polymers, we begin with starting materials that are naturally occurring and deemed safe. We have two different classes of polymers - polymers that deliver bioactives and polymers derived from bioactives.

As polymers that deliver bioactives, nanoscale amphiphilic macromolecules (AMs) were initially created to encapsulate hydrophobic drugs and improve drug water-solubility and improve bioavailability. Our current work builds upon the discovery that the AMs themselves are bioactive – they actively coordinate with binding domains on macrophages to mitigate formation of atherosclerotic plaques. They also display novel mechanisms for mitigating biofilm formation.

As polymers derived from bioactives, PolyActives are designed to biodegrade into therapeutically useful or bioactive molecules. The first example was a poly(anhydride-esters) that yielded salicylic acid, the active component of aspirin. This concept has been expanded to include PolyAntibiotics, PolyAntiseptics and PolyOpiates useful for localized, controlled bioactive delivery for pharmaceutical, personal care, and commercial applications.
Towards translation of superhigh-capacity polymeric micelles for chemo/immunotherapy of cancer

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Poly(2-oxazoline) (POx) based polymeric micelles (PM) enable unprecedented high loading of water-insoluble drugs, enhancing their solubility, stability, efficacy, and safety. Micelle morphology affects drug performance, with spherical micelles accumulating quickly in tumors and showing greater anti-tumor effects than worm-like micelles, which accumulate slower and release drug in the blood. Co-loaded two-drug micelles exhibit superior antitumor activity compared to single drug micelles or their combination, as well as free drug combination. This approach enables "drug design by co-formulation" and offers potential for cancer immunotherapy. To facilitate the translation of drug-loaded micelles, we will discuss approaches for their scale-up and manufacturing, including lyophilization and spray drying. Challenges in the storage, stability, and reconstitution of drug-loaded PMs must be carefully addressed. The relationship between drug loading, partitioning between micelle and serum proteins, pharmacokinetics/toxicokinetics, and efficacy will be discussed. These innovations accelerate the translation of novel PMs for therapeutic applications in cancer and other diseases.
Using charge patterning to modulate the solution self-assembly and structure of sequence-defined peptoid polymers

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Biomolecules such as polysaccharides and intrinsically disordered proteins have been shown to use charge patterning, i.e., the number and relative position of charged groups along a chain-like molecule, to modulate their structure, dynamics, intra/inter-molecular interactions, and biological functions. By contrast, much less is known regarding the roles of charge patterning in synthetic polymer assemblies, despite the unique opportunity for tailored morphologies, tuned only by the charge sequence of molecularly equivalent chains. In this presentation, we will discuss our recent efforts in the solution self-assembly of sequence-defined ionic peptoid block copolymers with discrete or dispersed chain lengths in water under dilute and semi-dilute regimes. A combination of transmission-electron microscopy, scattering (SANS/SAXS) characterization as well as molecular dynamics simulations were employed in the study. We have found that the charge patterning significantly affect the micellar aggregation, intra-micellar assembly, intermicellar interaction potential, and the micellar structural response towards environmental stimuli (e.g., solution pH). The mechanisms by which the positionally defined charges along the chains modulate the micellar structures will be discussed.
Diblock polypeptide hydrogels as bioinks for 3D printing in tissue engineering

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The use of 3D printing in tissue engineering (bio-printing) has rapidly increased throughout recent times, namely due to its ability to construct more complex, cell-viable 3D structures.\(^1\) Hydrogels are a prominent choice for bio-ink formulations as they can be engineered to simulate the native extracellular matrix (ECM).\(^2\) Furthermore, their mechanical properties can be altered to optimize printability and cytocompatibility properties. For particular applications, the choice of hydrogel used in bio-printing processes encompasses several important considerations, particularly that its strength is stable and suitable for the printing process, whilst also being comparable in strength to that of the native tissue it is replacing.\(^2\)

Here we present a range of amphiphilic star-shaped diblock co-polypeptides consisting of methacrylamide functionalized poly(L-glutamate)-b-(L-leucine) with different star architectures. The hydrophobic side chains of the L-leucine blocks drive the self-assembly of the polypeptides in water, spontaneously forming stable hydrogels. The mechanical properties of these materials are readily tuned by varying the star architecture and the monomer feed used. They also possess shear-thinning and self-recovery properties, indicating their suitability for extrusion based 3D printing. Complex 3D printed structures can be readily generated and then photo-crosslinked using visible light (405 nm) in the presence of comonomers. Printed hydrogels show good biocompatibility and represent viable bio-ink material platforms for tissue engineering.
Water-soluble polymer-collagen hybridizing peptide conjugates for targeting tumor extracellular matrix

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Water-soluble polymeric carriers with pendent peptide side chains have been used for targeted delivery of bioactive and imaging agents to solid tumors. The targeting moieties in these systems are typically used to home to the surface of tumor cells or to angiogenic blood vessels. While these strategies have shown promise in localized drug delivery and imaging of solid tumors, there is very little research on targeting carriers to the extracellular matrix (ECM). ECM targeting provides distinct advantages for drug delivery and cancer therapy. One approach to target the ECM is by utilizing collagen hybridizing peptides (CHPs) that selectively bind to denatured collagen. The advantages of attaching CHPs to the side chains of water-soluble copolymers is that such conjugates provide multi-valency, opportunity to attach multiple drugs and imaging agents as well as increase in circulation time and tumor uptake. In this work we describe our recent efforts in targeting breast tumors, osteosarcoma and pancreatic tumors by N-(2-hydroxypropyl)methacrylamide (HPMA) copolymers with side chains terminated in fluorinated CHPs. These conjugates showed increased tumor localization compared to copolymers with scrambled peptides and increased retention in the tumor compared to free CHPs. Such strategy provides opportunities to image the tumor ECM or target drugs acting on the ECM and the tumor environment with improved efficacy and reduced toxicity.

Figure 1. Schematic of HPMA copolymer-CHP conjugates for targeting tumor ECM.
Orally administered polymer micelle-type antioxidants that scavenge the intestinal ROS lead to health

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Reactive oxygen species (ROS), which are inevitably produced by oxygen respiration for life to gain energy, are essential signaling molecules at normal levels but overproduced ROS oxidizes cellular components and causes various diseases. Conventional antioxidants did not achieve a remarkable medicinal effect due to the rapid clearance, and dysfunction of intracellular redox homeostasis. We have designed amphiphilic block copolymers in which antioxidant moieties were covalently introduced in the hydrophobic segment. The obtained block copolymer spontaneously forms polymer micelles in an aqueous solution (RNP). As RNPs have several tens of nanometer size and PEG surface layer, they improve bioavailability and prevent damage in the intracellular redox balance, and they show a remarkable therapeutic effect on various oxidative stress-related diseases. Recently, we have found that orally administered RNP localized in the gastrointestinal tract ameliorated stress-induced depression and athletic performance by eliminating gastrointestinal ROS. For example, in stress-induced depression model mice, intense inflammation of the gastrointestinal tract was induced, but the oral administration of RNP strongly suppressed it. When mice were made to run on the treadmill until they could no longer run, their GI tract was damaged significantly (so-called EIGS). After oral administration of RNP, the intestinal damage was recovered significantly, and the running time was extended by 40-50% compared to normal mice. Therefore, we conclude that the effective elimination of ROS that is overproduced in the GI tract is extensively involved in maintaining health. The author appreciates Mr. Naoki Saigo, Dr. Yutaka Ikeda (depression) and Dr. Takuto Toriumi (Exercise) for their collaboration.

Fig. A) TEMPO (●)-installed amphiphilic block copolymer and self-assembles in water, with a size of several tens of nm. B) Toxicity to zebrafish. Survival rate (above), mitochondrial staining photographs (below)
Responsive amphiphilic block copolymers for selective sensing at liquid-liquid interfaces

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Complex emulsions with responsive surfactants provide a unique sensing platform that leveraged tunable interactions at liquid-liquid interfaces. In this presentation, we report our progress toward the fabrication of distributed, real-time sensors by incorporating complex emulsions with responsive amphiphilic block copolymers as selective recognition units. Specifically, we modified a common block copolymer via post-polymerization functionalization with the ability to undergo bioinspired conformational changes upon exposures to targeted analytes. Such interactions significantly alter the interfacial tensions at the interface of complex emulsions, drive macroscopic morphological changes, and produce distinctive optical signals. We will discuss our recent effort to detect different classes of biomolecules and environmental contaminants. We anticipate that the incorporation of responsive all-liquid materials into sensing platforms will provide a cost-effective, easily tunable, and portable alternative to laboratory-based analytical methods for on-site sensing applications.
Nature-inspired synthetic polymers for customized biomedical applications

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Synthetic polymers are promising candidates for customized biomedical applications due to versatility of structural modifications to meet the need of specific applications. In this talk, we will be presenting our recent developments of nature-inspired polymers for artificial bones, cardiovascular applications, and tissue recovery. Poly(thioether-co-carbonate) materials were synthesized from tris(alloc)quinic acid (TAQA) and multifunctional thiols. Quinic acid is abundant in coffee beans and plant-based food and can be metabolized by bacteria in guts. The TAQA polymers showed storage modulus of 1.4 GPa, which can be comparable to moduli of cancellous bones, and provided viable environment for preosteoblast cells. Degradation compounds from the polymer were also tested to be benign to cells. Poly(honokiol carbonate) (PHC) and a series of thermosets were synthesized from tree-based honokiol and magnolol and tested for cardiovascular applications. 3D-printed PHC and magnolol thermosets were tested with vascular endothelial cells, which maintained a monolayer of viable cells on the substrate even after a month. Furthermore, magnolol thermosets showed scavenger effect for reactive oxygen species (ROS). Hydrolytic degradation and swelling properties of magnolol thermosets also exhibited great potential as a drug-eluting material for vascular stents and coatings. Soft polymers have different categories of biomedical applications such as artificial tissue for wound healing and tissue rejuvenation. A hydrogel system from poly(ethylene glycol)-block-poly(dl-allylglycine) (PEG-b-PDLAG) mixed with fibroblast cells were tested for viability. As the hydrogel degraded in cell culture medium, cells were released to the cell culture plate and proliferated on the substrate. Cells showed high viability even after captured for a week in the hydrogel due to the porous structure of the hydrogel that allows penetration of nutrition and air. Our study showed that nature-inspired synthetic polymers can be environment-friendly tools for on-demand materials to meet the need of specific applications with relatively simple and cost-effective synthesis methods.
Polypept(o)ides: From defined polymer architectures to better therapies

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Polypept(o)ides combine the stealth-like properties of polypeptoids such as polysarcosine (poly(N-methyl glycine)) with the multifunctionality and intrinsic stimuli-responsiveness of synthetic polypeptides. This class of copolymers can be synthesized by controlled living ring-opening polymerization of the corresponding α-amino acid N-carboxyanhydrides (NCAs) and N-substituted glycine N-carboxyanhydrides (NNCAs). While polysarcosine provides a benefit with respect to the current concerns of poly(ethylene glycol) (PEG), e.g., acute immune responses, the polypeptide part can provide a plethora of reactivity or functionality, allowing to tailor the polymer for specific tasks. In this presentation I will provide an overview on recent developments in the synthesis, self-assembly and biomedical application of polypept(o)ides for diagnosis and therapy of cancer, inflammatory disorders, and bacterial infections.

Figure 1: Overview on different polypept(o)ide architectures, nanoparticles and biomedical applications
Synthesis and characterization of erythropoietin-polyester conjugates

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Erythropoietin (EPO) is a glycoprotein hormone useful for the treatment of anemia in patients with chronic kidney disease and in cancer patients who are receiving chemotherapy. The accessibility of the glutamine (Gln, Q) residues of recombinant human erythropoietin (rHuEPO) was studied towards a thermal stable form of microbial transglutaminase (mTGase), TG16. The aim is the development of new rHuEPO conjugates with potentially enhanced plasma half-life and in vivo efficacy. As a model system, we studied the reaction of rHuEPO with a low molecular weight amine groups containing substrate, monodansyl cadaverin (MDC). Analysis by SDS-PAGE and mass spectrometry confirmed the conjugates formation. Furthermore, we examined the conjugation of rHuEPO with a biodegradable and biocompatible polyester, poly(D-sorbitol adipate) (PDSA). Here, PDSA was enzymatically synthesized using lipase B from Candida antartica (CAL-B), chemically modified with side chains having free primary amine (NH2) groups that can be an acyl acceptor substrate of TG16. It was carefully characterized by 1H NMR spectroscopy, and then used for the TG16-mediated conjugation reaction with rHuEPO. rHuEPO conjugates formed by this technique were identified by SDS-PAGE proving that the amine-grafted PDSA is accepted as a substrate for TG16. The successful conjugation was further confirmed by the detection of high molar mass fluorescent bands after labelling of amine-grafted PDSA with rhodamine B-isothiocyanate. In summary, this enzymatic procedure is considered as a suitable approach to synthesize biodegradable rHuEPO-polymer conjugates.
For over 100 years, NCA polymerization has been a reliable method to prepare polypeptides. Classic amine and alkoxides initiators present challenges in achieving high molecular weights and low dispersities. Transition metal initiators were developed to overcome this issue but could not initiate amino acid NCAs lacking an NH proton such as proline, or N-functionalized monomers for preparation of polypeptoids. We have now intercepted in intermediate in the initiation cycle to allow controlled polymerization of proline NCAs and N-functionalized NCAs. This method has opened doors to preparation of new functional materials with unique conformations and biomedical applications. Polymerization mechanisms and characteristics will be discussed, as well as material properties of the resulting polyproline and polypeptoids.
Minimally invasive biomaterial based approaches to manage osteoarthritic pain

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Pain is considered the most common disabling symptom of osteoarthritis (OA). Currently employed interventions to manage osteoarthritis pain include physiotherapy, anti-inflammatory drugs, intra-articular corticosteroid injections and visco-supplementation such as hyaluronic acid injection. As the prevalence of OA is steadily increasing, there is an urgent need to explore novel therapeutic strategies to manage osteoarthritic pain. The overall goal of our studies is to develop minimally invasive, non-addictive approaches to manage OA pain. Our studies on combining biomaterial based approaches with local anesthetics and anti-inflammatory/analgesic pain modulators and periarticular delivery in a minimally invasive manner will be discussed.
Near-field electrospinning of polydioxanone to fabricate tissue-specific in situ regeneration templates

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The ideal biodegradable, polymeric-based regeneration template should be engineered to mimic (fiber diameters and overall orientations) the extracellular matrix (ECM) of native tissues to coordinate the cellular response and ultimately guide in situ functional regeneration. The near-field electrospinning (NFES) method allows for the “direct writing” of fibers, thus, adding the missing capacity in generating tissue template specificity and tailorability. Mechanical properties, pore size, and fiber orientation can be tightly programmed/controlled to bring about desired cellular responses. Two NFES apparatuses were custom designed and fabricated. For one design, the stock filament extruder was replaced with a custom three-dimensional (3D) printed adapter to accommodate a syringe pump. Fibers could be directly written onto a flat collector and sequentially stacked to create 3D, fibrous constructs. The polymer polydioxanone (PDO) was chosen as a candidate material due to its superior inflammatory response, mechanical properties, and in vivo degradation rate of 6-8 weeks. Subsequently, a second NFES system was constructed to create regeneration templates with more complex 3D geometries by including a rotating cylindrical mandrel driven by a stepper motor. This platform allowed a fiber to be written onto a cylindrical collector with a wind angle as the resultant vector between the translational 3D printer and the rotational mandrel. The direct writing of PDO fibers resulted in orderly sheet templates with tailored fiber sizes with the average fiber diameter ranging from 4.1 ± 1.1 to 8.0 ± 2.1 µm. When creating cylindrical vascular regeneration templates, the resultant mechanical properties depended on fiber diameter, orientations, and spacing (regulated pore sizes uncoupled from fiber size). In conclusion, we have demonstrated that solvent-based NFES of PDO is a viable technique to precisely create multiple types of 3D, fibrous tissue regeneration templates. The fabrication of seamless, cylindrical templates has numerous biomedical applications in vascular, neural, gastrointestinal, and urinary tissue engineering fields.
Facile end-group diversification of poly(2-oxazoline)s towards applications in nanomedicine

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The precise control over the end-groups of biocompatible polymers has been proven key in enabling polymer-based therapeutics and nanomedicine, most notably in the form of PEGylation. Nevertheless, the diversification of the end-groups can be a synthetically exhaustive process, especially for polymers prepared via ionic polymerization mechanisms, due to the limited functional group tolerance of the polymerization. Towards this end, we explored a single-step post-polymerization modification approach for facile end-group diversification of poly(2-oxazoline)s (POx) with a wide array of nucleophiles by exploiting the differential reactivity towards O, N, and S-nucleophiles of a pentafluorophenyl α-terminus and the living oxazolinium ω-terminus. This attractive route towards POxylation was subsequently applied in the synthesis of polypeptide-POx blockcopolymers and lipid-POx conjugates, which are well-suited platforms for drug and gene delivery. Finally, the application of a lipid-POx conjugate for the formulation and delivery of mRNA lipid nanoparticles was investigated, which underlines the value of POx as a biocompatible polymer platform.

Figure 1: Synthetic scheme showing facile end-group diversification of poly(2-oxazoline)s via a combination of the nucleophilic termination reactions and para-fluoro substitution of a pentafluorophenyl α-terminus.
Poly(2-oxazoline): Based double network hydrogels as artificial cartilage

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Poly(2-oxazoline)s (POx) are pseudopeptides with excellent biocompatibility. We have rendered POx in various ways to create potent switchable enzyme inhibitors, highly active and selective biocides or antibiotic conjugates that overcome bacterial resistances. Here, the work on POx-based double network hydrogels (DNH) as artificial cartilage is presented. Osteoarthritis is one of the most prevalent diseases in our rapidly ageing population, affecting the articular cartilage in load bearing joints such as hip and knee; and therefore, it is a currently leading cause of disability for more than 500 million people worldwide. So far, no material can substitute the non-regenerable cartilage, mostly because of its highly demanding mechanical properties, being a hydrogel with an average water content of 70% and compressive strength values between 14 and 59 MPa. The only water-swollen material class that can in principle exhibit such a strength is a DNH. To date, no DNH with sufficient strength in physiological environment has been described. A DNH composed of end group cross-linked poly(2-methyl-2-oxazoline) and subsequently polymerized poly(acrylic acid) (PAA) within the primary network shows not only a remarkable compressive strength of up to 60 MPa in phosphate buffered saline or egg white, but also shifts the pKa value of PAA from 4.7 to above 7.4. This makes the DNH applicable in physiological environment. Additionally, the DNH is not cytotoxic to stem cells and exhibits a compressive modulus, water content, coefficient of friction, and a dynamic load behavior that is similar to the challenging cartilage.
Programmable synthesis and supramolecular self-assembly of stable DNA nanoparticles

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The enzyme terminal deoxynucleotidyl transferase (TdT) can synthesize both natural and unnatural polynucleotides in a template-independent manner. We harness this ability in a reaction we term TdT-catalyzed enzymatic polymerization (TcEP) to create self-assembled DNA nanoparticles. We demonstrate the use of TcEP to synthesize aptamer-containing polynucleotides and micelles that deliver the cytostatic nucleobase analog 5-fluorouracil. We find that the micelles exhibit high nuclease resistance and greater tumor cell cytotoxicity than free drug. Further, we show how we use TcEP to initiate polynucleotide brush growth on the surface of DNA origami nanostructures (DONs). We find that brush-functionalization increases nuclease resistance and that we can spatially program stability of DONs through site-specific growth of brushes. We combine TcEP with restriction enzyme cutting to achieve spatiotemporal control of brush growth and cleavage on DON surfaces. Finally, we show how we use TcEP to modify the DON surfaces by growing hydrophobic brush patches to drive DON self-assembly into mesoscale structures (Fig. 1). We demonstrate that self-assembly behavior is governed mainly by the number-density and location of initiation sites on the DON surface. We exploit non-specific, hydrophobic interactions between hydrophobic polynucleotides to assemble DONs into flexible, supracolloidal nanostructures. Overall, our research provides guidance for constructing DNA nanoparticles for drug delivery applications and presents an innovative pathway for generating stable and programmable polynucleotide brush-functionalized DNA nanostructures for potential applications in smart nanoscale delivery systems.

Fig 1: (A) synthesis of patchy DNA origami nanostructures by enzyme-mediated site-specific growth of polynucleotide brushes, and (B) supramolecular assembly of hydrophobically modified DNA origami rods into micellar mesostructures.
Programming bacterial surface behavior with biosurfactant-mimetic polyurethanes

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Designing materials that can modulate the behavior of living systems can have a positive impact on the efficiency of biomanufacturing processes. Over the past couple of decades, it has been demonstrated that the industrial production of small molecules and synthetic macromolecules can be achieved through microbial engineering. Due to the chemical and physical tunability, ease of manufacturing, and bioactivity, synthetic polymers to direct bacterial behavior have been utilized as materials or synthetic matrices to design engineered living systems. Herein, we report a platform of synthetic, water-soluble, amphiphilic peptide-like polyurethanes as a means of regulating a variety of bacterial surface behaviors. Our research demonstrated that various hydrophilic functional groups can dramatically influence the surface motility of bacteria. Polyurethanes with carboxyl (-COOH) functional groups showed considerably enhanced surface swarming area in both *P. aeruginosa* (16x increase) and *E. coli* (10x increase). Furthermore, these polyurethanes were used to manipulate bacterial spatial migration to achieve designed spatial patterns of bacterial growth. The polyurethanes with -COOH group improved the surface wetting of agar and enhanced extracellular polymeric substance (EPS) production without limiting bacterial growth. Our approach to spatial programming bacteria via synthetic polymer stimulus is an exciting approach to designing active and responsive biomaterials.
Delivering polymer nanomedicines using living cells

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Cells provide attractive opportunities to develop innovative drug delivery systems. Red blood cells e.g. are uniquely designed to circulate in the bloodstream for extended periods of time. Immune cells, in particular lymphocytes from the adaptive immune system, are attractive as they potentially provide possibilities to home in to the disease site in a highly selective manner. Modifying the surfaces of these cells with synthetic polymers or polymer nanoparticles provides manifold opportunities to further enhance their functionality. Successful polymer cell surface engineering, obviously, requires conjugation chemistries that proceed under biological conditions and in high yields and without compromising cell viability and function. This presentation will discuss various polymer cell surface modification strategies and compare these different approaches in terms of the possibilities they offer to modify cell surfaces as well as their impact on cell viability and function. It will be shown that under appropriate conditions live cells can be surface modified with synthetic polymers while retaining their viability and functional properties.
Poly(2-oxazoline)s: From fundamental research to biomedical applications

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The living cationic ring-opening polymerization of 2-oxazolines has been studied in great detail since its discovery in 1966. The versatility of this polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer properties that enable, for example, hydrophilic, hydrophobic, fluorophilic, as well as hard and soft materials. Moreover, the chemical versatility allows orthogonal end-group and side-chain modification of the polymers. However, this class of polymers was almost forgotten in the 1980s and 1990s because of the long reaction times and limited application possibilities. In the new millennium, a revival of poly(2-oxazoline)s has arisen because of their potential use as biomaterials and thermoresponsive materials, as well as the easy access to defined amphiphilic structures for (hierarchical) self-assembly (see Figure).

Recent developments from our research group that illustrate the potential of poly(2-oxazoline)s for biomedical applications will be discussed in this lecture. First, the preparation of defined high-molar mass polymers up to the use of such polymers as pharmaceutical excipients for oral tablets will be highlighted demonstrating the development of poly(2-oxazoline) based high-drug loading tablets for enhanced solubilization of hydrophobic drugs in so-called amorphous solid dispersions as well as high drug loading sustained release formulations of hydrophilic drugs, which were both demonstrated in in vivo dog models. Secondly, the development of a wide range of side-chain functionalized poly(2-oxazoline)s based on the modification of methyl ester side chains will be demonstrated. The resulting polymers have been developed for applications as hemostatic patches, as covalent polymer-drug conjugates and for biocompatible hydrogels.
Enhancing PDNA delivery with hydroquinine polymers by modulating structure and composition

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Quinine is a promising natural product building block for polymer-based nucleic acid delivery vehicles as its structure enables DNA binding through both intercalation and electrostatic interactions. However, studies exploring the potential of quinine-based polymers for nucleic acid delivery applications (transfection) are limited. In this work, we used a hydroquinine-functionalized monomer, HQ, with 2-hydroxyethyl acrylate (HEA) to create a family of 7 polymers (HQ-X, X = mole percentage of HQ) with mole percentages of HQ ranging from 12% to 100%. Biological delivery experiments revealed that maximum transgene expression, outperforming commercial controls, was achieved with HQ-25 and HQ-35 as these two variants sustained gene expression over 96 hours. HQ-44, HQ-60, and HQ-100 were not successful in inducing transgene expression, despite being able to deliver pDNA into the cells, highlighting that the release of pDNA is likely the bottleneck in transfection for polymers with higher HQ content. Using confocal imaging, we quantified the extent of colocalization between pDNA, and lysosomes proving the remarkable endosomal escape capabilities of the HQ-X polymers. Overall, this study provides guiding principles for improving monomer structure and polymer composition, supporting the development of the next generation of polymer-based nucleic acid delivery vehicles harnessing the power of natural products.
Exogenous application of salicylic acid-based poly(anhydride ester) in micro-tom for controlled release of salicylic acid against drought stress

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Drought stress is a major constraint for plant growth, development and food production which threatens food security worldwide. Salicylic acid is well known by its therapeutic properties, specially by its anti-inflammatory action. However, it is also a defense related plant hormone capable of mitigate the stress effects of water deprived plants. Exogenous application of salicylic acid favors plants under stress by regulating processes such as photosynthesis, membrane permeability, nutrient uptake, transpiration and the activity of antioxidant enzymes. Our group has developed an environmentally safe salicylic acid derived poly(anhydride ester) (SAPAE) that hydrolytically degrades to release salicylic acid in a controlled manner. Here, the effect of the controlled release of salicylic acid in plants under healthy and drought conditions was investigated by comparing the exogenous application of SAPAE polymer with the direct application of salicylic acid to the soil of micro-tom tomato plants. The exogenous application of all compounds was performed directly in the powder form to the soil at comparable concentrations during the seedling stage (~30 days of the life cycle). Plant growth and mortality was monitored from the day the plants were treated with SAPAE or salicylic acid through the remaining days of the plant cycle (total plant cycle ~74 days). Final measurements of plant height, water content, root length, and tomato production yield were also performed. Plants mortality right after treatment was higher for plants receiving salicylic acid when compared with SAPAE. Drought stress was mitigated by both compounds, however SAPAE appears to have a more significant impact in plant growth which has been further investigated by repeating the experiment with a larger sample number. It is hypothesized SAPAE will promote more attractive results especially at long term when the polymer degrades at considerable levels.
Sustainable polymers based on acrylic monomers from wide range of plant oils

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Plant oils are a complex, variable, and valuable feedstock for chemical modifications of double bonds to be applied in high-performance polymers production.

We developed method of synthesis of plant oil-based acrylic monomers (POBMs) using one step catalytic transesterification of crude oil and N-hydroxyethyl acrylamide. Fatty acid profile of oils remains preserved during transesterification and defines the chemical composition of resulted POBMs mixture. Resulting acrylic monomers contain both varying unsaturated and saturated fatty acid fragments. The latter provides an ability to tailor the thermomechanical properties and performance of POBM-based polymeric materials in a broad range, via either “on-demand” cross-linking or formation of crystalline domains. Current library of fifteen monomers from oils widely varying in fatty acid esters chemical composition can be applied in free radical polymerization (including emulsion process).

Incorporation of POBM fragments into polymers not only improves product sustainability, but also enhances its performance. This presentation discusses POBM-based polymers synthetic features and properties to demonstrate their potential to be applied for variety of industrial applications.
Polysaccharide-based macromolecules as safer chelation therapy for treating heavy metal poisoning

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Heavy metal poisoning remains a public health crisis. Exposure to heavy metals such as lead, cobalt, and mercury can occur through contact with metal sources or through trace amounts in the environment. Heavy metal poisoning is currently treated with chelation therapy, where a small molecule chelator is administered to bind the heavy metal to help remove it from the body. However, this treatment is currently indicated for only severe and life-threatening blood metal levels. This is because it is only in emergency situations that the benefit outweighs the risk: traditional small molecule chelators are innately toxic.

To create a safer chelation therapy, we designed a class of polysaccharide-based macromolecular chelators (BioBinders) by chemically linking biocompatible polysaccharides with known metal chelators. The polysaccharide backbone increases compatibility, bioavailability, and renal clearance. The chelator component retains its metal-binding ability while being sequestered, preventing toxicity (Figure 1a). Initially, we have targeted two specific heavy metals—cobalt and lead. We have synthesized and characterized candidate BioBinders and demonstrated the ability to accelerate clearance of heavy metals from the body (through the urine). Preliminary in vivo clearance has been demonstrated in rats with cobalt (a heavy metal with similar chelation characteristics). BioBinders show substantial binding in vivo and enable 10-fold faster and 2-fold larger renal clearance (Figure 1b).
Biobased and bioinspired polymers with controlled biodegradation conditions: From acetalated cellulose to polyphosphoesters – recent developments in molecular stability control

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The present lecture discusses the recent developments in molecular stability control with a focus on the utilization of lignin, polysaccharides, and synthetic degradable polymers. The use of biopolymers in the production of plastics dates back to the introduction of Celluloid and Cellophane, which marked the onset of the Polymer Age. However, the use of petroleum-based polymers has dominated this age owing to the poor properties of biopolymers for specific applications. Synthetic polymers have proven to be more versatile, allowing broad adjustments of their properties, including precise control over their degradation rates. Although biopolymers can be chemically modified to alter their properties, this often results in a drastic slowdown in their biodegradation rates. In contrast, synthetic polymers allow for more precise control over the degradation rates of the modified polymers.

This lecture will highlight recent strategies that have been developed for the reversible modification of cellulose using acetal groups. This approach has enabled the adjustment of the degradation behavior and mechanical properties of cellulose. The presentation will also cover other strategies for the chemical modification of biopolymers such as lignin and cellulose. These strategies aim to produce fully biodegradable macroscopic and microscopic polymers that can be utilized in packaging films or agrochemical delivery. In addition to these biopolymer modifications, synthetic approaches will also be presented. These approaches involve the development of lignin-like polymers that can be used in an emulsion formulation of agrochemicals, and copolymerization with esters, carbonates, and phosphoester breaking points.

Overall, this lecture presents a comprehensive overview of the recent developments in molecular stability control using different approaches, including modifications of biopolymers and synthetic degradable polymers. The strategies discussed in this presentation have the potential to lead to the production of fully biodegradable polymers with tailored properties that can be used in a wide range of applications.
Novel cyclodextrin-based nanoparticles delivering alpha-mangostin for the treatment of brain ischemia

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We discovered that cyclodextrin-based hyperbranched polymer nanoparticles (CDNPs) could solubilize various hydrophobic drug compounds by encapsulating them within the cyclodextrin cavity. Interestingly, the binding constant of the CDNP/drug complex is 100 times greater than those of native cyclodextrins. Alpha-mangostin (α-M) is an antioxidant compound extracted from the pericarp of the mangosteen fruit and has been shown to reduce neuronal toxicity in primary rat cerebral cortical neurons. We prepared α-M/CDNP particles and optimized their properties to extend blood circulation time. In vivo results indicated that α-M crossed the blood-brain barrier (BBB) with the assistance of CDNP. The released α-M from CDNP interacted with albumin during its prolonged blood circulation, forming an α-M/albumin complex that may cross the BBB through the absorptive-mediated transcytosis pathway.
Controlled accelerated degradation of phosphoester (Co-)polymers

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For any biomedical application, the stability and/or degradation rates of polymers in aqueous media are important factors. The polymer is required to stay intact for a certain amount of time and then to degrade or to degrade on-demand. Otherwise, potentially harmful accumulation could occur. Polyphosphoesters (PPEs) are highly compatible with biological systems and the ester bonds in the backbone make them hydrolytically degradable. We demonstrated that the degradation rate of various polyphosphoesters can be precisely controlled by a small change in the side-chain and the binding pattern around the phosphorous center in the polymer backbone. A systematic library of water-soluble PPEs was synthesized by ring-opening polymerization resulting in polyphosphates, and in-chain or side-chain polyphosphonates. Especially for the side-chain polyphosphonates we studied the influence of the side-chain (methyl, ethyl, allyl, iso- or n-propyl) on the degradation rates at pH=8 and pH=11. Importantly, the degradation mechanism is controlled by the type of and size of the side-chain and the pH. At pH=11 the hydrophilicity plays a key role, while at pH=8 the electron density on the phosphorus is crucial, following a random chain scission or a backbiting mechanism. Further changes of the binding pattern (in-chain phosphonates or phosphates) of the phosphorus or installation of additional “breaking points” allowed to tune the polymer half-life times from less than a day to several years. This study underlines the versatile stability of water-soluble PPEs, which makes them interesting for several different applications, in which different hydrolysis rates, e.g. during regrowth of tissue, are of importance. By copolymerisation of PPEs with common monomers the degradation properties can be tuned, while keeping the mechanical properties. In this way we improved degradation properties of poly lactic acid (PLA) and poly trimethyl carbonate (PTMC) in vitro and in artificial seawater.
Negatively charged dendritic polyelectrolytes in biomedical applications

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In 2023, the American Cancer Society approximated almost 2 million new cancer cases – another 600,000 patients will die – in the United States, making it the second leading cause of death after cardiac arrest. The development of high-performance chemotherapeutics encounters tremendous significance for maintaining global health. Over the last years, dendritic polyglycerolsulfate (dPGS) systems have emerged with great potential for biomedical applications; incredibly, as selective tumor-targeting nanomedicines. dPGS is a hyperbranched, polyanionic, synthetic polymer with excellent biocompatibility. It has been demonstrated that dPGS-based drug delivery systems have intrinsic targetability towards cancerous tissue, enabling the targeted delivery of several drugs. The selective accumulation of dPGS-based materials is due to the binding of sulfates with L-selectin, an overexpressed cell adhesion molecule in cancer progression. Different architectures ranging from unimolecular to micellar systems were designed, synthesized, and investigated with suitable in vitro and in vivo models.

For self-assembled systems, the critical challenge lies in the extreme dilution upon administration, causing the concentration to fall below their critical micelle concentration (CMC). Additionally, the nonspecific interaction with blood serum proteins alters the applied systems' stability and targeting properties. As a rule of thumb, the following criteria must be met: (i) the self-assembled systems must be in equilibrium, and dilution upon injection must not lead to disaggregation; (ii) the carrier system must deliver its cargo to the site of action with no leaching into the bloodstream; (iii) once the loaded carrier reaches its destination, the drug must be released selectively; and (iv) nonspecific interactions with the reticuloendothelial system (RES) and other systems within the body must be avoided. Recently, our group designed dPGS micelles stabilized by π-π interaction tailoring these limitations, showing extremely low CMCs in the low nanomolar regime, high drug-loading capacities, and no interaction with human serum albumin (HSA).
Novel hydrolytically degradable salicylic acid-based poly(anhydride-esters) for triggered release of retinol

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Salicylic acid-based poly(anhydride-esters) (SAPAE) is a class of biodegradable and environmentally-safe polymers that has previously shown effectiveness for controlling inflammation, promoting bone growth, and preventing biofilm formation due to the release of a therapeutically active compound, salicylic acid, as the polymers degrade. The versatility of these polymers is not only showcased in their abilities to be formulated into different geometries (e.g. powders, fibers, microspheres, disks, films, cardiac stents), but also in the tunable degradation and salicylic acid-release rate using various strategies to alternate the polymers’ chemical composition. Herein, we explore the synthesis and hydrolytic degradation characteristics at different pH of novel fast-degrading SAPAE copolymers formulated as microspheres. Our findings show that by increasing the hydrophilicity of the polymers through copolymerization, salicylic acid is released over relatively short periods of time (i.e., hours) compared to their homopolymer counterpart (i.e., weeks). We furthermore explore the encapsulation characteristics of these microspheres to encapsulate retinol as a model hydrophobic molecule, and the release rate of retinol is also discussed. These SAPAEs copolymers act as an effective protecting capsule for the encapsulated substrate of interest and readily degrade to release it with additional therapeutic benefits of salicylic acid at various rates, thus opening a wide range of opportunities for eco-friendly polymeric material.
Biodegradable and biocompatible polymers for electronic applications

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Electronic products enhance our lives and bring change in almost every field including communications, entertainment, and healthcare. However, the fast-growing surplus of electronic waste has become a serious challenge to the environment: the majority of these toxic materials are deposited directly into landfills or incinerated because recycling is difficult and/or expensive. Electronic devices manufactured with biocompatible and biodegradable polymers are in demand because they are environmentally safe, of low cost, of potentially large volume, and are disposable. In addition, biocompatible and biodegradable electronics may enable the use of electronic devices in implantable biomedical applications. This review is focused on polymer materials, both natural and synthetic, that are utilized in biodegradable and/or biocompatible electronic devices as substrates, dielectrics, conductors, or semiconductors. Specific application examples are highlighted, such as biodegradable electronic devices, implantable medical devices, and edible sensors.
Charles G. Overberger International Prize for Excellence in Polymer Research (Invited)

Using block copolymer templates to pattern crystallization - Estroff, Lara (Oral Only)

Block co-polymers as structure directing agents to use well-known substances to make materials with novel properties - Gruner, Sol (Oral Only)

Hybridization and mesotructuring as tools towards next-generation photocatalysts - Eder, Dominik (Oral Only)

Nano-material science by polymer self-assembly - Steiner, Ullrich (Oral Only)

Bottle-brush block copolymer templated porous carbons for energy storage and catalysis - Watkins, James (Oral Only)

Block copolymer self-assembly based functional porous materials - Wiesner, Ulrich (Oral Only)
Biomineralization, the study of how organisms form minerals such as bones, teeth, and shells, provides examples of strategies for controlling the growth of crystalline materials patterned at the nanoscale. In particular, the concept of crystal growth in confinement has led to many interesting synthetic structures. When confinement is coupled with patterned substrates, an additional level of control over the nucleation of the crystals is achieved. In this presentation, I will focus on our investigations using block copolymer substrates to template the surface-confined precipitation of crystalline transition metal oxides with periodicities on the order of 50 nm. Specifically, I will present results related to the characterization of the hydrated structures of the templates and the crystallization pathways leading to the growth of nanostructured crystals on these templates. These results are helping us to rationally design assembly pathways to obtain hybrid materials with well-defined materials structures and resulting properties.
Block co-polymers as structure directing agents to use well-known substances to make materials with novel properties

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A nearly quarter century long collaboration between the Wiesner and Gruner labs has focused on using block co-polymers (BCP) to create mesoscopically ordered structures that endow well-known materials with new properties. As a first example, BCP are used to form superconductors, such as niobium nitride or indium into mesoporous, 3-dimensionally (3-D) periodic gyroid structures with periodicities on length scales of tens of nanometers. The key insight is that macroscopic superconductor properties depend on the London penetration depth and coherence length of the constituent superconducting material; these length scales are comparable to the thickness of the gyroid walls. By using BCP to change the gyroid periodicity and wall thickness one can systematically alter the macroscopic superconductor properties without changing the constituent superconductor substance. Experiments demonstrating this behavior are described.

A second example, that has yet to be fully realized, is to use BCP to create a single-crystal gyroid structure consisting of two distinct constituent substances, each in single crystal form. A gyroid may be described as a 3-D periodic constant-curvature surface that divides space into two distinct, interpenetrating volumes. Now imagine one volume as consisting of a single crystal of some substance, such as a metal, and the other volume as consisting of another substance, such as another metal or metal oxide. This material is then simultaneously a mesoscopic gyroid, and single crystals of each of the two constituent substances. X-ray diffraction of piece of this material would yield a gyroid diffraction pattern in the small-angle scatter superimposed on single crystal wide-angle diffraction patterns indicative of each of the two constituent substances.

Gyroid
Hybridization and mesostructuring as tools towards next-generation photocatalysts

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Photocatalytic splitting of water into oxygen and hydrogen constitutes a key requirement to realizing the successful use of hydrogen as a clean energy source. Light-driven conversion of CO2 into chemical commodities for industrial production of fine chemicals would equally benefit our environment and economy. These processes often occur in liquid media, where ready access to active sites is often limited by reactant diffusion through narrow pores such as in nanoparticle aggregates or inherent to microporous materials. In this presentation, I will demonstrate various strategies to introduce hierarchical mesopores and discuss their impact on the photocatalytic performance towards hydrogen evolution (HER) and in waste water purification.

First, I will show how tailor-made triblock-terpolymers can be used as structure-directing agents and sacrificial templates to design transition metal oxide films with large mesopores arranged in ordered 3D-interconnected pore architectures. In the second part, I will focus on microporous metal-organic frameworks (MOFs) and demonstrate how we incorporated mesopores through selective ligand removal from mixed-ligand MOFs upon thermolysis without the typical framework collapse. We designed photoactive MOFs of the MIL-125-Ti family with two distinct hierarchical pore architectures resembling either large cavities or branching fractures. Both pore geometries significantly improved the photocatalytic HER rates of the MOFs by up to 400%. These pores also enhanced the potential to adsorb large molecules, such as glyphosate from waste water. In both cases, the enhancements are contributed to 1) the formation of new under-coordinated adsorption sites and 2) a better access to catalytic sites by facilitating reactant diffusion through the pores. This strategy provides a powerful tool for the purposeful engineering of hierarchical MOFs with advanced applicability in liquid media.
Nano-material science by polymer self-assembly

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Block-copolymer self-assembly allows the bottom-up assembly of 2D and 3D nano morphologies. While highly precise on the 10-100 nm length scale, creating materials that rely on long-range order has remained challenging, limited by removing ordering defects and their characterization. This presentation starts with an overview of how polymer self-assembly has evened over the years to provide a variety of nanostructured materials systems, organic and inorganic, and how this can be integrated into various technologies. The second part of the presentation focuses on recent developments in large-scale imaging of block-copolymer architectures, their control by substrate induced epitaxy, and their use in optical metamaterials.
Bottle-brush block copolymer templated porous carbons for energy storage and catalysis

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We use the cooperative self-assembly of bottle brush block copolymers (BBCPs) and carbon precursors along with subsequent processing by nanoimprint lithography, photothermal processing or rapid thermal annealing for the fabrication of energy storage devices and supported catalysts. The use of BBCPs as carbon templates enables access to pore sizes ranging from tens to hundreds of nanometers while photothermal processing enables the formation of graphene materials within a few milliseconds. Example applications include large pore, few-layer graphene materials for supercapacitors, patterned Li ion battery anodes, and metal-nitrogen-doped mesoporous carbon materials for highly efficient oxygen evolution reactions.
Block copolymer self-assembly based functional porous materials

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In this presentation the formation of block copolymer self-assembly derived advanced functional porous materials and devices is discussed from a combination of block copolymer self-assembly directed organic as well as inorganic materials precursors. The emphasis will be on the development of wet chemical methodologies towards controlled porous structures resulting in specific functions. Experiments will be compared to theoretical predictions to provide physical insights into formation principles and specific properties. The aim of the described work is to understand the underlying fundamental chemical, thermodynamic and kinetic formation principles as well as nanostructure-property correlations enabling generalization of results over a wide class of porous materials systems. Work will cover structure formation at or close to the thermodynamic equilibrium as well as approaches where systems are systematically driven away from equilibrium.
Chemical Recycling and Upcycling of Polymers

Connecting segment distribution and performance in thermoplastic copolyesters constructed via polyester upcycling - Pitet, Louis (Oral Only)

Electrochemical-assisted alkaline hydrolysis of polyethylene terephthalate (PET) - Bunke, Samantha (Oral Preferred)

Catalyst design to address Nylon plastics recycling - Ye, Liwei (Oral Preferred)

Polyurethane sustainability: Concurrent design of polymer and process - Long, Timothy (Oral Only)

Chemical upcycling of polyethylene terephthalate - Cho, Joungmo (Oral Preferred)

Selective deconstruction and upcycling of condensation polymers - Saito, Tomonori (Oral Only)

Evolution of chain structure during the glycolysis of amorphous and semicrystalline polyesters - Watson, Shelby (Oral Preferred)

Tunable functionalization and upcycling of polyolefins to polyurethanes - Robertson, Megan (Oral Only)

Nylon Hybrids from Plants or PET - Miller, Stephen (Oral Only)

At the homogeneous – heterogeneous catalysis interface. Processes for waste polymer deconstruction and upcycling in a circular economy - Marks, Tobin (Oral Only)

Conversion of polyketones to polyamides and polyesters via the Boyer-Schmidt-Aubé rearrangement - King, Andrew (Oral Only)

Polyethylene terephthalate (PET) waste: A new platform chemical - Foster, Jeffrey (Oral Only)

C-H bond functionalization of polyolefins to create new materials - Hartwig, John (Oral Only)

Improving the recyclability and upcyclability of carbonyl-containing polymers via molecular editing - Michaudel, Quentin (Oral Only)

Understanding innovative solution processing to upcycle polymers to additive manufacturing feedstock - Dadmun, Mark (Oral Only)

Closed loop recyclable and degradable polyethylene-like materials enabled by catalysis - Mecking, Stefan (Oral Only)

Chemically recyclable multiblock polymers - Zhao, Yucheng (Oral Preferred)

Upcycling of poly(methyl acrylate) through amidation - Hoogenboom, Richard (Oral Only)

Functionalization of polycyclooctene for progress towards upcycling to polyethylene copolymers - Radzanowski, Anne (Oral Only)

Environmental and economic implications of emerging plastic recycling technologies - Uekert, Taylor (Oral Only)
Chemical Recycling and Upcycling of Polymers

Design and synthesis of chemically recyclable polyolefins - Archer, William (Oral Preferred)

Upcycling of polybutadiene facilitated by selenium-mediated allylic amination - Elardo, Matthew (Oral Only)

Effects of support on polyethylene hydrogenolysis using Pt/MₓOᵧ - Lamb, Jessica (Oral Preferred)

Molecular characteristics of effective compatibilizers of semicrystalline polymer blends - Eberle, Bailey (Oral Preferred)

Ball milling at room-temp with trace transition metals and metal-oxides breaks down polyethylene to gases (C₁-C₆) and lighter waxy residues - Ghosh, Yagnaseni (Oral Preferred)

C-H functionalization of polynorbornenes - Gitter, Sean (Oral Only)

Selective hydrogenolysis via a processive mechanism using earth-abundant metal oxide catalyst - Huang, Wenyu (Oral Only)

Trick and tips for sustainable packaging materials - Rabnawaz, Muhammad (Oral Only)

Polymer-to-polymer chemical transformations to produce specialty plastics from waste polyolefins - Winey, Karen (Oral Only)

Supercritical CO₂ as a tunable fluid impacting plastics recalcitrance to enzymatic depolymerization - Gurrala, Lakshmiprasad (Oral Only)

Depolymerization and upcycling of lignin-derivable polymers - Christoff-Tempesta, Ty (Oral Only)

Chemically recyclable polymers based on nucleophilic aromatic ring-opening polymerization - Su, Yongliang (Oral Only)

Improving mechanical properties of polydithioacetals via aryl backbones - Kariyawasam, Lasith (Oral Only)

Fast and mild method for the generation of poly-thioesters from lactone feedstocks for polymer upcycling - Paul, McKinley (Oral Only)

Closed-loop recycling of single-sourced mixed plastics via orthogonal (de)polymerization - Shi, Changxia (Oral Only)

Sustainable mono-material product design with chemically circular and biodegradable polymers - Chen, Eugene (Oral Only)

Using AFM-IR to quantify the complex phase behavior of multicomponent plastic mixtures - Gu, Xiaodan (Oral Only)
Chemical Recycling and Upcycling of Polymers

Effect of 2,3-dihydrofuran on ring-opening metathesis activity of 1,5-cyclooctadiene: Towards degradable rubber and polyolefins - Starvaggi, Francesca (Oral Preferred)

Advanced recycling: Understanding fundamentals to valorize plastics waste - Epps, Thomas (Oral Only)

Molecular engineering in four dimensions: A mechanistic approach to reprocessable polymer networks - Kalow, Julia (Oral Only)

Reprocessable polyolefin thermosets accessed by amidyl radical mediated C—H functionalization - Neidhart, Eliza (Oral Preferred)

Dynamic crosslinking compatibilizes immiscible plastic mixtures - Clarke, Ryan (Oral Only)

Malleable thermosets with closed-loop recyclability via dynamic covalent chemistry - Zhang, Wei (Oral Only)

Covalent adaptable networks (CANs) of ethylene/octene copolymers (EOCs) made by simple free-radical processing with a dynamic covalent crosslinker - Chen, Boran (Oral Only)

Healable, reprocessable, and fusionable cross-linked polymers based on dialkylamino disulfide-based dynamic covalent exchange - Otsuka, Hideyuki (Oral Only)

Incorporating dynamic bonds for recyclable melamine-based thermosets - Pierce, Ian (Oral Only)

Viscoelastic guanidinium-based supramolecular networks: Tunable, reprocessable, and degradable - Larsen, Michael (Oral Only)

Robust and recyclable polymer materials through supramolecular co-assembly - Schrettl, Stephen (Oral Only)

Reprocessable networks with dissociative dialkylamino disulfide bonds: Effects of dynamic covalent crosslinker species and concentration and the ratio of static to dynamic covalent crosslinks - Torkelson, John (Oral Only)

Catalytic C—H amination creates tough, adhesive materials from polyethylenes - Ciccia, Nicodemo (Poster Preferred)

Synthesis and post-polymerization modification of bio-derived poly(ester amide) copolymers - Qu, Taoguang (Oral Preferred)

Chemical recycling, upcycling of polyesters by transesterification using homogeneous titanium catalysts - Ohki, Yuriko (Poster Only)

Precision-controlled deconstruction of polyethylene terephthalate (PET) using organocatalysts - Guan, Chao (Poster Only)

Depolymerizing plastics via electrified spatiotemporal heating - Dong, Qi (Oral Only)
Chemical Recycling and Upcycling of Polymers
Towards chemically recyclable resins for Vat photopolymerization additive manufacturing - Makar-Limanov, Anna (Poster Preferred)

Two-phase reactors and population balance models for polymer upcycling - Kim, Changhae (Oral Only)

Reaction mechanism and interfacial structure of chemically recyclable polymer - Ng, Ka Chon (Poster Preferred)

Converting unsaturated polymers into vitrimers via cross-metathesis - Hart, Daniel (Poster Only)

Design of a new class of degradable polymers using phenolic additives - Gurrala, Lakshmiprasad (Oral Only)

Chemical recycling of textile wastes - Le, Ngan (Oral Preferred)

Molecular dynamics simulations for understanding and improving non-equilibrium plastic recycling product selectivity - Lele, Aditya (Oral Preferred)

Biowaste-based, non-isocyanate Polythiourethane (NIPTU) networks: Enhanced performance, reprocessability, and end-of-life monomer recovery - Chen, Yixuan (Oral Only)

Low mass mechanical characterization for sustainable polymers - Wang, Yunfei (Oral Preferred)

Highly recyclable thermosets from dithioacetal polymers - Highmoore, Julian (Poster Only)

Towards the upcycling of PVC into thermoplastic elastomers - Mceachern, Dj (Poster Preferred)

Vibrational analysis of polyethylene crystallinity for molecular-level recycling - Stavinski, Nicholas (Poster Only)

Efficient polystyrene depolymerization enabled by inorganic nano-sheet catalyst - Mazhar, Hassam (Oral Only)

Recycling of dithioacetal polymers into monomer macrocycles - Kassim, Abdulwarith (Poster Only)

Covalent adaptable networks exhibiting stress-induced shape-shifting behaviour and reprocessability along with scratch-resistant ability - Upadhyay, Chandan (Oral Preferred)

Closed-loop recycling of carbon fiber reinforced dynamic covalent crosslinked polyurea composites with hyperbranched polymers - Jiang, Can (Oral Only)

High-pressure CO₂-H₂O media for the depolymerization of polyethylene terephthalate - Osei, Dacosta (Oral Preferred)

High-density polyethylene (HDPE)-based Vitrimers - Ash, Subhaprad (Poster Only)
Connecting segment distribution and performance in thermoplastic copolyesters constructed via polyester upcycling

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Enormous quantities of polyesters are discarded every year in the form of single-use packaging and textiles. This represents an appalling misuse of potentially valuable resources. We have shown that through transesterification, post-consumer polyester waste can be directly transformed into a variety of performance enhanced thermoplastic copolyesters. During transesterification, segment redistribution occurs, as long polyester chains are cleaved and reformed, leading to multi-block backbone architectures. The equilibrium segment length is a critical determinant of final properties, including thermal behavior and mechanical performance. We have demonstrated that this segment distribution can be fine-tuned by choice of comonomers, feedstock ratios, and process conditions. Here we will present our various strategies for manipulating properties of these copolyesters in a systematic manner, through careful choice of ingredients and synthetic protocols. This includes the selection of the source of post-consumer or post-industrial feedstocks that chosen for implementing in the upcycling process.
Electrochemical-assisted alkaline hydrolysis of polyethylene terephthalate (PET)

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Decades of uncontrolled plastic production and disposal have led to large environmental discharges, runaway ecological effects, and an unsustainable industrial ecology. Conventional mechanical recycling melts plastic waste, which degrades the polymers’ properties and upholds an unsustainable plastic economy that requires virgin feedstocks. Chemical recycling offers a pathway of circularizing this industry by utilizing reactive processes to recover high-quality monomer feedstocks for repolymerization. One chemical recycling method, alkaline hydrolysis, has been demonstrated to effectively depolymerize common plastics such as polyethylene terephthalate (PET) through the use of commercial bases and reactive distillation. However, this method remains infeasible for industrial applications due to high energy demands and costs. We aim to investigate electro-assisted hydrolysis to reduce the environmental impacts of chemical recycling via alkaline hydrolysis, generate valuable by-products, and achieve a more sustainable plastic economy.

Electrochemical water splitting in a two-chamber cell separated by a cation-exchange membrane is used to generate high pH (pH>11) in the cathode chamber for alkaline hydrolysis. In this process, acid and hydrogen gas are also produced, which are valuable products that can be utilized for other industrial purposes. We investigated the effects of several operation variables on the degree of PET depolymerization, including reaction time, temperature, electrolyte, organic solvent, and hydrolysis catalyst. Both hydroxide ions and methoxide ions act as depolymerization agents, which resulted in three major products: terephthalic acid, dimethyl terephthalate, and monomethyl terephthalate. We revealed that the degree of depolymerization improved with increasing reaction time, temperature, and organic solvent percentage in the cathode chamber. We also observed no noticeable improvement in performance with the increasing percentage of phase transfer catalyst in the system. In addition, we found that depolymerization degree can be enhanced by adding a buffering agent (e.g., sodium phosphate) to the anode electrolyte, which reduces proton transfer to the cathode chamber. We will apply the knowledge gained from this study to other common and novel plastic designs to expand the scope of this work and advance the circular plastic economy.
Catalyst design to address Nylon plastics recycling

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Rational tailoring of catalytic systems offers highly desirable transformations targeting the growing environmental challenges associated with plastics pollution. For example, the identification of efficient catalysts to address alarming end-of-life Nylon pollution remains underexplored. Nylon-6 is a non-biodegradable high-performance engineering plastic with centuries chemical persistence, resulting in millions of tons of waste accumulation. Here we report the rational manipulation of organolanthanide catalyst structure to achieve a highly efficient, solventless, and scalable Nylon-6 depolymerization process, affording monomer caprolactam in up to 100% yield. Specifically, a lanthanocene catalyst operates at catalyst loadings as low as 0.2 mol% and temperatures as low as 220 °C. For efficient deconstruction of more recalcitrant commodity Nylon-6 end-of-life articles such as fishing nets, carpets, and clothing, a robust and thermally stable yttrium catalyst effects 100% conversion of these items into caprolactam monomer. The collected product can be readily re-polymerized to afford pristine Nylon-6 with comparable molecular masses and structural regularity, providing an important upcycling pathway for end-of-life Nylon plastics.
Polyurethane sustainability: Concurrent design of polymer and process

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Polyurethanes (PU) are a highly versatile material and remain critical in a multitude of specialty applications. Their tunable chemistry enables use as a robust elastomer in construction and automotive applications, while their foaming provides cutting-edge materials for comfort and insulation. The versatility of the formulation and structure of PUs complicates recycling and engenders the need for further development of circularity by bolstering degradability and introducing greener pathways for synthesis. PET depolymerization product bis(hydroxyethyl) terephthalate adds sites for premeditated degradation in the form of ester linkages. Base-catalyzed alcoholysis of model urethane compounds established an empirical relationship for location-specific degradation of the ester and preservation of the urethane linkage while investigation into the base, concentration, and temperature elucidated reactivity differences between the urethane and ester. Model studies successfully achieved selective degradation and formation of small molecules suitable for collection and future polymerization into new polymers.

In related work, efforts in non-isocyanate polyurethanes (NIPUs) provided novel synthetic pathways for PU synthesis. Biscarbonylimidazolide monomers enabled the synthesis of thermoplastic and thermoset PUs at high yields and in the absence of isocyanates. This polycondensation reaction leveraged existing polyester reactor infrastructure and provided facile routes toward high conversion. Additionally, an in-situ blowing method enabled the synthesis of NIPU foams with varying thermomechanical properties and pore structures. Alternatively, specific chain extenders with neutralizable moieties enable polyurethane dispersibility to form waterborne polyurethanes (WPU). Commonly used for coatings and adhesives, WPU replaces organic solvents with water improving sustainability while providing low viscosity high molecular weight polymer processing.
Polyethylene terephthalate (PET) is the most widely practiced plastics for recycling. Chemical recycling of PET can be achieved by various chemical routes of transesterification where an excessive alcohol is commonly used as a reactive solvent. Methanolysis of PET produces dimethyl terephthalate (DMT) and ethylene glycol (EG), which can be utilized to repolymerize them into PET. Conventionally, methanolysis of PET has been carried out under severe reaction conditions at which methanol is supercritical or near-supercritical. In the process, depolymerization is assumed to take place at random positions of polymer chains till their molecular sizes are reduced to smaller fragments. However, a relatively high amount of non-volatile oligomers and other impurities costs energy-intensive separation steps.

In this presentation, we will be discussing our recent study on the low-temperature methanolysis converting waste PET into crude dimethyl terephthalate (DMT) and the second transesterification converting DMT into several other valuable terephthalate derivatives. Both reactions can be achieved at a relatively low reaction temperature (<100°C) utilizing a single inexpensive catalyst. In this hybrid process (called ‘Bacterian’ as it involves two reaction steps of low activation energy), a relatively pure monomer product (e.g. BHET, BHPT, BHBT, DOTP) with high production yield (>90%) was obtained. We will also introduce our recent effort to build a demonstration plant for the technology.

Low-temperature methanolysis of PET and upcycling into valuable monomers
Selective deconstruction and upcycling of condensation polymers

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Condensation polymers such as poly(ethylene terephthalate) (PET), polyamides (PA), polyurethanes (PU), and polycarbonate (PC) comprise ~30% of the global plastic production. The catalytic deconstruction is one of the major paths for chemical recycling of condensation polymers. Although there has been progress on chemical recycling of condensation polymers especially PET, most condensation polymers are not recycled because of the difficulty in depolymerization to pure building blocks especially from mixed state in an energy efficient manner. Here, we have developed a tailored organocatalyst to enable low energy depolymerization pathways for condensation polymers. Our catalyst allows glycolysis of PET, PA, PU, PC and their multiple mixture at moderate temperature with high yield. A wide range of post-consumer plastics waste, such as bottles, packaging, foam, carpet, etc. is readily deconstructed into monomers with high efficiency. The Life Cycle Assessment indicates that the reproduction of various condensation polymers from the deconstructed monomers will result in a significant reduction in greenhouse gas emissions and energy input. Furthermore, we have developed a path to deconstruct those condensation polymers to selective length of oligomers. We have utilized those deconstructed building blocks to synthesize upcycled polymers, and the upcycled polymers can be further deconstructed to reusable building blocks. Such circular design contributes to establishing new closed-loop circularity of polymers by energy efficient selective deconstruction and upcycling of various commodity plastics.
Evolution of chain structure during the glycolysis of amorphous and semicrystalline polyesters

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Polyethylene Terephthalate (PET) is one of the most used commercial polymers and has the potential to be chemically recycled industrially. The depolymerization is often pushed to formation of monomer, which requires extensive time and energy. Our research seeks to track the evolution of chain structure during the depolymerization process of PET with varying crystallinity to offer insight into the availability of intermediates in the depolymerization process that can be used to fabricate value added materials. Our results for PET Glycolysis show that the heterogenous reaction is governed by the diffusion of the glycol into the polymer, not the PET surface area. From our interpretation, the depolymerization of PET occurs first in the amorphous polymer before breaking up the crystalline polymer. Understanding how crystal size affects depolymerization offers pathways to tune the reaction to isolate intermediates of a targeted chain length and dispersion. Increasing the crystallinity of PET alters the depolymerization progress to generate reaction intermediates with higher M_n at similar depolymerization times, further demonstrating the importance of glycol diffusion into the amorphous PET on the depolymerization process. The highly crystalline yet low disperse polymer intermediates that emerge from the depolymerization were repolymerized to regenerate PET that regained 90% of their original chain length. This provides an opportunity to repolymerize PET without pushing the reaction to pure monomer, using less time and energy. Further research focuses on the impact of PET crystallinity and lamellar size on the evolution of chain structure during glycolysis. Ongoing studies indicate that increased crystallinity increases the M_n of isolated reaction intermediates at similar depolymerization time. Similarly, ongoing studies focus on the variation in the depolymerization process in amorphous polyesters. These results show that the chain length decreases, and the dispersity increases, in the depolymerization of amorphous polyesters relative to that of semi-crystalline polyesters.
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Tunable functionalization and upcycling of polyolefins to polyurethanes

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Polyolefins represent the largest contribution to plastic production, use, and generated waste worldwide, yet their recycling rates are low. More efficient methods of recycling polyolefins have been underexplored, due to significant technological, scientific and economic challenges. We are exploring chemical functionalization and processing strategies for converting waste polyolefins to high value materials for advanced manufacturing and use. In this work, maleic anhydride grafted polypropylene was hydroxylated and subsequently cured with a diisocyanate to form thermoset polyurethane films. The physical properties of the resulting polyurethane films were evaluated and benchmarked to conventional polyurethanes. The complementary roles of the crosslinked network and crystallization behavior on the mechanical properties of the films were examined.
Nylon Hybrids from Plants or PET

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Nylon hybrids are polyamides that possess additional functional groups within the main-chain. These additional functional groups can be used to tune the polymeric thermal properties and degradation behavior. Described here are polyesteramides that derive from (1) brassylic acid, an increasingly-available C13 diacid from *Brassica carinata*, a seed oil crop studied for aviation biofuel production, or (2) post-consumer polyethylene terephthalate (PET). Aminolysis of dimethylbrassylate or PET with ethanolamine yields bis-hydroxyethylbrassylamide (HEBA) or bis-hydroxyethylterephthalamide (HETA), respectively. These diols can be copolymerized with a variety of diacids to yield aliphatic or semi-aromatic polyesteramides having thermal properties with either high glass transition temperatures (*e.g.*, $T_g = 125 \, ^\circ\text{C}$) or high melting temperatures (*e.g.*, $T_m = 138 \, ^\circ\text{C}$), which render them potential replacements for high $T_g$ or high $T_m$ commodity plastics, such as polystyrene (PS) or high density polyethylene (HDPE). These polyesteramides undergo ester hydrolysis under environmentally relevant conditions, yielding oligomers that are water soluble and thus can proceed to biodegradation to carbon dioxide. For example the all aliphatic polyesteramide built from HEBA and adipic acid loses 37% of its number average molecular weight ($M_n$) over the course of one year in seawater. Moreover, it was discovered that HEBA or HETA are capable of homopolymerization—whereby amide functional groups are converted to ester functional groups with loss of ethanolamine. The formed polymers are also polyesteramides with 50% amide and 50% ester functionality; their aminolysis with ethanolamine yields the original monomers HEBA or HETA—demonstrating their potential for chemical recycling.
At the homogeneous – heterogeneous catalysis interface. Processes for waste polymer deconstruction and upcycling in a circular economy

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The current increase in plastics production/consumption has generated unimaginable quantities of waste plastics with severe environmental consequences. Since >90% of these plastics come from fossil feedstocks, the impact on finite natural resources is also a concern. In a traditional linear economic model in which plastics are discarded after use, by 2050, the ocean will contain more plastics than fish, and plastics production will consume ~20% of the global petroleum production. To avoid such scenarios, a circular economy in which waste plastics are recycled and repurposed is urgently needed. Polyethylene terephthalate (PET), Nylon, as well as polyethylene, α-olefin-ethylene copolymers, and isotactic-polypropylene are the most consumed plastic materials worldwide, having multi-billion-dollar markets, hence a rising need for recycling. As an example of this daunting challenge, PET is currently the most recycled plastic, yet only ~7% is currently recycled bottle-to-bottle.

In this lecture, mechanistic and thermodynamic based strategies are presented, using structurally well-defined earth-abundant molecule-derived heterogeneous catalysts and complementary DFT analysis, of new efficient ways to deconstruct/recycle PET and other polyesters, linear and branched polyolefins, and Nylons. These catalytic processes are solvent-free, proceed in high conversions and selectivities under relatively mild conditions, and the catalysts are multiply recyclable. In all cases details of the reaction mechanisms and factors governing catalytic selectivity are emerging. In many cases these catalysts effectively deconstruct mixed polymers.
Conversion of polyketones to polyamides and polyesters via the Boyer-Schmidt-Aubé rearrangement

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Polymer backbone editing is a powerful tool for fundamentally changing a material by directly modifying the polymer backbone. Ideally, commodity plastics could be edited to allow for upcycling or recycling of these materials, but no examples currently exist. In this work, we target the rearrangement of polyketones—a large class of commodity plastics—into N-substituted polyamides and polyesters using the Boyer-Schmidt-Aubé rearrangement. Specifically, we investigate non-alternating aliphatic polyketones that can be sourced from either oxidation of polyethylene or copolymerization of carbon monoxide and ethylene. The mechanism of the rearrangement and the material properties of the rearranged polymers are explored. Additionally, cleavage of polymer chains at the ester and amide linkages is investigated to determine how rearrangement may facilitate degradation. Thus, this work opens the door for upcycling and recycling of commodity plastics by conversion between classes of commodity materials, which engenders new materials properties and mechanisms for chain cleavage.
Polyethylene terephthalate (PET) waste: A new platform chemical

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The production of commodity polymers in the US alone requires an estimated 3,400 PJ (3 quads) of energy annually and generates 104 MMT CO\textsubscript{2}e of greenhouse gas (GHG) emissions. Despite this significant energy cost and GHG production, most plastics are discarded after a single use, wasting the feedstock resources and energy consumed for their production. As such, plastics recycling/upcycling represents a significant opportunity for resource preservation and energy savings. Further, efficient processes for plastics recycling/upcycling promise to combat the accumulation of plastic waste in the environment.

Significant progress has been made with respect to chemical recycling of polymers. Efficient catalysts have been discovered to deconstruct waste polymers into their constituent monomers. An alternative strategy for chemical recycling is to transform waste polymers into entirely new feedstocks for novel polymer production. In particular, the rich aromatic content of poly(ethylene terephthalate) (PET) represents an ideal and abundant feedstock to produce aromatic building blocks including new monomers. In this contribution, we report the direct deconstruction of PET to bis-alkene monomers via transesterification using a TBD:TFA catalyst system. These monomers can be readily polymerized using acyclic diene metathesis (ADMET) polymerization, affording semi-aromatic polymers with a broad range of accessible properties. The obtained unsaturated polymers can be hydrogenated to produce PET-like materials, selectively depolymerized back to monomers using either transesterification or cross-metathesis chemistries, or modified through their backbone unsaturations to create robust vitrimer materials. This work highlights the potential for new paradigms in chemical manufacturing, where waste plastics are used as platform chemicals to produce a broad variety of chemical building blocks.
C-H bond functionalization of polyolefins to create new materials

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Our group has been seeking to exploit our experience with the functionalization of alkyl C-H bonds to create new polyolefins with unusual properties by converting C-H bonds along the polymer chain to C-O or C-N bonds by oxidation or amination or C-B bonds by borylation. This seminar will include recent results on the use of products from oxidation to create new materials and the generation of new materials from the amination and borylation of the C-H bonds in polyolefins. The influence of the installed groups on polymer properties and distinction between reactions on small molecules and macromolecules will be discussed.
Improving the recyclability and upcyclability of carbonyl-containing polymers via molecular editing

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Chemical recycling and upcycling methods are crucial in addressing the global plastic waste crisis, as they offer a sustainable solution to reduce the amount of plastic waste that ends up in landfills and oceans. Recycling involves the depolymerization of used plastic materials back to their initial building blocks, while upcycling allows the transformation of plastics into value-added polymers or fine chemicals. The current rate of recycling for most commodity polymers in the US and in the world is largely mismatched with their scale of production. The development of the next generation of plastics exhibiting improved recyclability, while maintaining desirable thermal and mechanical properties will be a crucial step in minimizing that mismatch. Our group is focused on the synthesis of polymers that are structurally analogous to carbonyl-containing polymers (e.g. polyesters) through the substitution of the repeating carbonyl –CO– by a –SO2– group. This small molecular editing of the polymer backbone is anticipated to provide polymers with similar properties but improved recyclability. This presentation will highlight our efforts in developing efficient and modular syntheses of polysulfamides. Polysulfamides form a family of polymers with largely unknown physical properties, that can be seen as analogs of polyureas commonly used in the coating, clothing, and adhesive industries. We will discuss the invention of polymerizations processes capitalizing on Sulfur(VI) Fluoride Exchange (SuFEx) click chemistry. The influence of hydrogen bonding and polymer composition over thermal properties and crystallinity will be demonstrated through a variety of experimental data and our attempts to predict polymer assembly via computational methods will be covered. Finally, the design of complementary processes for the recycling or upcycling of the synthesized polysulfamides will be presented.
Understanding innovative solution processing to upcycle polymers to additive manufacturing feedstock

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Powder Bed Fusion (PBF) is crucial technology in polymeric additive manufacturing. However, there exist limited polymers available for PBF, where most efforts use nylon. This work seeks to understand and control the rational development of scalable processing protocols that use liquid-liquid phase separation (LLPS) to reproducibly fabricate polymer powders that are suitable for powder bed fusion from polymers in the waste stream. In this process, the solvent quality of a polymer solution is reduced by a temperature quench or addition of non-solvent, causing the polymer to precipitate via phase separation. This results in the formation of polymer particles suitable for PBF that can be easily recovered, which also enables reclamation and reuse of solvent. Understanding the fundamental driving forces that guide the variation of final particle size with polymer solution concentration, polymer crystallinity, solvent type, and quench temperature provides pathways to rationally control the size and manufacturability of the final particles. This process has been used in our group to create powders that are suitable for PBF from products in the waste stream including polypropylene pill bottles, polyethylene terephthalate water bottles, high density polyethylene milk jugs, and low density polyethylene sandwich bags. The process of powder formation is driven by the phase separation of polymer solutions, which involves spinodal decomposition followed by Ostwald ripening and droplet coalescence. Control of powder formation requires understanding which of these processes regulates particle size in the precipitation process. We will discuss results that determine the impact of temperature, solution concentration, and molecular weight on formed particle size and offer important fundamental understanding into the phase separation processes that govern particle formation. This in turn offers insight that will enable the rational design of thermodynamic conditions required to create polymer powders that are suitable for powder bed fusion for a broad range of polymers from the waste stream using the LLPS process.
Closed loop recyclable and degradable polyethylene-like materials enabled by catalysis

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An introduction of low densities of functional groups in the main chain can endow polyolefins with desirable additional traits while retaining their mechanical strength and durability. For example, recyclability can be achieved and environmental accumulation can be prevented. Catalytic approaches can introduce such functionality into the hydrocarbon chains under mild conditions, either during polymerization directly or in a post-polymerization fashion. As a direct approach, a step-growth polymerization of long-chain monomers, obtained from natural oils, yields polyesters or polycarbonates with solid state structures and materials' and processing properties similar to polyethylene (HDPE). At the same time, these materials can be closed-loop recycled under mild conditions via the low-density of in-chain functional groups. The rates of degradation by microorganisms can be tuned over a wide range by the choice of monomers and repeat units, and through blending. Non-alternating chain-growth copolymerization of ethylene with carbon monoxide by state-of-the-art nickel(II) complexes provides access to polyethylenes with isolated keto groups in the chain (keto-PEs). Due to their high molecular weights, their properties are on par with HDPE, but the in-chain keto groups render the material photolytically degradable. Applications that particularly call for closed-loop recycling and biodegradability are also discussed.
Chemically recyclable multiblock polymers

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Polyolefins are among the most significant and high-volume plastics that are produced globally. Despite some progress in recycling, the extensive use of these plastics and their low recycling efficiency remain major challenges for the recycling industry. To address this issue, we developed an approach to create chemically recyclable polyolefin-like materials that offer diverse properties by constructing multiblock copolymers from hard and soft telechelic oligomers. Our synthesized multiblock polymers exhibit a wide range of mechanical properties, which can be adjusted by varying the ratios of segments, with a high melting temperature and low glass transition temperature. This feature makes them suitable for various applications, such as elastomers and thermoplastics. After use, these multiblock polymers can subsequently be mixed and deconstructed back into hard and soft segments. This approach allows for closed-loop recycling and has the potential for scaled-up production. Overall, the ability of this approach to generate diverse materials could offer new possibilities for the development of diverse sustainable plastics.

Multiblock polymers possessing broad material properties can be synthesized, used, and subsequently mixed together for chemical recycling representing a system for closed-loop recycling of diverse plastic waste.
Upcycling of poly(methyl acrylate) through amidation

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The amidation of polymers with non-activated ester side chains provides potential for creating higher added value materials through the introduction of more complex amide side-chains, which would be much more expensive, complicated and sometimes even impossible through direct polymerization of the corresponding monomers. However, despite that polymers with methyl ester side chains, such as poly(methyl acrylate) and poly(methyl methacrylate) (PMMA) are widely available, the non-activated side chain ester groups have low reactivity for transesterification or amidation.

In this lecture, the recent progress from our group in this area will be discussed. First of all, we developed a 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyzed procedure allowing efficient full or partial amidation of the side chains of poly(methyl acrylate), allowing accurate control over the introduction of functional side chains, such as allyl or cyclohexenyl groups that allowed further crosslinking. Moreover, we discovered that the amidation is strongly accelerated when a secondary hydrogen bond donating or accepting group is present on the utilized primary amine-containing reagent (see Figure). Furthermore, efficient introduction of secondary amine groups was achieved through amidation with N-ethyl-ethylenediamine, whereby selective amidation of the primary amine occurred.

These results from our results provide a sound basis for future development of functional polymer materials through amidation of poly(methyl acrylate) and also provide a first step towards future development of protocols for amidation and upcycling of the bulk polymer PMMA as is ongoing in our laboratories. The amidation of PMMA is, however, much more challenging due to the enhanced sterical hindrance of the polymer backbone.
Functionalization of polycyclooctene for progress towards upcycling to polyethylene copolymers

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The recycling rate for polyolefins remains critically low, despite their status as the most abundant polymers worldwide. The lack of reactive sites along the polymer backbone leads to challenges in chemical upcycling, while repeated mechanical recycling leads to a significant loss in material properties and eventual downcycling. Our strategy for the upcycling of polyolefins is a two-step process of dehydrogenation and then functionalization resulting in polyethylene copolymers with extended lifetimes. Following catalytic dehydrogenation, the selective transformation to polyethylene copolymers by alkene functionalization along the backbone can be performed. Polycyclooctene, synthesized by ring-opening metathesis polymerization, is used as a model polymer for unsaturated polyolefins with moderate molecular weight and solubility in organic solvents for polymer characterization. Our first strategy involves functionalization of the polycyclooctene via a one-pot, two-step hydroboration and oxidation protocol introducing hydroxyl groups along the polymer backbone. The hydroxylated materials then undergo hydrogenation by a diimide reduction to synthesize linear poly(ethylene-vinyl alcohol) (EVOH) analogues with randomly distributed hydroxyl groups and levels of functionalization from 4-24 mol%. Our second protocol for functionalization involves epoxidation. Epoxidized polymers in the range of 4-25 mol% functionalization can be further chemically elaborated by reactions at the epoxide prior to hydrogenation. The resulting polymers are characterized by nuclear magnetic resonance and Fourier transform infrared spectroscopy to evaluate molecular weight and level of functionalization. Thermal and adhesive properties of these materials are also investigated as they are important characteristics for polymer processing. The resultant properties are compared to commercial polyethylene copolymer materials.
Environmental and economic implications of emerging plastic recycling technologies

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Recycling will play a crucial role in mitigating plastic pollution and promoting a circular economy for polymers. Quantitative analysis can help guide the optimization and implementation of these plastic management strategies, enabling increased circularity while minimizing costs, energy use, greenhouse gas emissions, and other environmental impacts. This talk will outline the Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE) Consortium’s approach to analysis-guided plastic recycling research. Stringent process modelling, life cycle assessment, and techno-economic analysis are used to benchmark the technical feasibility, environmental impacts, and costs of chemical and biological recycling technologies in comparison to conventional fossil fuel-based plastic manufacturing. Across emerging recycling strategies, several key challenges become apparent – including plastic feedstock pretreatment requirements, high energy or chemical use, and recycled plastic yields and quality – highlighting opportunities for future innovation. Through this consistent and in-depth analysis approach, BOTTLE aims to provide the plastics community with key metrics and insights to drive plastic recycling innovation towards a more sustainable and circular economy.
Design and synthesis of chemically recyclable polyolefins

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Polyolefins are one of the most prominent classes of plastics due to their low cost, light weight, and chemical resistance. Most polyolefins (e.g., HDPE, EPDM, iPP) and other hydrocarbon polymers (e.g., SBR) employed in countless applications are derived from abundant, inexpensive, petroleum-derived monomers. However, many of these polymers were developed to maximize material properties without considering end-of-life in the material design. Chemical recycling, in which a material is reverted to monomer, theoretically enables access to closed-loop recycling. We are investigating the design and synthesis of chemically recyclable (co)polymers containing (α,ω-divinyl)oligocyclobutane (DVOCB), a chemically recyclable oligomer derived from butadiene, a commodity monomer. DVOCB is semicrystalline and comprises a polyolefin-like saturated hydrocarbon backbone. To that end, we have synthesized a host of elastomeric copolymers containing octenylene and DVOCB segments by combining ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization. In addition to reporting the thermomechanical behavior, we will discuss the polymerization–depolymerization behavior of these materials.
Upcycling of polybutadiene facilitated by selenium-mediated allylic amination

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The accumulation of post-consumer plastic waste is one of the largest environmental concerns facing society today. One promising approach to this emerging challenge is the chemical modification of post-consumer waste via post-polymerization modification methodologies. This strategy allows for the impartation of new functionalities into existing polymeric waste, with the end goal of repurposing post-consumer polymer waste into new, value-added materials in a process known as chemical “upcycling”. While promising approaches for the upcycling of a variety of commodity polymers exist, parallel approaches towards the repurposing of unsaturated polymers (such as 1,4-polybutadiene, the chief component of tire rubber) are elusive due to the heightened reactivity of the C=C π bond. In this work, we describe a novel post-polymerization modification reaction for the chemical upcycling of polybutadiene via a mild, metal-free allylic amination reaction. Uniquely, our method results in the retention of the original polymer microstructure, with no olefin saturation, olefin transposition, or backbone cleavage via chain-scission. The resulting materials have distinct and tunable thermal and surface wetting properties that are dependent on both the identity and density of the grafted sulfonamides. Based on these results, we anticipate future applications for the repurposing of commercial elastomers and vulcanized, industrial rubbers.

Allylic amination of PBD using selenium catalysis.
Polyolefins constitute over half of the industrial plastic market, with ~80% utilized in single-use products. Current plastic waste management options are typically limited and consist of incineration, pelletizing- and molding-based recycling, and disposal into overflowing landfills. Furthermore, these methods often lead to hazardous emissions, downcycled products with restricted applications, and widespread environmental concerns. Therefore, there is a substantial need to seek alternative processes to upcycle used plastics into value-added products.

This work targets the deconstruction of polyethylenes using supported platinum nanoparticle catalysts via hydrogenolysis. The support plays a vital role in determining catalyst activity and product properties, with platinum grafted onto silica-alumina giving the highest conversion to liquid products. Furthermore, the products of these reactions are monodisperse with significantly reduced molecular weights and increased branch density. The product properties are also independent of the polyethylene feedstock, allowing the potential to upcycle multiple streams of waste polyethylenes into a single product.

Current and future routes for addressing plastic waste
Molecular characteristics of effective compatibilizers of semicrystalline polymer blends

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Managing end-of-life plastics is a challenging problem for a variety of reasons, including the complexity of recycling mixed waste streams. Most polymer pairs don’t mix, and any product made from such a mixture will exhibit poor properties. These polymer mixtures can be enhanced by their compatibilization with proper polymeric interfacial modifiers. A compatibilizer strengthens the interface between immiscible polymers to stabilize the blend. Previous research by our group has examined the ability of chlorinated polyethylene (cPE) to compatibilize poly vinyl chloride (PVC) and polyolefin elastomers (POE). However, the impact of the sequence distribution and composition of the cPE on the compatibilization process is not fully understood. This presentation will discuss results that demonstrate that several molecular design characteristics must be considered in the design of an effective compatibilizer. A crucial factor is the composition of the compatibilizer, as well as the sequence distribution which impacts the formation of entanglements and co-crystallization at the biphasic interface. This presentation will focus on elucidating the relative importance of these factors by determining and interpreting the interfacial adhesion between POE/cPE, PVC/cPE and of the POE/cPE/PVC trilayer. This work therefore seeks to provide insight into the molecular design of compatibilizers that can stabilize phase separated crystalline polymer blends, including those that are most relevant for mixed waste streams in polymer recycling.
Ball milling at room-temp with trace transition metals and metal-oxides breaks down polyethylene to gases (C$_1$-C$_6$) and lighter waxy residues

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Plastic waste is a big peril to our environment. The stability and durability of plastics makes them inert to attempts of degradation or breakdown into constituent monomers or smaller carbon chain containing chemical forms. This results in accumulation of waste plastics in landfills and leakage into oceans and waterbodies causing harm to marine animals. The most widely used recycling process is mechanical breakdown of plastics into useful materials, which relies heavily on multiple human and machine mediated steps which are cost intensive processes riddled with many chances of failure.

Plastics can be degraded into constituent monomers in a closed loop recycling process, such as pyrolytic cracking, which employs very high-temperature melting/degradation of the polymers to crack them into constituent smaller hydrocarbon chains. This is an energy intensive process and is both expensive and adds to carbon footprint of an otherwise sustainable closed-loop recycling process.

In order to address the challenges of current plastics degradation methods, researchers at Aramco Americas have a new and energy-efficient way of converting polyethylene (PE), a major component of most widely used plastics, to constituent smaller hydrocarbons. This process employs solid-state ball-milling to degrade PE in the presence of zeolites, silica, sand etc. and leads to the formation of small and medium chain hydrocarbons. In this work, we demonstrate that solid-state ball-milling of PE with a grinding media of silica in the presence of trace amounts of widely used TM and TM-oxide catalysts such as Fe, Fe$_2$O$_3$, Cu, CuO, Ni, Pd, Pt, etc., lead to conversion of PE into smaller alkanes and alkenes, such as C$_1$-C$_6$ gases, and lighter waxes and other residues. GC-FID and NMR analyses prove the effectiveness of room-temperature ball-milling on the degradation of PE. Our goal is to effectively degrade all types of polymers and ultimately single use plastics into useful olefins, alkanes and fuels using this mild and energy + cost-effective process.
C-H functionalization of polynorbornenes

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With a society that is increasingly reliant on plastics for everyday use, the need to divert end of life materials to new uses has rapidly expanded in recent years. A promising approach to circumvent waste streams is C-H functionalization of commodity polyolefins, resulting in upcycled materials with new properties. However, these approaches have largely focused on fully saturated polyolefin feedstocks, leaving a need for new methods to functionalize alkene containing polyolefins. During this talk we will discuss our method for catalytically functionalizing polynorbornenes produced by ring-opening metathesis polymerization (ROMP). Highlights of our method include high and tunable degrees of functionalization, tunable materials properties, and functional group compatibility enabling further functionalization. Ultimately, our method provides a synthetic route to polymer structures that are otherwise difficult to access, while simultaneously representing a new approach to upcycling ROMP materials.
Selective hydrogenolysis via a processive mechanism using earth-abundant metal oxide catalyst

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Over 4900 million metric tons (MMT) of plastics wastes were discarded between 1950 and 2015, either in landfills or in the natural environment. Unfortunately, this number is expected to rise, as we produce over 400 million metric tons of plastic annually, and around 79% of it is quickly disposed of. The accumulation of plastic waste in the environment has raised numerous environmental and health concerns. On the other hand, plastic waste also contains a significant amount of energy and carbon resources that could be used as feedstock for the chemical industry, and chemical upcycling has emerged as a promising solution to the plastic waste crisis. To contribute to this solution, we have discovered that earth-abundant metal zirconia nanoparticles can catalyze the selective hydrogenolysis of polyethylene, a widely used plastic, to yield a narrow distribution of small hydrocarbon molecules. The selective cleavage of C-C bonds in polyethylene can produce valuable chemicals, such as linear alpha-olefins, hydrocarbon solvents, liquid fuels, lubricates, and waxes. The discovery is significant as it provides a sustainable and economically viable route for valorizing plastic waste. We conducted extensive structural characterization and employed density functional theory calculations to better understand the catalyst’s structure, active sites, and reaction pathways. Their work demonstrated the potential of Earth-abundant metal oxide catalysts for the efficient and selective conversion of plastic waste into high-value chemicals.

Zirconia, an earth-abundant, non-reducible, metal oxide, was discovered to catalyze the hydrogenolysis of aliphatic hydrocarbon polymers with activity rivaling that of precious metal nanoparticles (Nat. Catal. 2023, 6, 161-173.).
Trick and tips for sustainable packaging materials

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Polymeric materials have transformed our world and are widely used in applications ranging from packaging to medical supplies and from disposable to durable goods. In this presentation, I will provide an overview of problematic materials in packaging and what are the alternatives. I will provide information on when to choose glass, plastic, paper, and metal for packaging. I will also share trends in the packaging world and some winning solutions related to sustainable packaging materials.
Polymer-to-polymer chemical transformations to produce specialty plastics from waste polyolefins

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Recent advances in the dehydrogenation of polyolefins are opening new opportunities for polymer-to-polymer chemical recycling of waste plastics. Functionalizing the C=C bonds using a variety of synthetic strategies, including thiol-ene click chemistry, provides viable routes for incorporating associating groups that enhance mechanical or adhesive properties. For two specific associating groups, we demonstrate this approach by functionalizing polycyclooctene with (1) hydroxyl groups to mimic poly(ethylene-co-vinyl alcohol) copolymers or (2) carboxylic acid groups to mimic poly(ethylene-co-acrylic acid) copolymers. The reagent stoichiometry and reaction time control the level of functionalization up to ~ 25 mol% based on ethylene monomeric units. The level of functionalization controls the glass transition temperature, melting temperature, percent crystallinity, and surface properties. These new associating polymers with hydroxyl groups compare favorably with poly(ethylene-co-vinyl alcohol) copolymers of similar hydroxide content in surface polarity and lap joint shear tests. The properties of the acrylic-acid copolymers are being explored as a function of pendant length and flexibility. Overall, these studies with the model substrate polycyclooctene demonstrate the viability of combining dehydrogenation and functionalization of polyethylene’s to produce specialty plastics from waste polyolefins.
Supercritical CO₂ as a tunable fluid impacting plastics recalcitrance to enzymatic depolymerization

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Developing effective and sustainable recycling approaches for plastic waste is not only critical to solve a growing environmental problem, but also to meet the opportunity for plastic valorization. The enzymatic recycling processes for waste polyesters, including polyethylene terephthalate (PET), are hampered by transport-limiting reaction kinetics. This is because the enzyme activity is highly affected by PET properties, which is often present in a semicrystalline morphology, having low affinity to water required for hydrolytic depolymerization. To overcome these challenges, a supercritical CO₂ process was developed to modify the semicrystalline PET aiming to facilitate the enzyme access to the substrate, thus increasing hydrolysis rates. In this work, we report that semicrystalline PET pretreated with supercritical CO₂ led to a 2-fold increase in TPA yield relative to the untreated PET substrate after 96h of enzymatic hydrolysis and using a commercially available enzyme (Humicola insolens cutinase, Novozymes 51032). In addition, CO₂-pretreated PET showed a much faster depolymerization kinetics relative to the control (untreated PET). In the light of these observations, further studies were performed to understand how supercritical CO₂ pretreatment impacts PET morphology, its surface chemistry, and how those changes impact enzyme adsorption to the substrate and water affinity to the substrate’s surface. The aforementioned factors were correlated with the kinetic rates of enzymatic hydrolysis to determine their relative contribution for overcoming PET recalcitrance by supercritical CO₂ pretreatment.

Enzymatic depolymerization kinetics of untreated semicrystalline PET versus CO₂-pretreated semicrystalline PET. Reaction conditions: PET (25 mg, < 50μm), enzyme solution (0.3 mL), buffer (0.7 mL), temperature (55 °C).
Depolymerization and upcycling of lignin-derivable polymers

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The chemical deconstruction of lignocellulosic biomass offers an abundant source of renewable compounds from materials that are currently burned or otherwise discarded. Previously, we have demonstrated the synthesis of lignin-derivable polymers with tunable, high (> 100 °C) glass transition temperatures for applications ranging from boiling water-stable to deformation-resistant plastics. However, these polymers lack an intrinsic propensity for biodegradation, necessitating the development of an advanced recycling approach to enable materials circularity. Here, we present strategies for the chemical recycling of lignin-derivable polymers to reclaim and repolymerize their constituent monomers. Pathways to depolymerize in high yields are achieved through optimization of reaction kinetics over a range of industrially relevant conditions. Furthermore, we demonstrate methods to ‘upcycle’ free-radically polymerized versions of these polymers by depolymerizing to monomer and then repolymerizing to macromolecules with narrower dispersities via controlled polymerization techniques, closing the loop on their use. The results from this work are a significant advance towards realizing greater materials circularity in bio-derived polymer systems.
Chemically recyclable polymers based on nucleophilic aromatic ring-opening polymerization

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The development of chemically recyclable polymers with desirable properties is a long-standing but challenging goal in polymer science. Central to this challenge is the need for reversible chemical reactions that can equilibrate at rapid rates and provide efficient polymerization and depolymerization cycles. Based on the dynamic chemistry of nucleophilic aromatic substitution (SNAr), we report a chemically recyclable polythioether system derived from readily accessible benzothiocane (BT) monomers. This system represents the first example of a well-defined monomer platform capable of chain-growth ring-opening polymerization through an SNAr manifold. The polymerizations reach completion in minutes, and the pendant functionalities are easily customized to tune material properties or render the polymers amenable to further functionalization. The resulting polythioether materials exhibit comparable performance to commercial thermoplastics and can be depolymerized to the original monomers in high yields.

SNArROP: Nucleophilic Aromatic Ring-Opening Polymerization
Improving mechanical properties of polydithioacetals via aryl backbones

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We recently reported polydithioacetal (PDTA) as a promising candidate for chemically recyclable polymers. There, we synthesized linear PDTAs comprising aliphatic backbones. They yielded a mixture of homologous macrocycles via ring-closing depolymerization. The entropy-driven ring-opening polymerization of macrocyclic monomers subsequently furnished the virgin PDTA. However, the mechanical properties of these polymers were low. Therefore, herein we report the synthesis of PDTA copolymers comprising both aliphatic and aromatic backbones to improve their mechanical strength. Our preliminary results indicate that the copolymer tacticity could be controlled by the combination of appropriate acid catalyst and reaction time. Furthermore, these copolymers are also depolymerizable in solution with acid catalysts to a mixture of macrocycles, which are polymerizable back to the parent polymer. In this presentation, we will highlight the syntheses of the PDTA copolymers, efficiencies of the reversible ring-closing and ring-opening processes monitored by $^1$H NMR spectroscopy and GPC, and the material properties.

Synthesis of PDTA copolymers and their reversible ring-closing depolymerization and entropy-driven ring-opening polymerization

Ar = aromatic
R = alkyl
Fast and mild method for the generation of poly-thioesters from lactone feedstocks for polymer upcycling

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Polythioesters have recently emerged as a promising class of materials for recycling and upcycling applications. However, their synthesis often involves multiple steps and is non-generalizable to other substrates. To address these limitations, we report a two-step route to prepare diverse polythioesters from lactone feedstocks. Firstly, lactones are thionated to generate thionolactones, and then the easily-prepared tetrabutylammonium thioacetate salt is added to initiate polymerization via an SN2 reaction. This process is driven by C=S to C=O isomerization, enabling polymerization to occur without the presence of ring strain. This method enables the synthesis of previously inaccessible polymeric materials and allows for tuning the thermal properties of polythioesters. Additionally, the resulting polymers can be readily depolymerized to small molecule thiolactones in good yields.
Chemical recycling of polymers into their constituent monomers presents a promising solution to the end-of-life issue of plastic waste, thereby promoting the development of a circular material economy. To date, many chemical recycling methods have focused on the selective depolymerization of single plastic streams. However, in reality, plastic products typically consist of mixed plastics with diverse chemical structures and material properties. These characteristics complicate and raise the costs of separation techniques necessary to isolate individual polymers for recycling. Upcycling mixed plastics into valuable products is an alternative strategy that could bypass this limitation and substantially enhance plastics reclaimation and recycling infrastructure, but most current strategies adopt an open-loop framework. This work introduces a closed-loop recycling of mixed plastics via orthogonal (de)polymerization in a circular manner. More specifically, we designed a bicyclic lactone/olefin bifunctional monomer (BiL=) comprising “nonpolymerizable”, low-temperature substructures of a five-membered lactone toward ring-opening polymerization (ROP) and six-membered cyclohexene toward ring opening metathesis polymerization (ROMP). This monomer design not only enables the efficient polymerization of “nonpolymerizable” parent monomers but also renders orthogonal mechanistic pathways to generate two classes of polymers with distinct material properties and full chemical recyclability. More importantly, their physical blend can also be sequentially depolymerized back to their constituent monomer (BiL=). The implementation of orthogonal (de)polymerization of multifunctional monomers, which can produce different classes of recyclable polymers with distinct material properties, offers an alternative solution to mixed plastics recycling.
Sustainable mono-material product design with chemically circular and biodegradable polymers

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The traditional product design of plastic materials that employs multiple, often non-biodegradable or non-recyclable materials of different chemical compositions significantly complicates both mechanical and chemical recycling processes. Here we describe the sustainable mono-material product design that utilizes biodegradable polyhydroxyalkanoate (PHA) or redesigned chemically recyclable PHA materials. This approach employs polymer stereomicrostructure engineering to transform PHAs to different classes of polymers, from strong and rigid thermoplastics to flexible plastics, to stretchable elastomers, to tough thermoplastic elastomers, or to even adhesives, without changing their chemical composition.
Using AFM-IR to quantify the complex phase behavior of multicomponent plastic mixtures

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Plastic waste is a significant environmental challenge, and upcycling is emerging as a promising solution to mitigate this problem. Upcycling refers to the process of transforming discarded plastic waste into higher value products. This approach is gaining traction due to its potential to reduce plastic pollution, conserve resources, and promote sustainable development. The current mechanical recycling typically results in a reduction in material's performance. The recyclability of commodity plastics found in plastic waste streams is intimately linked to their complex morphology which can be comprised of multiple components. Although many advancements in morphology characterization have been made in the areas of scanning probe microscopy, electron microscopy, and advanced scattering techniques, many of these techniques characterize only a fraction of information held within a polymer blend or composite. Specifically, the surface roughness, local phase separation size, and chemical content can all be determined individually through a variety of techniques, but few techniques can determine all three properties simultaneously. In particular, it can be challenging to interrogate blends containing polymer isotopes due to the blend components sharing similar chemical environments. Fully comprehending, not only the nanoscale distribution and geometry, but also the composition of these components is critical for the advancement of polymer recyclability and the circular economy.

In this work, we seek to measure a series of two isotope blends using atomic-force microscopy paired with infrared spectroscopy (AFM-IR) to determine the phase separation size between the deuterated and non-deuterated components and local chemical miscibility. By targeting the unique infrared signal of the deuterated component, the local phase separation size is readily acquired across the surface of a thin film blend. Additionally, by taking a series of localized infrared spectrums across the surface of the blend, the local chemical composition and relative miscibility can be determined using quantitative techniques based on Fourier-transform infrared spectroscopy.
Enol ethers have been commonly used as quenching agents for Grubbs catalysts in olefin metathesis reactions. However, we recently showed that cyclic enol ethers, such as 2,3-dihydrofuran (DHF), can be effective monomers to undergo homo- or copolymerization via ROMP, resulting in degradable polymers due to the presence of acid-hydrolyzable enol ether linkages. The presence of enol ethers in the ROMP system converts the Grubbs catalyst into a Fischer carbene that has different reactivity from the original catalyst. In this work, we investigated the copolymerization between DHF and the common ROMP monomer 1,5-cyclooctadiene (1,5-COD). We characterized their copolymerization kinetics and copolymer microstructures as a function of DHF loading and polymerization conditions. Electron deficient quinone was found to greatly enhance the polymerization kinetics by suppressing undesired olefin isomerization of 1,5-COD. Nearly quantitative conversion of 1,5-COD and high molecular weights can be achieved under optimized conditions. The resulting copolymers provide access to degradable polybutadiene, producing hetero-telechelic polymers upon degradation.
Approaches that valorize plastics waste have continued to emerge over recent years. One common strategy is deconstruction, whereby polymers are degraded into smaller molecules by various reaction pathways. The dynamics of these complex systems of molecules, with evolving molecular weights and molecular weight distributions that span the range from monomer up to commodity polymer, are a strong function of process technology. Hence, efficient development of plastics deconstruction technologies will benefit from simple and descriptive models that link process parameters (e.g., reaction time) to physical properties (e.g., kinetic rate, solubility) and product distribution. As part of this work, we use a simple mathematical model and gel permeation chromatography combined with thermal analysis of the resulting products to gain a greater picture of deconstruction solids and further understand catalytic deconstruction more quantitatively. As another aspect of our work, it is recognized that functional additives are major impediment to the valorization of plastics waste. For instance, catalytic processes that convert discarded polyolefins into value-added products can enable a range of upcycling opportunities; however, widespread implementation of these technologies is often limited by the fact that plastic waste formulations tend to poison catalysts. Detailed and quantitative analysis of additive effects on catalytic properties (e.g., site chemistry) or process outcomes (e.g., yield, selectivity) are required to guide the design of efficient conversion strategies. As one case study in this vein, we examine the role of base additive formulation and antioxidant chemistry/concentration on the hydrocracking of high-density polyethylene (HDPE) with a platinum on tungstated zirconium catalyst.
Molecular engineering in four dimensions: A mechanistic approach to reprocessable polymer networks

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Enhancing the sustainability of thermosetting plastics by incorporating them into a circular economy faces many scientific, economic, and policy obstacles. The primary scientific obstacle is that the strong covalent crosslinks that give thermosets their outstanding thermal and mechanical properties cannot be reformed when the material is damaged or ground, preventing repair and reprocessing. Dynamic covalent crosslinks have emerged as a promising approach to provide the necessary thermal and mechanical performance under service conditions, while enabling topology reconfiguration under heating. The Kalow Lab seeks to bridge the molecular-level understanding of exchange chemistries and the macroscopic observation of flow and healing by combining physical organic studies and mechanical characterization. We have developed a tunable catalyst-free associative exchange reaction based on conjugate addition–elimination of thiols. In this talk, I will discuss strategies to upcycle polymer waste through incorporation of these dynamic bonds, and the effect of topological defects on dynamic networks.
Reprocessable polyolefin thermosets accessed by amidyl radical mediated C—H functionalization

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Polyolefin thermoplastics comprise the majority of global plastic production; are recycled at negligible rates in the United States. Upcycling represents an alternative to current recycling strategies wherein post polymerization modification introduces desirable material properties that might incentivize recycling. To date, there are limited methods to access covalently crosslinked polyolefins while maintaining reprocessability, an approach that would expand the property space accessible via post polymerization modification. In this work, we leverage amidyl radical mediated C—H functionalization of polyolefins to install dynamic covalent crosslinks. Crosslinks induce a toughening effect, representing a desirable change in material properties. The dynamic nature of the installed crosslinks affords a reprocessable thermoset despite covalency indicating the potential for dynamic polyolefin thermosets in a circular plastics economy. We investigate the structural underpinnings of toughening and reprocessability through characterization physical crystalline crosslinks and dynamic covalent crosslinks. This new synthetic method to access polyolefin vitrimers yield unexpected micro and macro structure outcomes which ultimately expand the chemical toolbox for polyolefin upcycling.
Dynamic crosslinking compatibilizes immiscible plastic mixtures

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A significant fraction of plastic waste exists in incompatible mixtures, presenting a significant challenge in tackling the global plastic waste problem. Such mixtures, especially polar/apolar, will undergo phase separation yielding micro- or macro-domains under high interfacial tension, sabotaging resultant material performance. Compatibilization is thus a promising approach for direct mixed polymer upcycling without the need for time-intensive and costly separations and de-/re-construction. This discussion will encompass our compatibilization strategy operating on installment of universal dynamic crosslinkers (UDC) into immiscible polymers during reactive melt blending and simultaneous in situ formation of compatibilized “living” graft multi-block copolymers from binary and ternary polyolefin (apolar) and polyester (polar) blends. Dynamic thermosets and thermoset blends demonstrate intrinsic reprocessability as well as enhanced tensile, thermomechanical, and rheological performances relative to virgin/untreated blends. Noteworthy, UDC tolerance to commercial additives/plasticizers/colorants is probed by blending post-consumer polyethylene bags and polylactic acid cups, revealing a high degree of compatibilization by electron microscopy and mechanical testing. Other experimental and modeling studies will be discussed, along with opportunities for future design and development.
Malleable thermosets with closed-loop recyclability via dynamic covalent chemistry

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The past decades have witnessed a dramatic increase in global usage of conventional polymers, which can be classified into thermoplastics and thermosets. Thermoplastics typically have melting points and can be reprocessed and recycled, but are not durable enough for many applications. On the other hand, thermosets are mechanically tough but are not able to be recycled. Malleable crosslinked polymers are a new class of materials, wherein reversible covalent bonds are employed. These materials can exhibit mechanical properties of typical thermosets under ambient conditions, yet at elevated temperatures or under other stimuli they can be reprocessed and 100% recycled through a cross-link exchange and rearrangement process. This presentation will focus on our recent work in the development of novel thermosets consisting of cyanurate or spiroborate dynamic covalent linkages, which become malleable upon activation of the bond reversibility, thus enabling their unique processability and full recyclability while retaining good mechanical properties.
Covalent adaptable networks (CANs) of ethylene/octene copolymers (EOCs) made by simple free-radical processing with a dynamic covalent crosslinker

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Permanent crosslinking of ethylene-based copolymers such as ethylene/1-octene copolymers (EOCs) is practiced in industry to enhance elasticity but comes at the cost of their recyclability. Few studies have sought to overcome the recyclability issues of permanently crosslinked EOCs (EOCXs) by incorporating dynamic covalent crosslinks into their structures to produce EOC covalent adaptable networks (EOC CANs). Using a simple, radical-based reactive process, we have synthesized EOC CANs directly from EOCs of varying 1-octene content and melt flow index (MFI). The EOC CANs are made capable of dialkylamino disulfide dynamic covalent chemistry via incorporation of dissociative bis(2,2,6,6-tetramethyl-4-piperidyl methacrylate) disulfide (BiTEMPS methacrylate) crosslinker during reactive processing with dicumyl peroxide, a radical initiator. While EOCXs cannot be reprocessed into healed films, the EOC CANs are reprocessable and fully recover their thermomechanical properties after successive compression molding cycles, including robust network character at intended use temperatures. We studied structure-property relationships of the EOCs and EOC CANs. Increases in 1-octene content and MFI in EOCs are generally accompanied by reductions in crosslink density in the resulting EOCXs and EOC CANs. At elevated temperatures where the dynamic chemistry is active, decreasing crosslink density in EOC CANs results in greater fractional losses of crosslink density with increasing temperature; this response is cause by the strictly dissociative nature of the BiTEMPS methacrylate dynamic crosslinks.
Healable, reprocessable, and fusionable cross-linked polymers based on dialkylamino disulfide-based dynamic covalent exchange

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Cross-linked polymers exhibit excellent mechanical properties as well as good chemical and solvent resistance. However, their recycling, reprocessing, and fusion remain difficult. One promising approach to overcome this limitation is to introduce dynamic covalent linkages that enable chain-exchange reactions and network-structure rearrangements in the polymer networks, resulting in self-healing and reprocessing properties. Dialkylamino disulfide (BiTEMPS) units are known to undergo bond exchange reactions via stable radicals at temperatures above 80 °C, and therefore, they can work as dynamic covalent linkages under heating conditions.

Cross-linked polymers with BiTEMPS units at the cross-linking points were prepared by free-radical polymerization of methacrylate monomers using dimethacrylate derivatives of BiTEMPS as the cross-linkers at <30 °C in the presence of the low-temperature radical initiator V-70 to prevent the homolytic dissociation of BiTEMPS. The reprocessability of the cross-linked polymers incorporated with a series of BiTEMPS-containing cross-linkers was systematically investigated. Also, we developed a new method to fuse different cross-linked polymers using the thermal bond-exchange reactions of BiTEMPS. Furthermore, we realized reversible interconversion between the cross-linked polymers and corresponding single-chain nanoparticles.

Reprocessable and fusionable cross-linked polymers based on BiTEMPS-based dynamic covalent exchange.
Incorporating dynamic bonds for recyclable melamine-based thermosets

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The simple combination of 1,3,5-triazine-2,4,6-triamine (melamine) and formaldehyde forms a thermoset resin with desirable mechanical and thermal properties for applications including dinnerware and construction materials. Despite the ubiquity of this material, methods for its recycling remain sparse due to the chemical resistance of the permanent crosslinks. Incorporating dynamic bonds to form covalent adaptable networks (CANs) has quickly become a popular strategy for developing reprocessable materials. Here, I will discuss efforts to incorporate reversible crosslinking into melamine-based systems by reacting silyl ethers with hexamethylol melamine, an intermediate formed during melamine-formaldehyde resin curing. Free hydroxy groups have been shown to exchange with silyl ether bonds and the resulting topological rearrangement can result in reprocessing under thermomechanical conditions. However, the crosslink density and high glass transition temperature of our melamine-based systems prevent efficient mechanical reprocessing. Instead, the networks can be chemically recycled back to unincorporated triazine small molecules by dissolving in methanol. The properties and potential applications of these materials will be presented.
Viscoelastic guanidinium-based supramolecular networks: Tunable, reprocessable, and degradable

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Many applications of bulk polymer materials rely on viscoelasticity, an intrinsic property of the macromolecular nature of polymers. However, this macromolecular structure also results in challenges in degrading or recycling polymers; for example, unwanted decreases in molar mass can occur during reprocessing, and large chains with little functionality can be difficult to biodegrade. Circular strategies such as chemical recycling to monomer rely on reversible conversion of polymer chains to their constituent small molecules and vice versa. An alternative is construction of a supramolecular material entirely from small molecules, held together by reversible non-covalent interactions. Such materials are inherently degradable and reprocessable, as no covalent bonds need be broken or formed. We have developed a new class of supramolecular networks based on guanidinium-phosphonate interactions which display polymer-like viscoelasticity. These materials have high glass transition temperatures ($T_g > 100 \degree C$) and degrade rapidly in the presence of a suitable solvent. The materials can be reprocessed multiple times and their properties tuned by alterations to their structures. Rheological characterization by small-angle oscillatory shear measurements indicates the presence of Maxwell-like behavior above $T_g$, including a rubbery plateau and terminal region.
Robust and recyclable polymer materials through supramolecular co-assembly

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Supramolecular polymers can be formed by assembling monomeric building blocks through directional, non-covalent interactions. The linkages between the monomers can be disrupted by heat, light, mechanical force, or certain chemical stimuli, resulting in significant changes in the material's properties and a temporary or complete disassembly. Due to their ability to offer both functional features, such as reversible adhesion or healing, along with recyclability, supramolecular polymers are ideally suited for developing advanced materials. However, most supramolecular polymers have mechanical properties similar to those of elastomers and cannot replace commodity plastics.

This presentation focuses on how to obtain supramolecular polymers that exhibit the mechanical properties of commodity plastics. By blending two building blocks with complementary mechanical properties that share the same metal-ligand complex as a binding motif, strong, stiff, and tough materials can be created. Co-assembling these two components creates microphase-separated hard and soft domains, and adjusting the composition can fine-tune the bulk mechanical properties. Some blends display significantly higher strength, toughness, or failure strain than either metallosupramolecular polymer alone. This approach produces bulk supramolecular materials with properties similar to those of commodity polymers, such as polyethylene, while also displaying useful responsive functions and recyclability. Additionally, we report how introducing completely new building blocks that mimic commodity plastics can further improve the mechanical properties.
Reprocessable networks with dissociative dialkylamino disulfide bonds: Effects of dynamic covalent crosslinker species and concentration and the ratio of static to dynamic covalent crosslinks

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Conventionally crosslinked polymers or thermosets cannot be melt-processed because the permanent covalent crosslinks prevent melt flow. Covalent adaptable networks (CANs) employ covalent bonds that undergo dynamic reactions, commonly high temperature, enabling network recycling. Here, we consider CANs made via radical polymerization with dialkylamino disulfide (DDS) crosslinks that undergo dissociative dynamic chemistry at high temperature but are robust at use conditions. Poly(hexyl methacrylate) networks with 5 mol% DDS crosslinks can be melt-state reprocessed multiple times with full crosslink density recovery. Additionally, the elevated-temperature stress relaxation of such networks has an Arrhenius activation energy equal to the DDS bond dissociation energy (BDE). Elevated-temperature creep response is strongly suppressed in these systems, with the creep flow viscosity activation energy also equal to the DDS BDE. Replacing a fraction of dynamic crosslinks with static crosslink leads to networks with the same rubbery plateau modulus and thus the same crosslink density but with different stress relaxation behaviors. As the ratio of dynamic to static crosslinks goes from 5:0 to 4:1 to 3:2, there is surprisingly a reduction in average stress relaxation time over the temperature range of 120-140 degrees C. In both 5:0 and 4:1 networks, there is no permanent residual stress, and both networks exhibit the same stress relaxation activation energy. However, in 3:2 networks, stress does not fully relax because of the permanent crosslinks, and there is a major reduction in stress relaxation activation energy. Importantly, although the 3:2 networks do not fully relax their stress, they can be melt-reprocessed by compression molding with full recovery of crosslink density, indicating the important role of pressure in achieving reprocessability. Finally, we note that dynamic crosslink density can play important roles in stress relaxation, with increasing average relaxation times with increasing dynamic crosslink density even with a common activation energy.
Catalytic C–H amination creates tough, adhesive materials from polyethylenes

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Polyethylenes are ubiquitous commodity polymers, but the lack of polar groups in the materials generally restricts their use to low-value applications and necessitates additives that complicate recycling. The introduction of nitrogen-based functional groups into polyethylenes is an important goal because the non-covalent interactions of amines, amides, and imides are known to create valuable properties in other classes of polymers and, therefore, could improve the value and reusability of polyethylenes. However, methods for the synthesis of nitrogen-containing polyethylenes are limited; copolymerizations of N-vinyl monomers and ethylene are plagued by catalyst poisoning and direct amination of preexisting polyethylene architectures by catalytic methods are unknown. We report a Cu-catalyzed C–H amination of a series of polyethylenes, including waste plastic, to incorporate a range of nitrogen-based functional groups into more than 4 mol% of the monomer units. Unusual variations to the catalyst structure proved critical to achieve high efficiency without competing scission or crosslinking of the polymer chains. The resulting nitrogen-containing materials offer a valuable combination of bulk and surface properties, including large increases in toughness (up to 8-times tougher) and newfound adhesion to various metal surfaces. This catalytic amination illustrates principles of catalyst design to facilitate reactions in the viscous solution of polyethylenes and should motivate and inform the translation of additional light alkane functionalizations as a means to address the broad challenge of converting plastic waste to higher-value materials.
Poly(ester amide)s (PEAs) are a type of polymer that contains both ester and amide groups. PEAs offer biocompatibility, biodegradability, good mechanical properties and thermal stability, making them a promising material for various applications, particularly in the biomedical field. In this work, PEAs were synthesized via a newly developed polyaddition method between terephthalaziridine (TP-Az) and a variety of dinucleophiles. The step-growth polymerizations were performed under mild conditions and open-air, and are compatible with many functional groups without the need for any protecting group chemistry. Example functional groups include alkenyl, hydroxyl, ether, aldehyde, ketone, ester, disulfide, and siloxane. In addition to the hydrolysis of the ester linkages, some functional PEAs exhibited the characteristic of programmed degradation (e.g., in the presents of fluoride or dithiothreitol). Additionally, an alkenyl-containing PEA was chosen as a template for intermolecular thiol-ene coupling to introduce extra functionality and tailor the physical properties of PEAs. Overall, this work not only broadens the synthetic methods toward functional polymers but also expands the reaction scope of aziridine in polymer synthesis. Further studies based on chiral diaziridines toward the preparation of optically active PEAs with superior thermal properties are currently in progress.
Chemical recycling, upcycling of polyesters by transesterification using homogeneous titanium catalysts

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Chemical recycling of poly(ethylene adipate) (PEA) and poly(butylene adipate) (PBA), by transesterification with ethanol at 150 degree celsius in the presence of Cp'TiCl3 (Cp' = Cp, Cp*) catalyst, afforded the corresponding diethyl adipate (DEA) and diols [ethylene glycol (EG), butane diol (BD)] exclusively. NMR spectra of the reaction mixture showed resonances ascribed to DEA and EG or BD without any other by-products. Depolymerization with the other alcohols showed the similar results. The depolymerization of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) with ethanol also afforded diethyl terephthalate (DET) and EG or BD exclusively, demonstrating a wide applicability of this catalysis. Since the reaction mixture after transesterification of PBA with ethanol (DEA, BD) contained titanium catalyst, high molecular weight PBA was resynthesized by the condensation polymerization. This result suggests a possibility of one pot (acid-, base-free) closed-loop chemical recycling.
Precision-controlled deconstruction of polyethylene terephthalate (PET) using organocatalysts

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Over 400 million metric tons of plastics are generated globally every year, but only ~9% are recycled. This not only causes environmental pollution but also leads to the waste of valuable resources. The performance of recycled products inevitably diminishes because of the undesired oxidation and degradation in the traditional mechanical recycling processes. Therefore, it is urgent to develop efficient methods to upcycle waste plastics rather than downcycle them. Condensation polymers, such as PET, are considered one of the ideal candidates for precise degradation due to their relatively high reactivity. Given that, we have developed a new route for the controlled deconstruction of PET to a series of well-defined oligomers using organocatalysts. These well-defined building blocks can be used to separate specific small molecules selectively and further upcycled to higher-performance polymeric materials. Therefore, this closed-loop technology via the precision-controlled deconstruction of polymer waste would provide a solid basis for a circular economy and benefit the environment.
Depolymerizing plastics via electrified spatiotemporal heating

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Nearly 9 billion metric tons of plastics have been produced in the human history, the majority of them have become waste that lacks proper treatment. For example, over 14 million tons of plastic waste end up in the ocean every year, threatening biodiversity and wildlife. Moreover, microplastics and its microfibers have been often detected in air and municipal drinking water, causing long-term health concerns. With the continuing heavy demand of plastic products, it is urgent to develop efficient plastic recycling strategies to ensure a sustainable future. In this talk, I will present a catalyst-free, electrified depolymerization method via the pyrolysis reaction that can convert model polyolefin and polyester plastics to their monomers with high yield (Nature 2023, accepted). This pyrolysis process is realized by two critical features: (1) a spatial temperature gradient and (2) a temporal heating profile. The spatial temperature gradient is enabled by a bilayer structure made of porous carbon felts, which promotes continuous melting, wicking, vaporization and reaction of the plastic in a candle-like fashion. In the meantime, we apply pulsed electrical heating through the top heater layer, creating a temporal heating profile that features periodic high temperatures (e.g., ~600 °C) to enable high reaction rate and conversion, while reducing unwanted side products and keep the reaction under far-from-equilibrium conditions. With this process and setup, we converted polypropylene and polyethylene terephthalate to their monomers via the pyrolysis reaction. We achieved monomer yields of ~40%, among the highest compared to conventional thermochemical methods even with catalysts. Due to the high tunability of the electrified heating (e.g., temperature, timescale), this approach potentially offers a unique platform to convert plastic waste and a range of polymeric species to value-added chemicals.

Depolymerization performance by the electrified spatiotemporal heating approach
Towards chemically recyclable resins for Vat photopolymerization additive manufacturing

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Vat photopolymerization additive manufacturing, including Continuous Liquid Interface Production (CLIP), produces cross-linked thermosets that cannot be recycled by traditional methods, such as melt reprocessing. With the advancement of these technologies, it is critical to design new materials with end-of-life in mind. In particular, chemical recycling to monomer is a promising strategy for addressing polymer waste. This work presents the design of oligomeric star-shaped, CLIP-compatible methacrylate-functionalized resins synthesized by ring-opening polymerization. The effect of monomer composition and molecular weight on thermomechanical properties will be discussed.

Graphical abstract showing the proposed chemical recycling scheme from resin synthesis, to additive manufacturing, to chemical depolymerization of the printed part back to monomer.
Polymer upcycling efforts attempt to drive selectivity towards high-value liquid hydrocarbons, rather than light gases. In cases where polymer cleavage is affected by a heterogeneous catalyst in the polymer melt, the volatility of products can be exploited to tune selectivity. Specifically, products that partition into the headspace gas will not be further cleaved, since the catalyst resides in the polymer melt. We formulate and solve population balance models of two-phase reactors to quantify the effects of product volatility on the selectivity of polymer upcycling. We incorporated vapor-liquid partition coefficients into population balance equations to describe polymer upcycling in two-phase reactors. The models consist of vapor-liquid equilibrium models and rate equations that can be nondimensionalized and generalized to a wide range of systems, including batch reactors and flow reactors with several different catalysis strategies.

Phase partitioning can be used to tune selectivity. Specifically, the heaviest volatile species will accumulate, since the catalyst resides in the polymer melt.
Reaction mechanism and interfacial structure of chemically recyclable polymer

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Chemical recycling of plastic has attracted attention because the polymer can be more efficient in synthesis, retain better mechanical properties, be environmentally friendly and less expensive. Among the selected polymers, polydiketoneamine (PDK) is a novel polymer that can be highly chemically recycled. PDK is depolymerized by strong acid and forms triketone monomer and triamine with a recycling efficiency of above 90%. However, the properties of such polymers are less investigated.

In this study, we employed Raman spectroscopy to observe in-Situ PDK depolymerization in strong acid and sum-frequency generation (SFG) to monitor the interfacial structure of PDK. In our observation, hydrochloric acid (5M) rapidly reacted with PDK, resulting in a new peak, from C=O at 1590 cm⁻¹. Compared to depolymerized products, triketone monomer and triamine, we proposed this newly formed peak is due to the intermediate. Time-dependent study showed that the intermediate exists for at least ten hours. From our proposed reaction mechanism, we assign that the peak at 1590 cm⁻¹ is due to the single carbonyl group after the rapid hydrolysis of PDK.

Interfacial structure and interaction of anion of PDK is observed at PDK-aqueous interfaces by sum-frequency generation (SFG). Our SFG results indicate that the intensity of CH stretch of PDK changed depending on the anion identity. We observed the intensity of the asymmetric CH stretch of PDK at 2950 cm⁻¹ followed by the order of Cl⁻ > Br⁻ > HSO₄⁻, representing the interfacial dipole of CH has decreased. In addition, a similar trend is also observed for the swelling rate of PDK in HCl, HBr and H₂SO₄. We proposed the intensity of CH stretch could be an indicator of reaction rate of PDK depolymerization.
Converting unsaturated polymers into vitrimers via cross-metathesis

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Unsaturated polymers, such as polybutadiene and polyisoprene, are used in a variety of everyday applications, ranging from automobile tires to construction materials. These polymers are often vulcanized, or permanently crosslinked with sulfur, creating thermoset materials that have enhanced mechanical properties, but are also rendered non-recyclable. As a result, millions of tons of these materials accumulate in landfills every year. Polymer networks crosslinked with associative dynamic bonds, known as vitrimers, have been proposed as a circular alternative to conventional thermosets. Due to the dynamic nature of the chemical crosslinks, these networks rearrange in response to increasing temperature, allowing the material to be reprocessed. In previous work in the Kalow lab, a dynamic, catalyst-free dithioalkylidene bond was developed and applied to silicone vitrimers, but the structure of the original crosslinker limited its use to polymers containing free thiols. We are interested in finding ways to broaden the scope of polymeric materials in which this dithioalkylidene bond can be incorporated. Here, I will present new dithioalkylidene crosslinkers that can undergo olefin metathesis. These crosslinkers may be incorporated into several types of unsaturated polymers, including polyisoprene and polybutadiene. The resulting networks may be dynamically crosslinked. I will discuss the mechanical and chemical re-processability of these materials, as well as efforts to convert previously crosslinked systems into vitrimers.
Design of a new class of degradable polymers using phenolic additives

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Polyethylene terephthalate (PET) is one of the world's most used thermoplastics with a global current mass production of 62 million metric tons per year [1]. However, less than 19% of waste PET is recycled in U.S., which means that approximately 80% of waste PET ends up in landfills [2,3]. In this work, we aim to address low recyclability rates for waste PET by engineering new polymer materials to alter their solvation mechanisms and reactivity at solid-liquid interfaces during chemical recycling. We designed an additive to be introduced into PET to promote aqueous degradation of PET at controlled reaction conditions. Firstly, various phenolic additives functionalized with a thermally-labile group were synthesized and their thermal degradation mechanisms and thermal properties were investigated. Through solution-blending techniques, the optimized additive was introduced in PET at varying compositions (up to 50 wt.%) and the blend was recrystallized by adding water. The blends were characterized for composition and additive dispersity and showed comparable thermomechanical and barrier properties relative to virgin PET. The prepared PET blends were exposed to various thermal conditions, such as temperature and heating rate (up to 700 °C and 5-20 °C/min), to investigate the thermal decomposition of the additive in PET. The effect of the thermal degradation of the additive on PET morphology (i.e., crystallinity) and surface area, as well as on the depolymerization rates of PET in the presence of water will be presented. This approach has the potential to simplify the entire plastics recycling process and address major rate-limiting challenges of the current chemical recycling methods.
Chemical recycling of textile wastes

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Chemical recycling of textile wastes is challenging because they are often discharged as a mixed stream of different fibers with intractable impurities such as colorants. Due to chemical and physical incompatibilities between the fabric materials, sorting the wastes into homogeneous materials should be considered as an essential part of recycling. In practice, the presence of dyes and other organic impurities also affects the quality of recycled product, which must be improved by energy-intensive purification steps.

In this presentation, we will discuss our recent technology, so called “chemical sorting”, utilizing an inexpensive and fully recyclable green solvent to separate polyester from a mixed textile waste stream. The solvent enables a complete separation of disperse dyes from polyester-based textiles while dyes from other fabric materials remain unaltered. As a consequence, a clean polyester can be selectively collected from complex textile wastes, initially containing various natural and synthetic fibers, colorants, and other impurities. Then, a low-temperature glycolysis reaction system can be applied to depolymerize the sorted polyester into pure bis(2-hydroxyethyl) terephthalate (BHET). In this reaction system, the identical chemical compound adopted in the “chemical sorting” can be utilized as a co-solvent to lower the activation energy of catalytic decomposition of polyester. The reaction system can be efficiently integrated with the chemical sorting process to produce high-quality recycled monomers from post-consumer textiles regardless of the complexity of materials and impurity level in the waste stream.
Molecular dynamics simulations for understanding and improving non-equilibrium plastic recycling product selectivity

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Recycling plastic waste is a major challenge facing humankind. Thermochemical conversion of plastic waste into valuable products is a promising solution to this issue. However, conventional recycling processes such as pyrolysis are limited by their lower product yields and selectivity. One of the reasons for this shortcoming is lack of understanding of detailed pyrolysis chemistry. Reactive molecular dynamics (MD) simulations provide a useful tool for gaining atomistic insight into the detailed reaction chemistry of polymer pyrolysis. We use ReaxFF reactive potential to perform the MD simulations of polymer pyrolysis. Firstly, in this work, these classical MD simulations are used to analyze the impact of reactor residence time on product selectivity of polypropylene (PP) pyrolysis under non-equilibrium conditions. We show that the mass residence time distribution could affect the product selectivity by up to 25%. Later, we use the ReaxFF MD simulations to guide the pyrolysis of polyethylene (PE) using a non-equilibrium reactor with PE leading the share of plastic waste. The atomistic insights gained into the pyrolysis chemistry of PE using MD simulations are validated by non-equilibrium reactor experiments. The validation includes the temperature and time dependence of major product formation (C₂H₄ and C₃H₆). Then the insights gained from the comparison between MD simulations and experiments are used to optimize the non-equilibrium reactor. We observed some of the highest major product yield (47%) compared to the literature using the optimized non-equilibrium reactor.
Biowaste-based, non-isocyanate Polythiourethane (NIPTU) networks: Enhanced performance, reprocessability, and end-of-life monomer recovery

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Traditional isocyanate-based polyurethanes (PUs) raise concerns about safety, sustainability, and the circular economy. Moreover, current development of the most prevalent isocyanate-free PU substitutes, polyhydroxyurethane (PHU), suffers from limitations associated with slow reaction and inferior properties, etc. Here, we present research on renewable non-isocyanate polythiourethane (NIPTU) networks derived from biowaste sources, e.g., cashew nutshell liquid, rice husk, and glycerol. We demonstrate the outstanding performance of the NIPTU networks in aspects of reactivity, mechanical properties, and water resistance superior to their PHU structural analogs. We address the recyclability of NIPTU networks crosslinked with dynamic covalent bonds of two types, thiourethane and disulfide, by showing full recovery of crosslink density and associated properties of NIPTU networks after multiple melt-recycling steps. The dynamic chemistries of reversible cyclic thiocarbonate aminolysis and transthiocarbamoylation were also have also been demonstrated for the first time via small-molecule experiments. Finally, via transcarbamoylation dynamic chemistry, we present the first case of “monomer” recovery from NIPTU using a facile solvolysis approach with 93 mol% recovery. From biowaste feedstock and robustly crosslinked, recyclable polymers and to end-of-life monomer recovery, our work highlights the potential of NIPTUs to contribute meaningfully to a true circular polymer economy.
Low mass mechanical characterization for sustainable polymers

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Mechanical properties are important for daily used materials which determine the range of usefulness. To accelerate material discovery, rapid and high-throughput mechanical property measurement is in urgent need. However, traditional tensile testing methods are mainly designed for bulk samples, which require a large amount of materials making them unsuitable for high-throughput measurement. In this work, we developed a film-on-water (also named pseudo-free standing) tensile tester, allowing measurement of polymer thin films (thickness < 100 nm), which only required at least 1000 times fewer polymers to study. We utilized polystyrene (PS) as the model polymer, successfully obtained stress-strain curves. Such results are comparable to those from traditional tensile testers. The measurement has also been extended to various conjugated polymers, obtaining elastic modulus and crack onset strain to help guide further design of stretchable semiconductors for wearable devices. Furthermore, such thin-film tensile testers were also used to perform hysteresis and fracture energy studies making it more universal. Due to the less material requirement and compatibility, the film-on-water tensile tester showed enormous potential for high-throughput mechanical property study.
Highly recyclable thermosets from dithioacetal polymers

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Thermoset polymers are widely used in consumer plastics for their durability and stability, but prove to be an undeniable issue regarding sustainability. This issue with consumer thermosets has prompted the creation of new classes of polymers: Covalently Adaptable Networks (CANs). These materials act as thermosets at low temperatures, giving comparable durability and stability to existing thermosets, but at higher temperatures they can flow under a mechanical load like thermoplastics, enabling them to be reprocessed and given new purpose without sacrificing the quality of the material. Another interesting quality of this class of materials is the possibility of reclaiming the material through depolymerization. The resulting monomers could then be collected and repolymerized without sacrificing the quality of the polymer. With this in mind, we have developed an efficient monomer-polymer recycling system using crosslinked polydithioacetal (PDTA). Pristine PDTAs can be synthesized from 3,4,5-trimethoxybenzaldehyde and alkyl dithiols, with teraphthalaldehyde introduced as a crosslinker in an acid catalyzed reaction. The system can undergo depolymerizability via ring-closing depolymerization into macrocycles. These macrocycles can then be repolymerized via entropy-driven ring-opening polymerization, all done with only the catalyst still present from the initial polymerization. The crosslinked networks also showed a penchant for thermal reprocessing enabled by acid catalyzed dithioacetal exchanges. As the system is mechanically reprocessed, the tensile characteristics improve with each cycle, a trend that is present in both the strictly mechanically reprocessed films as well as mechanical reprocessing of repolymerized macrocycles. This demonstrates PDTA as a viable foundation for the design and development of recyclable polymers critical to moving towards a sustainable future.
Towards the upcycling of PVC into thermoplastic elastomers

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Poly(vinyl chloride) (PVC) is among the most widely produced thermoplastics and is used in a wide range of applications. However, despite its widespread use, the post-consumer reuse or recycling of PVC is almost non-existent, and most post-consumer PVC is ultimately landfilled. Unlike other plastics, PVC is challenging to mechanically recycled due to its' low decomposition temperature.

The chemical structure of PVC lends itself to easy chemical modification and holds the potential to upcycle PVC into more valuable materials. Alkyl chains substituted onto the backbone of the polymer can act as plasticizing agents without the detriment of migrating out of the PVC over time. In addition, reactive moieties substituted onto the backbone of PVC can lead to advanced functionalities.

This presentation will detail our efforts toward modifying waste PVC into a thermoplastic elastomer. We will also discuss the effects of PVC dehydrochlorination, which is a common side reaction that occurs during the chemical manipulations of PVC.

\[ \text{CH}_2=\text{C}(-\text{Cl})\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{HS}-\text{R} \xrightarrow{\text{Base, Heat}} \text{CH}_2=\text{C}(-\text{SR})\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \]
Vibrational analysis of polyethylene crystallinity for molecular-level recycling

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Globally, only about 10% of postconsumer polymers are recycled, with the other 90% winding up in landfills, surrounding ecosystems, or incinerators. To mitigate the irreversible impact of the plastic waste crisis via new technologies, there has been a major shift in both academia and industry towards understanding the chemistry of mixed plastic waste. From a physical chemical viewpoint, the vibrational characteristics of polyethylene film plastics and bulk postconsumer plastics will be presented. Polymer crystallinity is the property-of-interest in these studies, as it may be leveraged for enhanced separation, purification, and recovery of recycled polymers. Thanks to a joint experimental and modeling approach, new insights from a phenomenological model reflecting the dissolution process of polyethylene were found to be supported by temperature-controlled Fourier Transform-Infrared (FT-IR) spectroscopy. Two-dimensional correlation spectroscopy was used to elucidate dynamic events occurring within the FT-IR cell at different temperatures, such as solvent diffusion, polymer swelling, chain disentanglement, and transformation from crystalline to amorphous domains. These insights may assist with the design of more efficient chemical recycling systems and processing conditions for dissolution-based packaging film separations. Moreover, understanding the fundamental mechanical properties of mixed plastic waste may also contribute to innovation in spectroscopic mechanical sorting systems.
The applications of plastics are diverse and widespread, spanning from industrial to domestic utilities. However, global annual plastic production surpassed 760 billion pounds per year in 2019, leading to a rapid buildup of waste and putting immense pressure on waste management systems. The negative implications of plastics on the environment and their inadequate recyclability have resulted in anti-plastic sentiments. It is alarming that approximately 85% of produced plastic is dumped in landfills or incinerators, posing a significant threat to ecosystems due to the release of microplastics and hazardous materials.

The United States is actively promoting plastic recycling due to various reasons, including the implementation of China's National Sword policy, brand owner commitments, and anti-plastic sentiments.

Polystyrene, a widely used polymer, had global production of about 15.6 million metric tons in 2019. PS caters to a vast range of industrial and domestic applications. PS stands out as the only commodity polymer that exhibits the potential for depolymerization into its styrene monomer. Catalytic pyrolysis and solvent-assisted pyrolysis have also been employed to overcome some of the challenges associated with PS depolymerization. Other methods, like microwave-assisted pyrolysis, vacuum conditions, and high pressure, have also been investigated as strategies to achieve PS degradation. However, these methods carry their own set of challenges, such as lower % styrene yields, the formation of a large number of byproducts, the requirement for high temperatures to achieve pyrolysis, and longer reaction times.

In this work, we present catalytic pyrolysis of PS using an inorganic nanomaterial as a catalyst. The depolymerization reactions were carried out under a vacuum with a few weight percent of the recyclable catalyst. The abstract shows preliminary results, as shown figures. Detailed experimental results referring to catalyst characterization and the product analysis through NMR and GC-MS will be presented at the conference.

The salient features of the catalyst based on the preliminary results were as follows:
- High monomer product recovered
- A high percentage of styrene monomer in the product
- Low coke formation during recycles
- High reaction rate
- Easy catalyst separation
- Easy catalyst regeneration
- Low-cost catalyst
Recycling of dithioacetal polymers into monomer macrocycles

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Polymers are widely utilized in modern society and are irreplaceable in many applications. These synthetic polymers are highly stable, and as a result, they persist in the environment for a considerable amount of time even after disposal. This makes the production of sustainable polymer materials through chemical recycling to monomers a very important process. Here, we present a method for highly efficient ring-chain recycling of linear polydithioacetal (PDTA) ring-closing depolymerization (RCD) and entropy-driven ring-opening polymerization (ED-ROP). PDTA polymers can be conveniently synthesized by a one-step reaction using 3,4,5-trimethoxybenzaldehyde and α,ω-alkyl dithiols with an acid catalyst. The synthesized pristine PDTAs undergo RCD by refluxing in toluene in the presence of an acid catalyst to yield a mixture of varying sized macrocycles with high conversions. At room temperature these macrocyclic monomer mixtures undergo ED-ROP forming the initial PDTAs, also reaching high conversions. The position of the ring-chain equilibrium is controlled with a combination of concentration, temperature, and size of the macrocyclic monomer. In this presentation, we will take a detailed look at the mechanisms of this ring-chain equilibrium.
Covalent adaptable networks exhibiting stress-induced shape-shifting behaviour and reprocessability along with scratch-resistant ability

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One of the prime areas of research in the field of polymer science is Covalent Adaptable Networks (CANs). Polymeric materials having self-healing, as well as shape-shifting ability, provide an alternative pathway for 4D printing technology to create a variety of complex shapes easily. However, shape-shifting materials enable a wide range of biomedical and engineering applications, but till now transformations require external agents such as light, temperature or chemicals to trigger a programmed shape. These conditions restrict their further utilization and application because it is impossible to implement such a control environment in complicated situations. Here, we demonstrate a thia-Michael adduct that can be exchanged at room temperature, and their corresponding CANs rearranged in topology on the application of nominal stress and ambient environmental conditions. These CANs have sufficient modulus (≤71.4 MPa) and tensile strength (≤6 MPa) for the adaptation of any targeted application. These CANs also have the ability to self-weld, self-heal and recycle under nominal stress. The self-healability along with transparent properties at room temperature conditions can be used in scratch-resistant coating materials. We have demonstrated the efficacy of these materials as an alternative to 3D/4D printing techniques by fabricating various 3D shapes and altering their shapes after fabrication.

In the absence of additional chemical stimuli or agents, the thia-Michael adduct based on highly activated Michael acceptors can be exchanged in ambient conditions. This enables the covalent adaptable networks with the aforementioned links to be flexible in response to environmental factors, display autonomous shape-shifting behaviour, and have the capacity for self-healing and reprocessing. These CANs can are transparent so they may be applied as coatings in display items with scratch resistance ability.
Closed-loop recycling of carbon fiber reinforced dynamic covalent crosslinked polyurea composites with hyperbranched polymers

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Carbon fiber reinforced thermoset composites have causing an environmental crisis, prompting the development of chemical recycling technologies for fully recovery of polymers and carbon fiber. Here, we synthesized thiol-terminated hyperbranched polymer (THBP) and isocyanate-terminated hyperbranched polymer (IHBP) for closed-loop recycling of dynamic covalent crosslinked polyurea composites, based on hindered urea bonds and hexahydro-s-triazine structure. Incorporation of THBP and IHBP dramatically improved the mechanical and reprocessing properties of composites. The generated composites exhibited tough behaviors as well as Young's modulus of 43GPa, a stress at break of 691MPa and a glass transition temperature of 100 °C due to the hyperbranched topological structure. The dynamic and hyperbranched topological structure contributed excellent repairability, reprocessibility and self-healing properties of composites. Importantly, the introducing dynamic covalent crosslinks and hexahydro-s-triazine into composites can dramatically tune the recycling behaviors with high recovery rates of 96 %. The regenerate composites retain the mechanical and thermal properties of pristine materials. Thus, this work provides a strategy for end-of-life upcycling of high-performance carbon fiber reinforced thermosets, while overcoming the environmental challenges associated with plastics pollution.
High-pressure CO₂-H₂O media for the depolymerization of polyethylene terephthalate

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Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic mostly produced for textile and single-use bottles. Mechanical recycling of PET has been implemented with limited success because it produces low quality recycled PET relative to the virgin counterparts. To address these issues, various chemical processes have been developed with limited success. Most of the processes require harmful solvents and generate deleterious waste streams. In this study, we propose to overcome these issues by developing a depolymerization process using solely green chemicals, such as CO₂ and H₂O. CO₂ dissolves in H₂O to create carbonic acid (H₂CO₃) in situ, which catalyzes polyester depolymerization via hydrolysis. At the end of the process, the H₂CO₃ formed can be dissipated readily by releasing CO₂ pressure. Here, we will present our research findings supporting substantial increase of PET depolymerization rate and terephthalic acid (TPA) yield upon exposure to high-pressure CO₂-H₂O media at elevated temperatures relative to H₂O-only reactions. A conversion of 98 wt% of PET and a TPA yield of 86% were observed at 200 °C, 208 psi of initial CO₂ pressure for 2 hours residence time. The purity of the produced TPA was evaluated by carbon and proton NMR.
High-density polyethylene (HDPE)-based vitrimers

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High-Density Polyethylene (HDPE) is presently the most-used commodity plastic by volume, and it is frequently used in consumer goods, construction, and electrical industry. In this poster, I will present HDPE based vitrimers and the impact of grafting agents on the performance of these vitrimers. Interestingly, the crystallinity of the polymers decreased which might find a great application in 3D printing owing to warping issues with conventional HDPE.
Circular Economy of Polymers

Precision native polysaccharides from living polymerization of anhydrosugars - Wu, Lianqian (Oral Only)

Verification of additive effects for biobased polylactic acid resin found by “chemicals Informatics” - Tsubouchi, Shigetaka (Oral Preferred)

Survey of machine learning strategies for improved polyolefin sorting using near-infrared spectroscopy - Sutliff, Bradley (Oral Preferred)

Property-advantaged (tetrahydro)furanic polymers from lignocellulose & CO₂ - Woroch, Cristian (Oral Preferred)

Biosourced dipicolinic acids in the redesign of soil release polymers - Mahon, C (Oral Preferred)

Data-driven design of circular polymers - Helms, Brett (Oral Only)

Renewable materials based on vitrimers from small and large molecules - Abetz, Volker (Oral Only)

Mechanism of synergistic catalytic PET glycolysis by urea/choline chloride - Chenxi, Zhu (Oral Preferred)

Practical and scalable epoxy-anhydride formulations for thermomechanically competitive and recyclable composites - Clarke, Ryan (Oral Only)

Influence of molecular architecture on the viscoelastic properties of polymers with phase separated dynamic bonds - Carden, Peyton (Oral Preferred)

Tough and recyclable glass fiber composites with a upcycled commodity thermoplastic - Mahappu Koralalage, Menisha (Oral Preferred)

Continuous one-pot melt extrusion approach for high-density polyethylene-based Vitrimers - Rabnawaz, Muhammad (Oral Only)

Polyester networks from structurally similar monomers: Recyclable-by-design and upcyclable to photopolymers - Wang, Chen (Oral Only)

Comparison of dilute solution properties of precision short-chain branched polyethylene copolymer compatibilizers - Orski, Sara (Oral Only)

Biobased and chemically recyclable polysulfones - Jain, Vitasta (Oral Preferred)

Modification and activation of PVC to enable efficient depolymerization to small molecule targets - Bara, Jason (Oral Only)

Environment controls kinetics of nano-confined enzyme plastic degradation and upcycling - Jayapurna, Ivan (Oral Only)
Circular Economy of Polymers

Elucidation of underlying chemistry for polyethylene terephthalate (PET) depolymerization between alcoholysis and hydrolysis - Kang, Donghyeon (Oral Preferred)

Recycling polystyrene into self-healing 3D printable resins - Weems, Andrew (Oral Only)

Facilitating a circular economy for textiles through a designer molecule approach - Wentz, Charlotte (Poster Only)

Composites of polyethylene-like polyesters with polar microphases for enhanced degradation in nutrient-poor environments - Bernabeu, Lea (Poster Only)

Mechanical recycling of waste polyolefins using a rheology modifier - Muzata, Tanyaradzwa (Poster Only)
Precision native polysaccharides from living polymerization of anhydrosugars

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The composition, sequence, length, and type of glycosidic linkages of polysaccharides profoundly affect their biological and physical properties. However, investigation of the structure-function relationship of polysaccharides is hampered by accessing well-defined polysaccharides in sufficient quantities. Here, we report a chemical approach to precision polysaccharides with native glycosidic linkages via living cationic ring-opening polymerization of 1,6-anhydrosugars. We synthesized well-defined polysaccharides with tunable molecular weight, low dispersity, and excellent regio- and stereoselectivity using a boron trifluoride etherate catalyst and glycosyl fluoride initiators. Computational studies revealed that the reaction propagated through the monomer a-addition to the oxocarbenium and was controlled by the reversible deactivation of the propagating oxocarbenium to form the glycosyl fluoride dormant species. Our method afforded a facile and scalable pathway to multiple biologically relevant precision polysaccharides, including D-glucan, D-mannan, and an unusual L-glucan. We demonstrated that catalytic depolymerization of precision polysaccharides efficiently regenerated monomers, suggesting their potential utility as a class of chemically recyclable materials with tailored thermal and mechanical properties.
Verification of additive effects for biobased polylactic acid resin found by “Chemicals Informatics”

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Hitachi High-Tech Solutions has developed Chemicals Informatics (CI) which utilizes artificial intelligence technologies and a huge amount of public data such as patents and papers to rapidly search for combinations of compounds and composite materials with promising characteristics. By conducting a search using CI, two promising additives, adipic acid and 3,3'-dithiodipropionic acid, were identified which improve both the yield strength and hydrolyzability of a biobased polylactic acid (PLA) resin. The effects of the found promising additives were clarified by molecular simulations. The results verified the mechanism of increasing the yield strength and hydrolyzability by arranging the PLA and strengthening the electrostatic attraction. The ordered molecular arrangement of the PLA showed that it was attributed to the distance between the carbonyl groups in adipic acid or 3,3'-dithiodipropionic acid is close to the distance between carbonyl groups in PLA. In an experiment conducted by making PLA resin containing the promising additives and comparative additives, isophthalic acid and terephthalic acid, the yield strengths of the PLA containing promising additives were improved by more than 10 MPa compared to that with no additives. The PLA resin with no additives and the comparative additives retain the shape until 595 h in immersion in 0.1 N NaOH aqueous solution at 60°C, while the resin pieces with adipic acid and 3,3'-dithiodipropionic acid were pulverized. As a result, it was experimentally demonstrated that the PLA resin with the promising additives found by CI achieve both yield sufficient strength and hydrolyzability. Furthermore, the results obtained from the analysis of the PLA resins with each additive before and after hydrolysis elucidated that the mechanism clarified by the molecular simulation is experimentally reasonable.

Yield strength and hydrolyzability in PLA resin pieces with (ref) no additives, (a) isophthalic acid, (b) terephthalic acid, (c) adipic acid, and (d) 3,3'-dithiodipropionic acid.
Survey of machine learning strategies for improved polyolefin sorting using near-infrared spectroscopy

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Polymers are ubiquitous, since they are cost-effective and exhibit a variety of useful properties such as chemical, shock, and impact resistance. Polyolefins, specifically polypropylene (PP) and polyethylene (PE), are some of the most stable and commercially available polymers, yet recycling rates remain low. Incompatible molecular architectures result in downgraded material properties in recycled resins or require compounding with more virgin resin to achieve desired properties. Improved sorting and more quantitative understanding of the impacts of architectural heterogeneity on resultant properties can circumvent this challenge. Here, we explore using machine learning (ML) along with the near infrared (NIR) measurements that are already in use at advanced materials recovery facilities to identify patterns that allow enhanced sorting of these polymer species beyond what is possible using NIR databases. In this work, NIR data of polyolefins was achieved using supervised classification algorithms for polymer sorting. The polymer samples included polyolefins spanning a range of branch content, processing conditions, and additives. Common scattering corrections and preprocessing steps such as multiplicative scatter correction, linear detrending and Savitzky-Golay filtering limited artifacts from scattering and noise prior to ML applications. Principal component analysis enabled reduction of the data for further comparison of preprocessing techniques and their effect on the accuracy of the classification models. The survey of preprocessing steps and ML algorithms combinations identified multiple data pipelines capable of successfully sorting polyolefin materials. Multiple combinations properly distinguished PP from PE, and separated subclasses of these polyolefins (high-, low-, and linear low-density PEs) while also reducing data from 4148 data points per spectrum to 4 principal components. This work discusses the effects of each data analysis step on the final classification results and proposes a standard method that can be employed at scale to maximize sorting efficiency of mixed polymers.
New performance-advantaged polymers derived from renewable feedstocks are needed to improve the sustainability of the plastics industry. Herein, we describe our efforts toward synthesizing chemically recyclable polyamides and polyesters sourced from carbon dioxide (CO₂) and furfural, a platform chemical derived from lignocellulose. The resulting polymers contain furan and tetrahydrofuran moieties which imbue them with exceptional thermal properties. Our previous work has demonstrated that polyamides containing furan and tetrahydrofuran moieties have exceptionally high glass transition temperatures (T₉). More recently, we have demonstrated that the tetrahydrofuran analog to polycaprolactone (PCL) named POTC also exhibits a T₉ 90 °C greater than PCL. In each case, the tetrahydrofuran or furan ring imbues the polymer backbone with increased rigidity that enhances its T₉ relative to other bio-derived polymers. Using experimental and computational techniques, we investigate how incorporation of tetrahydrofuran and furan rings can produce sustainable polymers with notable properties.
Biosourced dipicolinic acids in the redesign of soil release polymers

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The performance of fabric care formulations under environmentally favourable conditions of low wash temperatures and low water consumption relies upon a range of polymer additives which fulfil important functions. Soil release polymers (SRPs), for instance, enhance cleaning efficiency and improve the cleanliness of synthetic fabrics by modifying the surface of fabric to prevent the adsorption of soil in the subsequent wear phase. To complement the structure of polyester fabrics, conventional SRPs contain a poly(ethylene terephthalate) subunit capped by a hydrophilic methoxy-poly(ethylene glycol) unit to aid in the dispersal of the polymer in the solution whilst preventing the redeposition of the soil onto the fabric surface.

To improve their environmental footprint, a novel class of SRPs have been synthesized using lignocellulosic derived dipicolinic acids in a one-pot multi-step polycondensation reaction. The potential viability as potential replacements to current commercialized SRPs were assessed through soil release and anti-redeposition performance tests, to determine the stain removal index and whiteness maintenance of the fabric samples. Changing structural features of polymers including varying degrees of polymerisation and influencing regiosomerism resulted in significant variation in the performance of the SRPs. The differences in performance within this library of polymers has been explored through a range of molecular modelling studies, which have enabled structure-function relationships to be elucidated.
Data-driven design of circular polymers

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Here, I will describe a data-driven workflow for designing-in circularity in plastics from the bottom up. This workflow for designing involves collecting and analyzing data on plastic properties and recycling processes, identifying relationships between properties and recyclability, developing predictive models to understand deconstruction during chemical recycling, and using these models to guide the design of more sustainable plastics from the perspective of energy and resource requirements. I will show how this workflow has provided fundamental insights into the recyclability of polydiketoenamines, capturing phenomena dictated by specific features at the atomic and molecular scale as well as higher order effects tied to solvation, dynamics, and mechanochemical effects associated with polymer chains responding to reactive liquid environments. I will further show how these behaviors can be studied and quantified with precision using advanced X-ray and magnetic resonance techniques, revealing not only foundations for circularity, but also design rules for spatially controlled deconstruction of waste exhibiting hierarchical complexity.
Renewable materials based on vitrimers from small and large molecules

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Vitrimers are associative covalent adaptable networks introduced as a new class of soft matter a decade ago. They have received an increasing interest in the scientific community, as they offer a broad spectrum of thermal mechanical properties between the properties known from thermoplastics or thermoplastic elastomers on one side and thermosets (duroplasts) on the other side. They are malleable materials, which are characterized by keeping their crosslink density constant due to chemical exchange reactions upon deformation, as the crosslinks are reorganized in an associative way rather than dissociated and rebuilt upon deformation above a temperature characteristic for the chemical exchange reaction. Depending on the glass transition temperature and the temperature above which the exchange reaction takes place, the material can display a broad range of features, such as plasticity, shape memory and thermomechanical or chemical reprocessability. Here we present the concept of vitrimers using two different chemically reversible reactions based on vinylogous urethanes and Schiff bases. The basic components are multifunctional amines, aldehydes and alcohols and acetoacetates, which can be of petrochemical or biogenic origin. They may range from low molecular weight materials to polymers and block copolymers. The chemical basic reactions will be presented and the resulting materials properties will be discussed and related to the structure of the used building components.
Mechanism of synergistic catalytic PET glycolysis by urea/choline chloride

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The Metal free catalyst has attracted more and more attention in the catalytic degradation of polyethylene terephthalate (PET) due to its advantages of environmental protection and low toxicity. However, there are problems such as low monomer yield. In this paper, we report a cheap mixed catalyst of urea and choline chloride and find that adding 1/4 equivalent of choline cation could effectively improve the PET glycolysis efficiency of catalytic system on the basis of experimental and theoretical studies. PET conversion could reach 100% and BHET yield could reach 85.67% under the optimum reaction conditions. Also, the mixed catalyst has good reusability and maintain a high BHET yield after 5 times of use (83.49 %). Density functional theory (DFT) calculations and weak phase protection force (IGMH) analysis results showed that the excellent catalytic activity of PET glycolysis could be attributed to the synergistic catalysis of urea and choline cations. Urea activated ethylene glycol to improve nucleophilicity, and at the same time, the choline cation stabilized carbonyl oxygen through hydrogen bond interactions, promoting the formation/breaking of C-O bonds to form BHET.
Practical and scalable epoxy-anhydride formulations for thermomechanically competitive and recyclable composites

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At the intersection of thermoset performance and thermoplastic reprocessability, covalent adaptable networks are promising candidates for robust, recyclable materials. In this talk, I will discuss our recent trials in designing an ideal epoxy-anhydride formulation for performance-advantage polyester covalent adaptable networks (PECAN) with the objective of scaling in fiber-reinforced composites for wind turbine applications. Resin attributes toward high value proposition include low activation temperature, fast cure kinetics, long shelf life, low cure exotherm, and full conversion precluding high-temperature post-curing cycles – each which will be demonstrated point-by-point in context of precision formulation, curing mechanism, rational catalyst selection, and structure/property relationships of the resultant PECANs. Furthermore, PECAN materials are fully characterized by tensile, thermomechanical, and rheological means alongside commercial thermoset resins, revealing competitive or superior creep performance, crosslink density, and modulus. We ultimately define and identify an ideal candidate, which is advanced to composite manufacturing stage by infusion with fiber-glass panels. Several thermomechanical performance comparisons are established directly between the thermoset resins and corresponding composites, in addition to inter-composite panel comparisons, revealing the impact of composite reinforcement on long-term creep deformation probed by rheological time-temperature superposition, as well as other key properties.
Influence of molecular architecture on the viscoelastic properties of polymers with phase separated dynamic bonds

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Polymers with dynamic bonds attracted significant attention in recent years due to their recyclability, self-healing ability, extreme toughness and an added ease of processability. An understanding of parameters and mechanisms controlling the viscoelastic behavior of these systems is critical for the design of materials with desired properties. Polymers with phase separating dynamic bonds (stickers) present particular interest due to the added option to decouple mechanical and viscoelastic properties through control of relaxations in the clusters of stickers. In this work we analyze the dynamics and viscoelastic properties of polymers with phase separating stickers placed either as pendant groups or at the chain ends (telechelic systems). Our results revealed that segmental dynamics and rubbery plateau depend only on concentration of stickers regardless of their placement on the chain. This similarity between pendant and telechelic structures continues up to the point of a sticker pullout from a cluster. The difference between these two architectures appears only at longer times, when pulling a sticker from a cluster results in terminal relaxation for telechelic systems, while it results in the onset of sticky Rouse regime in pendant systems. Based on these results we propose a qualitative scenario describing viscoelastic properties of polymers with phase separating dynamic bonds that should aid in rational design of recyclable polymeric systems.
Plastic waste accumulation in landfills causes severe environmental hazards such as soil, water, and air pollution. Plastic upcycling is proposed as an effective approach to transform waste into valuable products. However, developing upcycled polymers with advanced properties, cost-effective upcycling schemes, and achieving closed-loop circularity are challenging. A tough vitrimer resin was developed by modifying a commodity thermoplastic elastomer (SEBS) with boronic ester (S-Bpin) and amine-based multiple diol crosslinker to address these challenges. The resin was incorporated into glass fiber reinforced polymers (GFRPs), which are commonly used in high-strength applications such as aerospace, automobile, defense, sports gears, and construction. GFRPs provide advantages such as lightweight, customizable, low-cost, easy installation, and environmental resistance. However, conventional GFRP materials with thermoset matrices, like conventional epoxy, cannot be reprocessed and reused due to the presence of permanent cross-linkages, leaving massive waste behind. Consequently, most of GFRPs end up in landfills or waste incineration. Another challenge of GFRPs is the weak fiber/matrix interfacial bonding in causing the debonding or delamination. To address these issues, we have developed a tough, recyclable vitrimer-reinforced composites with closed-loop circularity. The controlled Boronic ester functionalization created a polymeric network with tunable mechanical properties. Dynamic boronic ester exchange between the resin and fiber interface resulted in robust mechanical properties, strong fiber-matrix interfacial adhesion, and efficient closed-loop recycling of both fiber and resin. The interfacial shear strength of the GFRP increased by 43% compared to that of the control composite without dynamically exchangeable bonds. Boronic ester bonds with amine-based diol crosslinker resin rearrange the network integrity under a specific temperature, enabling fast thermoformability and repairability of micro-cracks of the composite matrix. Furthermore, this upcycled crosslinked polymer exhibits remarkable adhesion with numerous surfaces like glass, aluminum, and steel, making it suitable for use in multiple industrial applications. This study paves the way for the ongoing pursuit of recyclable, multitask structural materials.
Continuous one-pot melt extrusion approach for high-density polyethylene-based vitrimers

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In this presentation, I will discuss a continuous melt extrusion approach in one go for the synthesis of high-density polyethylene (HDPE)-based vitrimers. Vitrimers are produced with two grafting two agents, with maleic anhydride serving as a reactive agent to facilitate crosslinking while dimethyl maleate helped to lower the surface energy for better maleation. This improved property is reflected in the 2 wt% system, where the crosslinking density had doubled and enhanced the stiffness of the material. Overall, these vitrimers had enhanced tensile stress at break and impact resistance as compared to that of HDPE, while yet having a similar melting temperature and tensile stress at yield. The crystallinity of the polymers decreased and thus these materials may be strong candidates for 3D printing applications as they are less susceptible to the warping issues that are encountered with unmodified HDPE. These vitrimers are reprocessable with torque pf ~ 30 Nm, and thus they can be readily recycled despite the crosslinking of layers which imparts them with better mechanical and thermal properties.
Polyester networks from structurally similar monomers: Recyclable-by-design and upcyclable to photopolymers

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Epoxy-based polymer networks from step-growth polymerizations are ubiquitous in coatings, adhesives, and as matrices in composite materials. Dynamic covalent bonds in the network allow its degradation into small molecules and thus, enable chemical recycling; however, such degradation often requires elevated temperatures and costly chemicals, resulting in various small molecules. Here, we design crosslinked polyesters from structurally similar epoxy and anhydride monomers derived from phthalic acid. We achieve selective degradation of the polyesters through transesterification reactions at ambient conditions using an alkali carbonate catalyst, resulting in a singular phthalic ester. We also demonstrate upcycling the network polyesters to photopolymers by one-step depolymerization using functional alcohol.
Supporting the development of sustainable materials and processing methodologies requires accurate measurements and quantitative models of polymer structure-property-performance relationships. This involves understanding the impacts of distributions of molar mass, chemical composition, and topology on polymers and polymeric compatibilizers for mechanical recycling. To explore these contributions, we consider polyolefins where the landscape of recycled and mixed content continues to expand. The precise placement of branches along a linear polyethylene backbone offers important insight into how changes in intramolecular branch distribution dictate polyolefin behavior. Specifically, short-chain branching (SCB) is widely applied in polyethylene as a functional handle for tuning processability and final properties of the material; however, inter- and intramolecular variations in branch distribution make linear low-density poly(ethylene) (LLDPE) difficult to characterize effectively, especially when considering different branch distributions and copolymer structures (e.g., blocky, statistical). This presentation will highlight efforts to make systematically varied families of model polyolefins, including LLDPE-block-HDPE compatibilizers and comparable statistical copolymer analogs. Characterization of these model copolymers materials with high temperature size exclusion chromatography reveals a systematic decrease in intrinsic viscosity ([η]) with increasing branch content and a similar decrease in the radius of gyration (Rg) associated with the compaction of chains with increasing SCB content of the LLDPE block. Additionally, block copolymers have higher values of [η] than their statistical copolymer counterparts, indicating that branch distribution plays a role in the dilute solution properties of short chain branched polyolefins. These trends are compared to molecular dynamics simulations in which the branch distribution can be exactly specified and detailed insights about polymer conformations can be obtained.
Biobased and chemically recyclable polysulfones

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The production of polymers has increased significantly in the last few decades. Their synthesis uses petroleum-based resources and harmful chemicals like bisphenol A (BPA), linked to neurological and reproductive problems. Their end-of-life disposal is another concern as the resulting plastic waste causes environmental damage due to evolution of harmful chemical and toxic gases upon degradation. Due to these concerns, there is a need for making these polymers from biobased, green processes which can be recycled for a closed loop economy. Polysulfone (PSU) is a high-performance thermoplastic, industrially made from BPA. Studies have shown that BPA leaches into the system when using PSU in applications such as water filtration membranes. In the past some work has been done to make PSU’s more sustainable by making them partially biobased using lignin, or isosorbide. However, these studies do not close the loop since the product is not recyclable and is subject to the same problems as traditional PSU waste. In this work, a protocol to synthesize thermoplastic polysulfones that are biobased and chemically recyclable was investigated. A partially biobased alternative to BPA with an imine bond was made from vanillin and 4-aminophenol. This monomer was used with other biobased alternatives such as bisguaiacol (BGF) and a divanillin derivative to make PSU copolymers. Imine bonds are brittle in comparison to the free rotating methyl groups in BPA. The addition of BGF with its methylene bridge lend the copolymer flexibility and properties closer to traditional PSU. The recycling is achieved via dissociation of the imine bond under acidic pH and its subsequent recovery via base neutralization. This recycling capability and good thermal properties makes these biobased polymers a potential replacement to the traditional PSU for a circular economy.
Modification and activation of PVC to enable efficient depolymerization to small molecule targets

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While PVC is one of the most widely produced plastics worldwide, it also is one of the most challenging to recycle. PVC is unique among common thermoplastics (i.e., RIC 1-6) as it is far more susceptible to reactions, which can release HCl and/or result in crosslinking. However, we see advantages in this reactivity as a means for modifying and activating PVC for depolymerization reactions which can yield a range of small molecules. This talk will detail our approaches to working with PVC and strategies for depolymerization toward target small molecules which can be upcycled to new polymers as well as opportunities for obtaining rare and new molecules that are otherwise only available as natural products and/or via complex syntheses.
Environment controls kinetics of nano-confined enzyme plastic degradation and upcycling

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be exposed to in its lifecycle – from use to end-of-life in compost, landfill or as environmental pollutants. We explored the degradation of poly(caprolactone) by nano-confined lipase in variable moisture compost conditions. Results showed that environmental water controls the extent of reaction. Beyond a threshold of ~60% wet soil, complete degradation occurred, following a similar kinetic profile to that of ideal, aqueous environment degradation. In water deficient environments, diffusion-limited degradation products accumulate locally at enzyme active sites, shutting down catalysis. Moisture content can program specific degradation extents for top-down upcycling of plastic waste into mechanically sturdy, hierarchically porous films, with homogeneous, acidic surface chemistry. Several competing reactions could occur in real environments between reactive plastic surfaces and surrounding molecules. Controlled kinetics can drive the synthesis of porous polymer scaffolds functionalized with catalytically active metal nanoparticles for use in heterogeneous catalysis. We showed the diffusion of internally trapped products can be accelerated by external water, to re-activate enzymes and resume depolymerization with ideal environment kinetics. This process is not inhibited by metal nanoparticle functionalization, raising concerns over the natural in situ formation of metal nanoparticles on the surfaces of partially degraded biodegradable plastic waste that coexists in environments rich in heavy metal salts, and the subsequent release of the nanoparticles into natural ecosystems upon complete plastic degradation.
Elucidation of underlying chemistry for polyethylene terephthalate (PET) depolymerization between alcoholysis and hydrolysis

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Chemical recycling of polyethylene terephthalate (PET) into monomers is considered a crucial strategy for achieving plastic circularity. Over the last few decades, various chemical recycling methods have been developed, including hydrolysis, methanolysis, glycolysis, and other pathways. Recently, PET hydrolysis/alcoholysis using alcohol/base mixed solvents has garnered attention as a scalable process due to its low energy consumption, fast depolymerization rate, and simplicity. However, despite the progress made in PET depolymerization, the underlying chemistry of this process has not yet been fully investigated. To better understand and further develop the chemistry of PET depolymerization, it is crucial to scrutinize its fundamental aspects.

In this report, we propose that four critical factors can affect PET depolymerization when using base/alcohol solvents. First, regarding the differing reactivity of hydroxide and alkoxide, we have observed that methoxide is more reactive than hydroxide in PET decomposition, despite both having similar pKa values of their conjugate acids which are methanol and water, respectively. Second, the pKa values of the alcohols have been found to have a significant impact on PET depolymerization in base-catalyzed alcoholysis. Third, the affinity between PET and the solvent is also relevant to the rate of PET depolymerization reaction, as it affects the wetting of PET by the solvents. Finally, the steric effect of alkoxide can also influence the rate of PET depolymerization. In this presentation, we will discuss the detailed chemistry based on experimental results and molecular dynamics simulation. Through experimental results and molecular dynamics simulations, we have gained valuable insights into the underlying mechanisms of this process, which can aid in the design of more efficient and sustainable PET recycling methods.
POLY 3928859

Recycling polystyrene into self-healing 3D printable resins

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Polystyrene is one of the greatest contributors to the Plastics Pollution Crisis, both due to its poor degradability as well as the large volume it occupies as a foam. Green solvents, such as terpenes, may be used to dissolve polystyrene without degrading it, providing an upcycling method towards making a photoreactive nanocomposite material. The polystyrene composite is shown to offer a means of tailoring physical properties of the resultant thermoset, providing a higher value 3D printable resin ink. Ultimately, the use of this polystyrene filler provides an avenue towards self-healing considerations, where the thermoset may be repeatedly damaged and healed relying on the same design principles.
So called “fast fashion” and the low cost of clothing have significant environmental impacts within the textile industry such as increasing the amounts of waste, water consumption, and CO₂ emissions, among others. To help facilitate a circular economy (CE) for textiles one must consider end-of-life considerations through holistic material design and innovations. For example, covalent adaptable network (CAN) materials can play an impactful role in reducing the burden posed by synthetic fibers on the environment. CAN materials are both reusable and recyclable through innovative reversible linking mechanisms. Synthetic fibers are typically recycled through mechanical shredding or chemically recycled into monomer feedstocks, instead of CANs in their design. The resulting textiles would then have great potential as sustainable and zero-waste alternatives for polymer-based materials. Through this research, a hybrid method of recycling polyester materials is proposed in which covalent reversible linkages, such as Diels-Alder (DA) adducts are inserted into the polyester to reversibly unlink the bulk material at targeted lengths. Thus, allowing recycling into longer building block units instead of monomer constituents. DA is a well-known dissociative CAN, where the structures can be “delinked” at certain temperatures and linked at other temperatures. In this poster, preliminary results of this new hybrid recycling approach and comparison with commodity polyester materials will be shared.
Composites of polyethylene-like polyesters with polar microphases for enhanced degradation in nutrient-poor environments

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Plastics are a cornerstone of today's modern materials. Their ubiquitous use also results in environmental pollution. Even with the implementation of more responsible waste management in the future, this problem needs to be addressed. Compared to conventional plastics like polyolefins, biodegradable polyesters can be less persistent and less amenable to undesired accumulation if lost to the environment. However, degradation rates vary hugely depending on the specific environment and moreover a specific trigger would be desirable. We report on composites with semicrystalline, aliphatic polyesters with favorable polyethylene-like materials properties as a continuous phase, with polar microphases. Release of specific otherwise deficient nutrients from the latter is envisioned to promote the breakdown by microorganisms even in challenging environments like sea or freshwater.
Mechanical recycling of waste polyolefins using a rheology modifier

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The global production of plastics has greatly increased due to its numerous applications. This has resulted in the increased disposal of post-consumer plastic waste into the environment resulting in a major environmental concern. The amount of plastic used in the USA since the 1980s has surpassed more than 80 million metric tonnes annually. The amount of plastic disposed of is expected to be 142 million metric tonnes by 2060. The amount of post-consumer plastics being dumped into the environment need to be dealt with and one of the ways of reducing this plastic waste is by recycling. One of the major challenges in recycling post-consumer polyolefins is compositional fluctuations. These fluctuations usually result in inconsistent melt flow properties of the plastics. The melt flow index is an essential plastic property required to determine the processing parameters of the plastics. In this work, we intend to make use of an accurate, cost-effective, less time-consuming model to incorporate a specific amount of rheological modifier in the mixed polyolefins in an endeavor to establish a specific and consistent melt flow index and finally improve their mechanical properties.
General Topics: New Synthesis and Characterization of Polymers

Tough polymer gels by in-situ phase separation for 4D printing - Wang, Zhenwu (Oral Only)

Living polymerization of tube-like polyaramid foldamers - Kilbinger, Andreas (Oral Only)

Post polymerization modification of polyacrylamides through amide activation - Wekasinghe, Kasun (Oral Preferred)

3D printed porous polymer sorbents for cobalt recycling - Mason, Keldy (Oral Preferred)

Low intensity triplet upconversion 3D printing in ambient conditions - ODea, Connor (Oral Only)

GaBr$_3$-catalyzed reduction of esters towards uniform poly(ethylene glycol) - Bohn, Philipp (Oral Preferred)

Unlocking the full potential of 3D printing: Building complex multimaterials using cutting-edge photocuring techniques - Boyer, Cyrille (Oral Only)

Compounded sequence control: A breakthrough technique for the synthesis of complex copolymers by Lewis pairs - McGraw, Michael (Oral Only)

Overcoming monomer limitations in RAFT polymerization using photoredox catalysis - Figg, Adrian (Oral Only)

Industrial development of novel hyperbranched polymers via a proprietary technology - Diable, Matthew (Oral Preferred)

Synthesis and application of versatile aryl-functionalized polyolefins - Fischbach, Danyon (Oral Preferred)

Transfer-dominated branching radical telomerisation (TBRT): Studying the impact of multi-vinyl taxogen dimensions on the branching behaviour of high molecular weight polymers - Penrhyn-Lowe, Oliver (Oral Only)

Synthesis of $^{19}$F MRI nanotracers by dispersion polymerization-induced self-assembly of N-(2,2,2-trifluoroethyl)acrylamide - Manayath Panakkal, Vyshakh (Oral Preferred)

Introducing transfer-dominated branching radical telomerisation (TBRT) as a novel free radical polymerisation of multi-vinyl monomers yielding high molecular weight branched step-growth polymers - Rannard, Steve (Oral Only)

High molecular weight water-soluble polymers synthesised as low-viscosity latex particles by RAFT aqueous dispersion polymerization in highly salty media - McBride, Rory (Oral Preferred)

RAFT end group modification for self-immolative immunodrug delivery - Nuhn, Lutz (Oral Only)

Post-polymerisation modification of Poly(hydroxybutyrate) (PHB) using thiol-ene and phosphine addition - Al-Shok, Lucas (Oral Preferred)
General Topics: New Synthesis and Characterization of Polymers

New monomers for ring opening metathesis polymerization (ROMP) reactions from pyrrole Diels-Alder reactions - Hobbs, Christopher (Oral Only)

Engineering solvation in all-dry polymerization - Yang, Rong (Oral Only)

Synthesis of bio-based cyclic polycarbonate based on dynamic covalent chemistry and its applications - Yokochi, Hirogi (Oral Preferred)

Thiol end-functional ring-opening metathesis polymers - Kilbinger, Andreas (Oral Only)

Hydrophobic interaction energies of hydrophobically modified cellulose ethers derived from reversed phase liquid chromatography - Li, Yongfu (Oral Only)

Redox-switchable polymerization by chain transfer - Johnson, Stephanie (Oral Only)

Supersoft thermoplastic elastomers prepared by ring-opening metathesis polymerization with wide service temperatures - Cater, Henry (Oral Preferred)

Metathesis polymerizations for functionalized degradable polymers - Kim, Cheoljae (Oral Preferred)

Tale of two isomers: Microstructural variation in frontal ROMP - Suslick, Benjamin (Oral Only)

Performance advantaged PET co-polymers from lignin-derivable monomers - Rosetto, Gloria (Oral Preferred)

Synthesis and assembly behavior of a Poly(ionic liquid) and a stimuli-responsive weak polyelectrolyte block copolymer - Foley, Kayla (Oral Preferred)

Electron donor acceptor double cable covalent conjugates: Towards improved photovoltaic devices and accelerated artificial photosynthesis - Iftikhar, Suniya (Oral Only)

Synthesis of nanowire heterojunctions via self-assembly of multi-block conjugated polymers - Fokwa, Hilary (Oral Only)

Ultrahigh conductive covalent organic framework films - Kim, Yoonseob (Oral Only)

Rate accelerated chain extension in Cross-Dehydrogenative Coupling polymerization - Chakraborty, Baitan (Oral Preferred)

Oxidative molecular layer deposition of charged polymers for electrochemical applications - Young, Matthias (Oral Only)

Amphiphilic main-chain poly(fullerene xylene)s - Hiorns, Roger (Oral Preferred)

Optimized synthesis of poly(9,9-dioctyfluorene) via modified Grignard metathesis method - Ge, Jing (Oral Preferred)

Chalcogenophene heteroatom control of conjugated polymer microstructure and mixed-conducting properties - Paulsen, Bryan (Oral Preferred)
General Topics: New Synthesis and Characterization of Polymers

Investigations into alkylation of sulfoximines to produce sulfoxonium functionalized polymers for anion exchange membranes - Vinskus, Jessica (Oral Preferred)

(Oxa-)norbornene derived block copolymers for the preparation of functional nanogels with stimuli-responsive Immunodrug delivery properties - Kockelmann, Johannes (Oral Preferred)

Selective demicellization of poly(benzyl ether)-based surfactants via head-to-tail depolymerization - Kim, ji woo (Oral Only)

Functional group metamorphosis in the condensed state: A self-reinforcing mechanism to increase mechanical performance of thermoplastic polyurethane materials on demand - Ehrmann, Katharina (Oral Preferred)

Sustainable aloe vera-polyvinylpyrrolidone-green tea-iodine formulation against surgical site- and wound infections during crisis - Edis, Zehra (Oral Preferred)

Poly(2-ethylthio-2-oxazine): A versatile polymer platform for post polymerization modification reactions - Mertens, Ine (Oral Preferred)

Antimicrobial N-carboxyanhydride-derived polypeptide grafted solid surfaces - Zhang, Yurong (Oral Preferred)

pH-Responsive swelling of poly(methacrylic acid) multilayer hydrogels through controlling polyacid chain conformations - Nikishau, Pavel (Oral Preferred)

Synthesis of disubstituted γ-amide ε-caprolactone monomers for the amphiphilic diblock copolymers in drug delivery applications - Polara, Himanshu (Oral Preferred)

Poly (glycerol ester)-based polyplex nanoparticles for safe and effective gene delivery - Radzinski, Scott (Oral Preferred)

Towards enediyne substituted polycaprolactones in an attempt to generate Calicheamicin-like anticancer activity - Bhadran, Abhi (Oral Only)

Quadruple Hydrogen Bonded Silicone-based Polymer Blends - Czuczola, Michael (Oral Preferred)

Bottom-up design of functional polymer monoliths for effective adsorption of endocrine disruptors - Jeong, Songah (Oral Only)

Responsive nanotubes from asymmetric cyclic peptide-polymer conjugates - Cheng, Zihe (Oral Preferred)

Templating trapped entanglements in polymer networks using coordination complexes - Krist, Erin (Oral Only)

Trainable dynamic aza-Michael-based liquid crystal elastomers - Ghimire, Elina (Oral Preferred)
General Topics: New Synthesis and Characterization of Polymers

Using a hybrid monomer to bridge the gap between silicones and traditional organic polymers - Getty, Patrick (Oral Preferred)

Branching anionic polymerization of cyanoacrylate without suppressing its high reactivity: A practical approach - Roxas, Alexander (Oral Preferred)

Nanostructural evolution during sulfonation-induced crosslinking of thermoplastic elastomers for ordered mesoporous carbon synthesis - Robertson, Mark (Oral Preferred)

Novel poly(vinylpyridine N-oxide)-based block copolymers with highly immiscible segments - Angelopoulou, Polyxeni P. (Oral Only)

Direct synthesis of ultra-highly branched polyethylene materials via controlled chain walking polymerization - Dai, Shengyu (Oral Only)

Fused macrocycle-cage molecule for nanoporous membranes - Wang, Yuzhe (Oral Preferred)

Direct arylation polycondensation of β-fluorinated bithiophenes to polythiophenes: Effect of side chains in C–Br monomers - Zhang, Xuwen (Oral Preferred)

Elasticity modulation of hydrogen bond-tethered near-amorphous conjugated polymers - Zhao, Bin (Oral Preferred)

RAFT synthesis of polymers for regulating fluid loss in water and oil-based drilling fluids - Jian, Guoqing (Oral Only)

Impact of mathematical models on the accuracy of analysis of high molecular weight polymers by multi-angle light scattering - Alb, Alina (Oral Only)

New insights into coacervation: self-assembly of zwitterionic polysulfobetaine for multifunctional applications - Arjunan Vasantha, Vivek (Oral Only)

Polyethylene (PE) based food packaging film: Recyclable, unitary material composition, manufacturing processes, methods, and characteristics - Yoon, Younghoon (Poster Only)

Aqueous solution properties of linear and star poly(2-hydroxyethyl acrylate)-based polymers: from RAFT-PISA or solution RAFT polymerization - Hermosillo-Ochoa, Eduardo (Poster Preferred)

Substituted Poly(para)phenylenes: Where is the Journey going? - Kleybolte, Moritz (Poster Preferred)

Tandem ring-opening and ring-closing metathesis polymerization of cyclopentenes containing terminal alkyne - Podiyanachari, Santhosh Kumar (Poster Only)

Fluorescent polymeric viscoelastics for ocular research - Yuan, Lucia (Poster Only)

ROMP of a nitroso-Diels-Alder adduct leads to amino-and hydroxyl-functionalized "polyolefins" - Hobbs, Christopher (Poster Only)
General Topics: New Synthesis and Characterization of Polymers

Effect of oligo(ethylene oxide) functionalization on the phase behavior of two bicontinuous cubic lyotropic liquid crystal monomer platforms - Culley, Keira (Poster Only)

Synthesis of a catenane via the exchange reactions of bis(hindered amino) disulfide linkages and its polymerization - Takashima, Rikito (Poster Preferred)

Understanding the impact of vinyl and allyl species in the decrease of telogen content in transfer-dominated branching radical telomerisation - Smith, Corinna (Poster Only)

Understanding the influence of different chemical strategies on transfer-dominated branching radical telomerisation (TBRT) and the production of novel hyperbranched polymers - Linthwaite, Beth (Poster Preferred)

Polycaprolactone dimethacrylate functionalisation via transfer-dominated branching radical telomerisation - Lomas, Sarah (Poster Only)

Polymers based on Vitamin E - Jackson Hoffman, Brooke (Poster Preferred)

Improving food and vaccine safety: A temperature-sensitive indicator for cold supply chains - Kim, Semin (Poster Only)

Evaluation of biobased solvents for the synthesis of poly(2-oxazoline)s and poly(2-oxazine)s by cationic ring-opening polymerization - Lusiani, Niccolograve; (Poster Only)

Homo- and co-cyclopolymer containing symmetrical motifs of (diallylammonio) diacetate - Yaagoob Mohamed, Ibrahim (Poster Only)

GCMS-HS and Py for polymer compatibility studies - Chov, Ashleigh (Poster Only)

Preparation of novel nanosized polyelectrolyte brushes based on macromolecular photoinitiator - Guo, Xuhong (Poster Preferred)

Visible-light-mediated controlled radical branching polymerization in water - Kapil, Kriti (Poster Preferred)

Effects of variable crosslink density on material properties of guanidine-based covalent adaptable networks - Koenig, Adelle (Poster Preferred)

InsectERA: Converting cultured insect exuviae into valuable biopolymers - Martins, Luisa (Poster Only)

Synthesis and characterization of thioether-functionalized poly(2-alkyl-2-oxazoline)s for ROS-responsive nanomaterials - Bener, Semira (Poster Only)

Photo Pisa-mediated synthesis of enzyme-loaded polymeric vesicles with tunable membrane permeability for intracellular cascade reactions - Bener, Semira (Poster Only)

Bifunctional initiator for ring-opening metathesis polymerization - Saada, Benjamin (Poster Only)
General Topics: New Synthesis and Characterization of Polymers

Synthesis of biobased vitrimers from renewable D-isosorbide - Kopilec, Ondrej (Poster Only)

Synthesis, characterization, property, and processing of polyvinyl alcohol bottlebrushes - Xi, Yumeng (Poster Preferred)

Self-assembling multidomain peptide hydrogels with histidine functionalized cores - Saenz, Gabriel (Poster Preferred)

High sulfur incorporation into sulfur-based hydrogels via inverse vulcanization - Dunn, Jaclyn | Norby, Callan (Poster Preferred)

Evaluating poly(Anhydride-ester)s' hydrolytic degradation & encapsulation characteristics for retinol release - Safi, Lema (Poster Only)

Innovative glass fiber nonwoven reinforced polymer composites: Effects of addition of cellulose nanofibers on physical and mechanical properties - Yim, Yoon-Ji (Poster Only)

Catenane formation of a cyclic poly(alkyl sorbate) via Lewis pair polymerization induced by an N-heterocyclic carbene and ring-closing without extreme dilution - Yato, Hirotake (Poster Only)

Polymerization of cyclic ketene acetics in aqueous media: The competition between radical ring opening and hydrolysis - Ascherl, Laura (Poster Only)

Design of novel water-soluble purely organic photocatalyst for aqueous PET-RAFT polymerization - Lee, Yungyeong (Poster Only)

Active esters and post-polymerization modification in metal-free ring-opening metathesis polymerization - Li, Ruojia (Poster Preferred)

Synthesis and characterization of semi-fluorinated polymers for 19F MRI - Tunca Arin, Tuba Ayca (Poster Only)

Synthesis and characterization of silicone based segmented polyurethane/ureas - Brown, Hope (Poster Only)

N-functionalized polyureas by cationic ring-opening polymerization of iminooxazolidines - Bodinger, Catie (Poster Preferred)

Synthesis and self-assembly of folate-conjugated block copolymers of poly(ethylene glycol) and poly(L-Leucine) and their targeting efficiency - Akinmola, Adekunle (Poster Only)

Transamidation of poly(2-ethyl-2-oxazoline) to a random copolymer - Dahlstrom, Ashleigh (Poster Only)

Polymerizable channel-like stacks derived from cyclic tetrameric diacetylenes - Kulikov, Oleg (Poster Only)
General Topics: New Synthesis and Characterization of Polymers

Temperature responsive diblock polymer spherical brushes as nanoreactors to prepare and load silver nano-catalysts - Guo, Xuhong (Poster Only)

Expanding the applications of metal-free ring-opening metathesis polymerization through functional initiators and chain-transfer agents - Tetzloff, Meg (Poster Preferred)

Epoxy resin formulation and study using ammonium carbamates as latent curing and blowing agent - Bishwokarma, Manish (Poster Only)

Toughening elastomers by entangling the crosslinkers - Wang, Fu-Sheng (Poster Preferred)

Biobased aliphatic polyesters from renewable resources: Synthesis, properties and performance - Sahu, Pranabesh (Poster Only)

Investigating hydrophobic and hydrophilic poly glycerol esters for non-viral delivery - Costello, Caroline (Poster Preferred)

Polyester-based non-viral vectors for gene therapy: Characterization and optimization of poly (glycerol ester) polymers - Roadarmel, Benjamin (Poster Preferred)

Group 14 radical cointiators of photopolymerizations with alkyl and perfluoroalkylhalides - Dutta, Abhirup (Poster Only)

Grafting well-defined polymers onto poly(vinylidene fluoride) via thiol-ene click reactions - Lin, Ting-Chih (Poster Preferred)
Tough polymer gels by in-situ phase separation for 4D printing

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Polymer gels, consisting of cross-linked polymer network systems swollen by a solvent, show great potential in biomedicine, flexible electronics, and artificial muscles, due to their tissue-like mechanical properties. Due to the presence of a large amount of solvent, the improvement of the mechanical properties of the polymer gel has been a challenge. Moreover, combining high toughness with facile functions (like 3D printability or shape memory) in one polymer gel system is even more challenging. In this study, we developed a simple and efficient method for the fabrication of tough polymer gels by polymerizing 2-hydroxyethyl methacrylate (HEMA) in a mixture of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in one step. The polymerized elastic networks present distinct compatibility with PEG (compatible) and PPG (poorly compatible), resulting in in-situ phase separation at the microscale. The resulting phase-separated gel demonstrates high strength (8.0 MPa), favorable fracture strain (430%), and large toughness (17.0 MJ m⁻³). The separated hard phases with a high glass transition temperature (75°C) endow the whole soft polymer gel with shape memory property at room temperature. Finally, we combined the fabrication of tunable tough PEG gels with 3D printing as well as with shape memory properties, demonstrating the use of PEG gels for 4D printing.
Over the past decade, there has been significant progress in synthesizing helical aromatic amide foldamers, which can form stable tube-like structures that mimic natural water or ion channels found in nature. All synthetic efforts thus far have utilized classical step-wise organic methods such as solid supported synthesis or iterative solution coupling strategies. However, the production of long helical molecular tubes that can bridge the distance across the hydrophobic interior of a lipid bilayer, similar to channel proteins, has not yet been achieved through organic synthesis. The use of a polymer synthesis approach may aid in achieving the necessary degrees of polymerization that traditional organic synthesis has not yet been able to accomplish.

Recently, we reported a series of new highly reactive coupling reagents that allow for the living polymerization of AB-type aromatic amino acids.[1] This new polymerization method has enabled the synthesis of block copolymers and helical polymeric aromatic amide foldamers with degrees of polymerization higher than those previously reported by organic chemists. The new polymerization method is applicable to various AB-type aromatic amino acid monomers and provides control over molecular weight at low dispersities with full end-group control.

In this presentation, the latest results concerning new syntheses of polymeric helical “tube-like” structures will be reported. Monomer choices, polymer purification strategies, molecular weight limits of the new polymers and characterization methods for tube-like polymeric foldamers will be discussed.
Post polymerization modification of polyacrylamides through amide activation

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Post polymerization modification is a common approach towards incorporating novel functionality into synthetic macromolecules. This method typically requires specialized monomers designed to undergo further derivatization in subsequent steps. An alternative approach is the chemospecific activation of the native functionality of the polymers of interest (e.g., polyacrylamides, polyesters, etc) either through enhancing the leaving group ability or transformation to a reactive intermediate that can traverse multiple reaction pathways.

Inspired by the thriving advancements in the field of amide activation, we explore the utilization of keteniminium ion intermediates in the post polymerization modification of polyacrylamides as a new approach towards obtaining novel functionality. Individual amide repeat units in well-defined polyacrylamides were activated toward further reactivity through transformation to keteniminium ions using established approaches. The activated polymers are then derivatized through nucleophilic additions, cycloadditions, or electrophilic rearrangements to obtain copolymers comprised of mixed acrylamide and vinyl ketones, allyl amine, and/or spirocyclic microstructures.
Porous polymers possess exceptional properties, including high surface area, tunable pore size, and adsorption capabilities, making them ideal for various applications. This study advances the field by merging receptor and polymer chemistry to develop tailored porous polymers for cobalt recycling. Previous research has shown that immobilized receptors can catch and release metals via a solvent polarity switch mechanism. However, attaining high surface areas, controlling polymer geometry, and receptor loading has been challenging. In response, we utilized high-resolution digital light processing (DLP) to fabricate intricate and complex geometries with precise control over the 3D structure of the materials. We employed the polymerization-induced phase separation (PIPS) of a diacrylate and porogens to generate nanopores within a bicontinuous network. Copolymerization of the diacrylate with an acrylate-functionalized ion receptor was used to synthesize a polymer network poised for recycling critical materials, such as cobalt. This was leveraged to chelate and release cobalt via a solvent polarity switch mechanism with UV-vis absorbance monitoring in a flow system. The cobalt capture and release were achieved in isopropanol and water, respectively, making this a ‘green’ and safe recycling method. This study represents a significant technological step towards sustainable cobalt recycling, offering a promising solution to address the pressing challenge of limited cobalt resources for batteries, catalysis, alloys and more.
Low intensity triplet upconversion 3D printing in ambient conditions

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An upconversion based photocatalyst system is developed that enables low light intensity (<10 mW/cm²) digital light processing (DLP) 3D printing under ambient conditions. Traditional resins are based on type 1 photoinitiators that absorb ultraviolet (UV) light to directly generate radicals for fast initiation but require short-wavelength light that is prone to scattering and is biologically incompatible. Triplet-fusion upconversion is a process where two low energy photons are converted to a single higher energy photon that can locally initiate a UV-absorbing dye. This process is inherently sensitive to oxygen due to the mechanism going through a long-lived triplet state and typically requires high intensity light (>1000 mW/cm²) to reach the theoretical upconversion quantum yield. Catalyst concentrations can be tuned to overcome oxygen inhibition and achieve polymerization rates relevant for commercial 3D printing. The quadratic relationship of upconversion yield on power density can be leveraged to minimize overcure while operating within the appropriate intensity range where scattered light is too low energy to initiate polymerization. An upconversion based photopolymerization system allows for the same benefits of speed and reliability of type 1 photosystems without the need for additional opaquing agents or oxygen scavengers.
Poly(ethylene glycol) (PEG) is a water-soluble, biocompatible, and flexible polymer, which is used in wide-ranging fields, such as cosmetics, lubricants or plasticizers, and drug delivery. However, commercial PEGs lack uniformity, thus hampering the investigation of their structure-property relationships, for instance in biological applications. Especially for biopharmaceutical applications, a uniform structure is crucial to ensure consistent and predictable pharmacokinetics. Furthermore, uniform PEGs possibly induce less immune response, causing a decreased formation of anti-PEG antibodies.

Uniform PEGs are commonly prepared via iterative Williamson ether synthesis, requiring harsh conditions, leading to the formation of side products and thus a challenging purification. Here, we report an alternative approach for the synthesis of uniform PEGs based on the selective GaBr₃-catalyzed reduction of esters. The ester precursors, bearing a benzyl protecting group, are obtained via Candida antarctica Lipase B (CALB)-catalyzed transesterification. After reduction of the ester to the corresponding ether, the benzyl ether is cleaved to recover the alcohol and complete the reaction cycle. The procedure was optimized regarding mild reaction conditions, the suppression of side products, and thus simple purification steps. IR and NMR spectroscopy were shown to be powerful analytic tools for monitoring of the carbonyl reduction. Each reaction step can be performed on multigram scale and consistently delivers high yields. Careful characterization via NMR, HR-MS and SEC was performed to confirm the high purity of the products.
Unlocking the full potential of 3D printing: Building complex multimaterials using cutting-edge photocuring techniques

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Reversible addition-fragmentation chain-transfer (RAFT) polymerization is a highly advanced technique for synthesizing macromolecules with controlled topologies and diverse chemical functionalities. Despite its impressive capabilities, the slow polymerization rates of RAFT have hindered its widespread application in additive-manufacturing processes. However, in our talk, we will present a revolutionary approach to rapid visible light-mediated RAFT polymerization that has enabled us to overcome this limitation.

Our photosensitive resins incorporate a photocatalyst and a trithiocarbonate RAFT agent, allowing for polymerization without prior deoxygenation. Through optimization of the resin formulation via variation of the photocatalyst ratio, we were able to investigate a variety of 3D printing conditions for the production of functional materials. Our findings demonstrate that the incorporation of RAFT results in significant improvements in the mechanical properties of 3D printed materials, enhancing their strength and resilience.

Moreover, we discovered that the trithiocarbonate species incorporated into the polymer networks could be reactivated after the initial 3D printing process. This allowed us to post-functionalize the printed materials via secondary photopolymerization processes, opening up new possibilities for creating highly customizable and functional materials with exceptional mechanical properties.

To further enhance the precision of the materials, we employed polymers terminated by RAFT agent for the preparation of 3D printed multimaterials with precise control of the nanostructure. Our research demonstrates the immense potential of rapid visible light-mediated RAFT polymerization for additive manufacturing processes. This approach enables the production of complex, high-performance materials with precise control of their nanostructure, thereby opening up new possibilities for applications in fields such as biomedical engineering, electronics, and aerospace.

Figure: Overview of the potential applications of living 3D printing
Compounded sequence control: A breakthrough technique for the synthesis of complex copolymers by Lewis pairs

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Compounded Sequence Control (CSC) is a recent breakthrough in the field of Lewis Pair Polymerization (LPP). Utilizing the unique two-step propagation mechanism of LPP, both thermodynamics and kinetics are leveraged to compound two distinctly selective steps (monomer activation and conjugate addition) in order to furnish highly resolved block copolymers from one-pot comonomer mixtures. Since its conception (2020), CSC has achieved several impressive feats such as the one-pot/one-step synthesis of AB diblock, ABA triblock, and ABC triblock compolymers as well as analogous syntheses of cyclic AB-diblock and cyclic ABAB-tetrapblock copolymers. This presentation will detail the history and development of the technique as well as the mechanistic details, monomer scope and several of the most prominent examples.
Overcoming monomer limitations in RAFT polymerization using photoredox catalysis

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In typical reversible addition-fragmentation chain transfer (RAFT) polymerizations, more-activated monomers (e.g., methyl methacrylate (MMA)) must be polymerized before less activated monomers (e.g., methylacrylate (MA)). This requirement is due to the inherent degenerative chain transfer mechanism, limiting access to complex block copolymers. Recent efforts towards overcoming this limitation use photoirradiation to homolytically cleave the carbon-sulfur bond using the inherent absorption properties of thiocarbonylthio RAFT agents. However, the thiocarbonylthio species is typically lost in this process, preventing access to multiblock copolymers. This contribution details the use of photoredox catalysis to overcome the monomer limitations in RAFT polymerization. Multiblock copolymers of monomers containing different inherent reactivities are synthesized (e.g., PMA-PMMA-PMA-PMMA) where the conditions identified lead to high retention of the thiocarbonylthio RAFT agent after each block. Overall, this approach introduces a method to address a long-standing challenge of RAFT polymerization using photoredox catalysis.
Industrial development of novel hyperbranched polymers via a proprietary technology

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A new synthetic strategy, termed transfer-dominated branching radical telomerisation (TBRT), has been devised for preparing previously inaccessible, high performance hyperbranched polymers. The approach utilises industrially relevant free radical chain-growth chemistry, under modified telomerisation conditions, to form hyperbranched polymers containing chemistries conventionally formed under step-growth conditions – e.g., hyperbranched polyesters and polyamides. The polymers’ highly branched globular architectures, combined with high backbone and pendant functionality, lead to unique and highly desirable physicochemical properties, such as low viscosity, high solubility, tuneable intramolecular cavities and optional degradability. A considerable range of commercially available and registered feedstocks leads to a vast scope of industrially feasible polymeric materials and properties that can be prepared using TBRT. This provides the opportunity to impact many industrial applications, without the significant cost, regulatory or scale-up challenges commonly associated with novel polymeric materials. The patented technology, developed at the University of Liverpool, has been exclusively licensed to Scott Bader Co. Ltd, who have established Polymer Mimetics Ltd to focus on its commercial exploitation. Ongoing R&D at the Company has demonstrated applicability of this new generation of materials in a wide range of commercially important areas, from high performance additives in adhesives, composites and curable materials, to biodegradable polymers for medical and personal care applications. The talk/poster aims to demonstrate the versatility of TBRT and how this pioneering technology can support the development of effective, sustainable products and solutions for real-world issues.

TBRT technology transforms highly variable and widely available chemical feedstocks into high performance hyperbranched polymers in an industrially applicable process. Functionality can be easily modified to direct polymer properties to suit the desired application, whilst linking chemistries along the polymer backbone provide potential to engineer in degradability.
Synthesis and application of versatile aryl-functionalized polyolefins

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Polyolefins are produced at a massive scale of 300 million tons per year. While these materials are extremely commercially viable, their lack of chemical functionality leaves them with the major drawback of being nearly inert. By adding versatile functional groups with the ability to undergo a plethora of post-polymerization reactions, polyolefins can access a wider range of applications, as well as become more reactive to current processes such as chemical recycling. Here, a general strategy for the production of end- and main-chain aryl-group functionalized polyolefins is achieved through the stereoselective living coordinative (chain transfer) polymerization of ethene, a-olefins, and a,w-nonconjugated dienes using any combination of 4-aryl-1,6-heptadiene comonomers, diphenyl zinc as a chain transfer agent, and reactive quenching. This strategy yields a wide variety of polyolefin-based materials where traditional variables such as monomer choice, tacticity, and molecular weight are maintained while new variables such as the type, amount, and location of chemical functionality are added. The aryl groups further serve as synthons that can be ‘unmasked’ through simple and high-yielding post-polymerization reactions leading to applications in polyolefin-polyester block copolymers, reversible linking of lower molecular weight polyolefins, and UV-active labeling to name a few.
Transfer-dominated branching radical telomerisation (TBRT): Studying the impact of multi-vinyl taxogen dimensions on the branching behaviour of high molecular weight polymers

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The creation of complex macromolecular architectures via branching polymerisation strategies offers opportunities for innovation through the formation of polymers with novel physical and chemical behaviour. Transfer-dominated branching radical telomerisation (TBRT) employs conventional free radical chemistries to achieve the homopolymerisation of multi-vinyl taxogens (MVTs) to high vinyl conversion (>99%) by including an excess of thiol-based telogen to enforce telomerisation conditions upon the system. This dominant chain transfer mechanism effectively restricts the telomeric number-average degree of polymerisation and affords polymers with taxogen and telogen-derived functionality pervading throughout the macrostructure. It follows that the outcomes of TBRT are highly dependent on the selection of the MVT and telogen.

Here, the impact of MVT dimensions on hyperbranched polymers formed via TBRT is examined. A series of branched polymershave been prepared using three chemically comparable MVTs with varying physical dimensions. Initial polymerisations, conducted under identical reaction conditions, present starkly contrasting gelation behaviours with varying taxogen dimensions. Through a series of model reactions, the intimate branching behaviour of the MVTs is investigated. Kinetic studies and Mayo experiments highlight variations in the chain transfer ability of a common telogen with each MVT, leading to notable differences in the primary chain length of sub-structural telomers within each polymer. However, the telomeric primary chain length is found not to correlate with trends in gelation behaviour, exposing a more dominant factor: the physical dimensions of the MVT. With the aid of a ‘transfer perimeter’ model, supported by TD-SEC and NMR analyses, the dimensions of the MVT is proposed to alter the branching efficiency of the MVT through changes to the molecular volume of polymers formed, and by shifting the balance of intermolecular and intramolecular branching processes during TBRT.

Figure 1 a) The evolution of weight-average molecular weight with varying feedstock [MVT]₀/[DDT]₀ ratio. b) Schematic representation of the ‘transfer perimeter’ model.
Synthesis of $^{19}$F MRI nanotracers by dispersion polymerization-induced self-assembly of $N$-(2,2,2-trifluoroethyl)acrylamide

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Polymerization-induced self-assembly (PISA) is a recently established technique that allows the production of self-assembled polymer nanoarchitectures with governable structure, size, and morphology. Self-assembled fluorinated nanoparticles have recently outperformed conventional fluorine contrast agents as nanotracers in $^{19}$F magnetic resonance imaging (MRI). In this study, we propose a one-pot synthesis of amphiphilic block copolymer nanoparticles containing poly[$N$-(2,2,2-trifluoroethyl)acrylamide] (PTFEAm) core which can be used as a $^{19}$F MRI tracer. These nanoparticles were synthesized by aqueous dispersion RAFT-PISA of TFEAm using a polyethylene glycol-based macromolecular chain transfer agent. The resulting PEG-$b$-PTFEAm nanoparticles were characterized by various techniques, such as $^1$H and $^{19}$F NMR, size-exclusion chromatography, dynamic light scattering, and transmission electron microscopy. Finally, the $^{19}$F MRI performance of selected nanoparticles was studied using a 4.7 T MRI preclinical instrument. To sum up, we developed a sensitive $^{19}$F MRI nanotracers with significant potential for biomedical applications.
Introducing transfer-dominated branching radical telomerisation (TBRT) as a novel free radical polymerisation of multi-vinyl monomers yielding high molecular weight branched step-growth polymers

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Branched polymers are ubiquitous in industrial products and academic research. Commercial examples are generally formed via both step-growth chemistries (eg Hybrane and Boltorn) and chain-growth/ring-opening polymerisation (eg Carbomer and Lupasol). Their applications span paper production to gene transfection and have a considerable global value (eg Lupasol exp. US$436m in 2023; Carbomer exp. >US$1.8bn in 2028). In general, branched polymers from step-growth routes are generally relatively low molecular weight material, and those formed from chain-growth/ring-opening chemistries are typically high molecular weight non-degradable polymers.

We recently described a novel route to high molecular weight branched polymers with extended step-growth backbones that utilises highly scalable chain-growth chemistries. The approach builds on >70 years of synthetic development of free radical telomerisation – the formation of polymers with a number average degree of polymerisation (DPn) <5 monomer units. By controlling the kinetic chain length of telomers formed by radical propagation of multi-vinyl monomers to DPn <2, and using conventional free radical chemistries, TBRT is able to homopolymerise highly functional monomers (known as taxogens) to complete consumption of vinyl functional groups at high solution concentrations (including bulk reactions). The backbone chemistry of the final polymer is derived from the monomer linking chemistry, therefore dimethacrylates generate branched polyesters, and bismethacrylamides create branched polyamides. Additionally, the nominal repeating structure is synthesised during the reaction providing the ability to control properties by telogen selection.

TBRT offers entirely new approaches to branched polymer syntheses including novel copolymer structures and previously unavailable high molecular weight complex products. The background and scope of TBRT will be described in detail.

Figure 1. Dimethacrylate TBRT (100% vinyl group consumption) forming branched polyester structure (DPn
High molecular weight water-soluble polymers synthesised as low-viscosity latex particles by RAFT aqueous dispersion polymerization in highly salty media

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Further to our recent work with zwitterionically stabilized polymer nanoparticles, we report the synthesis of other sterically-stabilized diblock copolymer particles at 20% w/w solids via reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization in highly salty media. This is achieved by selecting a water-soluble polymer to act as the salt-tolerant soluble precursor block. A relatively high degree of polymerization (DP) is targeted for the salt-insoluble block, which leads to formation of a turbid free-flowing dispersion by a steric stabilization mechanism. ¹H NMR spectroscopy studies indicate that relatively high conversions can be achieved within a few hours at low temperature. GPC analysis using a refractive index detector indicates good blocking efficiencies and unimodal molecular weight distributions, although dispersities increase as the core block DP is increased. Particle characterization techniques include dynamic light scattering (DLS) and laser diffraction. ¹H NMR spectroscopy studies confirm that subsequent dilution using deionized water lowers the background salt concentration and hence causes in situ molecular dissolution of the salt-intolerant chains. This leads to a substantial thickening effect and the formation of free standing polymer solutions with a viscosity increase across orders of magnitude, as measured by rotational rheometry. Thus this polymerization-induced self-assembly (PISA) formulation enables high molecular weight water-soluble polymers to be prepared in a convenient, low-viscosity latex-like form. In principle, such aqueous PISA formulations are very attractive: there are various commercial applications for high molecular weight water-soluble polymers while the well-known negative aspects of using a RAFT agent (i.e. cost and toxicity) are minimized when targeting such high DPs.
RAFT end group modification for self-immolative immunodrug delivery

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Reversible modifications of reversible addition-fragmentation chain transfer (RAFT)-polymerization derived end groups are usually limited to reductive degradable disulfide conjugates. However, self-immolative linkers can promote ligation and traceless release of primary and secondary amines as well as alcohols via carbonates or carbamates in β-position to disulfides. Having combined these two strategies, we introduce the concept of self-immolative RAFT-polymer end group modifications for enhanced immunodrug delivery.

The biocompatible stealth-like monomer N,N-dimethylacrylamide can be polymerized under controlled radical polymerization conditions by hydrophilic or amphiphilic chain transfer agents (the latter can bind under physiological conditions to albumin and thereby control biodistribution and enhance cell internalization). The polymers’ trithiocarbonate end groups are reversibly modified in a one-pot reaction with model compounds (benzylamine, dibenzylamine, and benzyl alcohol) as carbamates or carbonates (confirmed by ¹H-NMR spectroscopy, size exclusion chromatography, and mass spectrometry). Their reversible release under physiological reductive conditions can successfully be monitored by diffusion ordered NMR spectroscopy or thin layer chromatography. This concept has further been expanded to immune modulating small molecules which can precisely be conjugated to the polymers’ end groups for enhanced delivery and control over their activity.

Additionally, by installing amine-reactive species onto the RAFT-derived polymer end groups a reversible bioconjugation to immune modulatory proteins can be obtained, too.

Altogether, we believe that self-immolative RAFT end group modifications can form the new basis for reversible introduction of various functionalities to polymer chain ends, particularly relevant for biomedical purposes towards stimuli-responsive control over delivery and activity.

Controlled immunodrug delivery mediated by RAFT polymerization derived self-immolative end group modification
Post-polymerisation modification of Poly(hydroxybutyrate) (PHB) using thiol-ene and phosphine addition

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As we face the issues associated with fossil-based polymers and their fate in the environment after their useful life, polyesters become more important as “greener” alternatives due to their potential hydrolytic and enzymatic degradability in various environments. Moreover, producing monomers from renewable resources has developed as significant field within polymer research as we look to improved sustainability in our world. During this work the potential to polymerise β-butyrolactone (βBL) via organocatalysis mediated by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) has been investigated. The chemistry results in a crotonate end group being generated through the TBD-mediation which can be used and is explored for post-polymerisation modification using thiol-ene and phosphine addition. Modification by Thiol-ene ‘click’ chemistry was successfully conducted under UV-initiation. Surprisingly, attempting the thiol-ene modification under thermal conditions using dimethylphenylphosphine (DMPP) as catalyst, resulted in the attachment of the phosphine, as shown via NMR and control experiments using crotonic acid. The functionalisation resulted in an increased amphiphilic behaviour which resulted in aggregation of the phosphine functionalised PHB. The aggregates were further characterised by dynamic light scattering (DLS) and transmission electron microscopy (TEM).
New monomers for ring opening metathesis polymerization (ROMP) reactions from pyrrole Diels-Alder reactions

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This talk will describe our recent efforts aimed at preparing new monomers for ROMP using pyrrole Diels-Alder reactions. Polymerization of these monomers with norbornene derivatives provides access to new copolymers containing a main chain N atom that, after deprotection, can undergo post-polymerization modifications.
Engineering solvation in all-dry polymerization

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Organic solvents have been widely used in the synthesis of polymeric materials, although their profuse use lengthens the purification steps and generates hazardous chemical waste. While all-dry synthesis techniques like chemical vapor deposition (CVD) polymerization eliminate the use of solvents and hence improve the environmental sustainability of polymer synthesis, only a narrow palette of material properties is accessible, which has been primarily limited by the available monomer chemistries. Inspired by the principles of solvent engineering in solution synthesis, we developed a novel strategy to broaden that palette via hydrogen-bonding-mediated vapor-phase complexing (namely vapor-phase solvation). We demonstrated broadened ranges of polymer chain length, mechanical strength, and a variety of film surface morphology. We further extended the concept to enable an unprecedented solvation modality, i.e., interfacial solvation, that is unique to all-dry polymerization. We systematically unraveled the molecular interactions, locations of solvation, and detailed kinetics of the coupled solvation-adsorption-polymerization process via combined molecular dynamic simulations and experimental validation of a theoretical kinetic model. The generalizability of the solvation strategy was demonstrated using a variety of methacrylate and vinyl monomers. Solvation in all-dry polymerization thus offers a new degree of freedom in polymer design and synthesis with improved environmental beingness, pointing to the accelerated discovery of novel polymer thin films by simply introducing active solvents in the vapor phase.

Vapor-phase solvation to control deposition kinetics and film properties.
(a) Schema of solvation-enhanced polymerization in initiated Chemical Vapor Deposition (iCVD). (b) Enhanced rate of polymerization of 4-vinylpyridine (4VP) by replacing Ar with hexafluoroisopropanol (HFIP) (vaporized solvent). (c) The molecular weight of p4VP deposited using iCVD, which was tunable in a much broader range, by replacing Ar with HFIP. (d) Improved hardness and indentation modulus of the p4VP films by replacing Ar with HFIP. (N=3 for (b); 100 for (d)).
Synthesis of bio-based cyclic polycarbonate based on dynamic covalent chemistry and its applications

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Bio-based polymers are attracting attention as environmentally friendly materials. In particular, poly(isosorbide carbonate) (PIC) is expected to be the alternative to conventional petroleum polycarbonates as it has excellent recyclability toward fertilizer, high thermal stability, transparency, and so on. However, PIC by itself is inferior to general-purpose petroleum-derived polymers in terms of functionality, and their implementation in the real world has been limited. In this study, we propose a method to functionalize PIC based on the dynamic behavior of the bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) linkage. For controlling the primary structure of polymers, which is important for functionalizing polymers, cyclic compounds with the dynamic nature of BiTEMPS have been reported to be powerful precursors. Therefore, we synthesize cyclic PIC with BiTEMPS linkage utilizing the difference in solubility between end structures and polymers. The simplicity of the present procedure and purification is demonstrated by the highly efficient gram-scale synthesis of cyclic PIC; i.e., no catalysts, no additives, and no complicated synthesis procedures are required, because the radicals generated from BiTEMPS upon heating (> 80 °C) are highly tolerant toward a variety of chemical species, including oxygen and olefins. In addition, dynamic cyclic PIC can be combined with other polymers or functional end groups through bond exchange reactions to impart the completely different properties of those polymers and/or to introduce functional groups at the polymer ends (Fig. 1).

![Schematic image of synthesis bio-based cyclic polycarbonate using the dynamic behavior of BiTEMPS and functionalize cyclic polycarbonate through bond-exchange reaction.](image)

**Fig. 1** Schematic image of synthesis bio-based cyclic polycarbonate using the dynamic behavior of BiTEMPS and functionalize cyclic polycarbonate through bond-exchange reaction.
Thiol end-functional ring-opening metathesis polymers

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Over the last few years our group has developed several new polymerization methods that allow the ring-opening metathesis polymerization (ROMP) to be carried out with catalytic quantities of Grubbs ruthenium complexes.[1-5] This means that each ruthenium carbene complex is “responsible” for the synthesis of several polymer chains, whereas in a classical living ROMP each Ru-complex produces exactly one polymer chain.

Based on these new polymerization methods for catalytic ROMP we have recently developed new reagents that allow the synthesis of ROMP polymers based on functional norbornene derivatives that carry exactly one thiol end group. Thiol end functional polymers have been used for several decades for the functionalization of macroscopic or nanoparticle gold surfaces. Reports for the introduction of thiol end-groups to ROMP polymers, however, have been extremely rare.

In this presentation we report several new methods for thiol end-functional ROMP polymers that are also catalytic in ruthenium. The synthesis of the reagents as well as mechanistic details of the polymerizations will be discussed. Furthermore, first results regarding the functionalization of macroscopic and nanoparticle surfaces will be reported. We believe that these new polymer syntheses will be of great use for polymer scientists and engineers with an interest in highly functional gold surfaces.
Hydrophobic interaction energies of hydrophobically modified cellulose ethers derived from reversed phase liquid chromatography

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Cellulose ethers (CE) are biobased materials that can bring unique properties in many applications such as painting, food, and pharma. The hydrophobically modified cellulose ethers (hmCE) were synthesized with various hydrophobes and degrees of substitution (DS). The introduction of hydrophobic moieties on the cellulose ether backbone at low enough levels to maintain water solubility was hypothesized to yield a material having associative thickening behavior to improve the performance in some applications. It is critical to understand the hydrophobic association of hmCE to correlate with its performance. As such, a reversed phase liquid chromatography (RPLC) method was developed to probe the hydrophobic interaction energy and separate the hmCE materials according to their hydrophobicity. In this talk, we will present the RPLC method development in the separation of hmCE having various hydrophobes and DS. We will demonstrate that the developed RPLC conditions can yield high resolution in separation of hmCE according to their hydrophobicity that enables the assessment of hmCE hydrophobic interaction strengths, and that there is good agreement between zero shear viscosity results from rheology experiments and RPLC data on the same hmCE.

Hydrophobic interaction strength probed by RPLC. The strength of hydrophobic interaction is Long linear alkane > Intermediate linear alkane > Long branched alkane > Short linear alkane > Short branched alkane.
Switchable polymerizations typically make use of a single active catalyst that exhibits orthogonal reactivity upon application of an external stimulus. Herein, we report a new type of switchable polymerization in which the redox-switching event triggers chain transfer between two separate catalysts that facilitate switchable ring-opening polymerization (ROP) of lactide, and the alternating ring-opening copolymerization (ROCOP) of propylene oxide and CO$_2$. The system consists of a potassium 2.2.2-cryptand alkoxide that performs lactide ROP when the catalyst system is in the reduced state and a cobalt(III) salen catalyst that performs ROCOP of propylene oxide and CO$_2$ when the catalyst is in the oxidized state. Liberation or capture of the propagating alkoxide chain end triggered through addition of redox reagents enables switching between the two polymerization reactions. This new polymerization method was used to make block copolymers between polyesters and polycarbonates when stoichiometric amounts of redox reagents are used. Additionally, when substoichiometric redox reagents are used, simultaneous ROP of lactide and ROCOP of propylene oxide and CO$_2$ occurs that produces statistical copoly(ester-carbonates) whose microstructure can be controlled by altering the amount of redox reagent added to the reaction. The redox-switchable polymerization by chain transfer (ReSPCT) results in the synthesis of a wide variety of copolymers containing poly(lactide acid) and poly(propylene carbonate) whose microstructures could be controlled through catalyst oxidation state.
Supersoft thermoplastic elastomers prepared by ring-opening metathesis polymerization with wide service temperatures

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Thermoplastic elastomers (TPEs) are valued for their rubber-like properties, whilst possessing the capability to be reprocessed and recycled like a thermoplastic. However, commercial TPEs are dominated by acrylic and styrenic derivatives which restricts their service temperatures and precludes high temperature applications. Additionally, current high temperature plastics have concomitantly high moduli, making them unsuitable for applications that require softness and flexibility, such as those that interface functional electronics with the human body (e.g., wearable health monitoring devices). In this work, ring-opening metathesis polymerization (ROMP) is employed to rapidly access ABA norbornyl-triblock copolymers consisting of glassy A-blocks and a soft B-block. This presentation will go through the synthesis and characterization of these novel TPE materials that withstand exceptionally high temperatures under uniaxial tension, while maintaining low stiffness and high strength, toughness, and elasticity. Moreover, structure-property relationships as they relate polymer composition and architecture to thermomechanical characteristics are systematically identified to inform further development and optimization of advanced supersoft TPE materials.
Photo-degradable polymers have been developed via metathesis polymerization from newly designed monomers. The cyclic monomers contained a ortho-nitrobenzyl ester as photo-degradable functionality, and the polymer was successfully synthesized by ring-opening metathesis polymerization. The resulting polymer was simply degraded under the presence of UVA light without any chemical processes. We also demonstrated a biodegradable polymer via a cascade metathesis polymerization with living polymerization manner from acetal-containing enyne monomer.
Tale of two isomers: Microstructural variation in frontal ROMP

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Frontal ring-opening metathesis polymerization (FROMP) of dicyclopentadiene (DCPD) provides high-performance structural polymers and composites. Despite rapid developments, precise understanding of the chemical-level nature (e.g., microstructure) of frontally prepared p(DCPD) remains elusive. In our efforts to find more reactive substrates, we discovered that the monomer stereochemistry dramatically affects both the polymerization process as well as the resultant polymer properties. Specifically, FROMP of \textit{endo}- and \textit{exo}-DCPD occur at different rates according to their reaction rates and enthalpies. While resins comprised of the \textit{exo}-isomer cure twice as quickly than their \textit{endo}-analogs, the resultant polymeric materials exhibit wildly different properties as evidenced in a > 40 °C difference in glass-transition temperature ($T_g$). A thorough analysis of model oligomers of DCPD suggested that the monomer stereochemistry influences the polymer microstructure and stereoregularity.
Performance advantaged PET co-polymers from lignin-derivable monomers

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The development of new sustainable polyesters is highly desirable, as the ester bond can be leveraged for chemical recycling, an important strategy for achieving a closed-loop plastic lifecycle. Polyethylene terephthalate (PET) is the most widely produced polyester and, by weight, is primarily petroleum-based owing to the terephthalic acid monomer used in its synthesis. Hence, the development of analogous monomers derived from renewable sources that could offer competitive properties in polymers is sought after. Lignin is an abundant renewable feedstock that can be transformed into a variety of platform molecules through chemical or biological catalysis. Aromatic building blocks from lignin depolymerization can be converted into aromatic monomers such as 2-methoxy terephthalic acid and 2,6-dimethoxy terephthalic acid or used in bacterial aromatic catabolism to make β-keto adipic acid. These lignin-derived dicarboxylate species have been explored as co-monomers with terephthalic acid and ethylene glycol to form novel PET-like co-polymesters with performance advantaged properties. The effect of their unique features, i.e., the methoxy and ketone functionalities, in the polymer synthesis and material properties are investigated by varying the monomer compositions. The rate of depolymerization by enzymatic degradation and methanolysis are established and compared to those for PET.
Synthesis and assembly behavior of a Poly(ionic liquid) and a stimuli-responsive weak polyelectrolyte block copolymer

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Poly(ionic liquid)s (PILs) are special type of strong polyelectrolytes that combine the diverse functionality and unique properties of ionic liquids (ILs) with the mechanical stability, long-range ordering, and processability of polymers. In recent years, PILs have found application in a variety of fields including battery electrolytes, separations, nanomaterials, and more. In one growing field, PILs have been combined with highly incompatible neutral polymers to form block copolymers (BCPs). These systems have been used in forming polymer films and membranes with unique nanostructures such as lamellae, cylinders, spheroids, and bicontinuous structures. Depending on the structure, these morphologies can enhance the properties of PILs materials, such as ion conductivity in battery electrolytes or interfacial behavior in coatings. However, only a few studies have investigated block copolymers composed of PILs with weak polyelectrolytes, which can modulate their charge density based on degree of protonation. Such materials show conformational changes in response to environmental stimuli such as changes in pH and salt. Synthesizing and characterizing PIL-b-polyelectrolytes will aid in the development of novel all-polyelectrolyte materials for applications in stimuli response, polymer battery electrolytes, and flexible electronics. In this work, (PIL-b-polyelectrolyte) BCPs are synthesized through the Cu(0) mediated atom-transfer radical polymerization (ATRP) controlled free radical polymerization technique. Specifically, poly[vinylbenzyl butyl imidazolium bis(trifluoromethanesulfonyl) imide] was polymerized utilizing a tertiary amine weak polyelectrolyte macroinitiator. The synthesized polymers were characterized for their chemical properties and molecular weight through GPC, NMR, and FTIR. The solubility and solution behavior of these block copolymers were investigated with DLS. Self-assembled films of the block copolymers on silicon wafers were analyzed with a combined FTIR-AFM technique.
Electron donor acceptor double cable covalent conjugates: Towards improved photovoltaic devices and accelerated artificial photosynthesis

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Tremendous amount of effort is being invested in improving the optical and electrical properties of semiconducting materials for use in diverse applications including photovoltaics, interfacing electrodes, and biosensing devices. These efforts have led to a remarkable development in the field of semiconducting materials offering versatile chemical and functional traits. In this context, various chemically and functionally distinct classes of organic semiconducting polymers (OSP) have been developed. Compared to inorganic counterparts, OSPs are easy to synthesize and present possibilities of installing chemically diverse functional groups as side chains and end groups. These provisions have resulted in the development of a toolbox of OSPs with tunable optical and chemical properties that can be customized for target application. In quest of expanding advantages offered by OSPs, current research is focused on development of side chain engineered OSPs via Grignard Metathesis polymerization. The overarching aim was to develop a variety of OSPs with controlled chemical nature of side chain functional groups for targeted applications. In the context of energy applications, a part of work is related to developing facile strategies for covalent conjugation of OSPs with fullerene for better electronic communication between donor-acceptor (D-A) for enhanced photovoltaic effect. The insight into the efficacies of electronic communication in D-A covalent hybrid systems was revealed through current generation in photodetector devices that will open new avenues to materials for advancing applications. Besides, OSPs developed were employed in the development of hybrids of OSPs and NiO nanoparticles (NPs) to synergize their distinct optical and electrical properties for (electro)catalysis. In-addition, light harvesting NPs systems based on covalent conjugation of OSPs with flavin moieties were developed for biophotovoltaic devices that mimic the natural photosynthesis. In summary, this work will lead to development of OSPs derived functional systems with precise molecular design for energy, environmental, and biological applications.
Synthesis of nanowire heterojunctions via self-assembly of multi-block conjugated polymers

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Nanowire heterojunctions (NWHs) constitute a device platform with the potential to advance energy harvesting and storage, communication, and computation. Most nanowire heterojunctions developed to date are based on inorganic materials, whose synthesis requires the use of toxic gases and specialized vapor deposition set-ups. Conjugated polymer nanowires present a promising alternative because such materials could be amenable to solution-based processing/fabrication. However, the synthesis and self-assembly of conjugated multiblock copolymers into NWHs remain scarcely studied. To address this gap in knowledge, we’ve synthesized conjugated block copolymers with varying electronics and investigated their self-assembly.
In this study, we present ultrahigh conductive covalent organic frameworks (COFs) films via vapor-assisted synthesis, denoted as CuPc-AQ-COFs, constructed by linking phthalocyanines and anthraquinones through ultrastable dioxins. The resulting 2D COFs film exhibited unprecedented electrical conductivity of 1534.9 S m\(^{-1}\) and carrier mobility of 601.5 cm\(^2\) V\(^{-1}\) s\(^{-1}\), orders of magnitude higher than the reported record. This is attributed to the porous 1D channel formed by the π-π conjugated stacking layers and to the unique molecular design of the CuPc-AQ-COFs. Insights into the mechanisms via density functional theory (DFT) analysis showed that the lower LUMO of anthraquinones-based linker, compared to the dimethyl-based linker used in the control group, facilitated greater electron transfer from the Cu-phthalocyanine fragment, leading to a better donor-acceptor system. Charge density results revealed that Cu played an exceptional role in electron delocalization to establish interlayer connections by comparing to Ni and Co. Above all, the highest experimental conductivity and mobility of CuPc-AQ-COFs film was confirmed compared to control groups. Overall, CuPc-AQ-COFs films not only set new records of COFs’ conductivity and mobility but also represent a significant step forward in developing COFs for electronic applications.
Rate accelerated chain extension in Cross-Dehydrogenative Coupling polymerization

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Focus on the synthesis of conjugated polymers has increased over the years due to their potential application as organic semiconductors in organic light-emitting diodes (OLED), organic photovoltaics (OPV), organic field-effect transistors (OFET) etc. Traditional cross-coupling reactions like Stille, Suzuki or Kumada coupling, as well as direct arylation reactions have been used efficiently for synthesizing conjugated polymers. However, use of organometallic reagents, and/ or the requirement of prefunctionalization of monomers cannot be ideal scenario for the polymerization. Recent introduction of cross-dehydrogenative coupling (CDC) strategy in conjugated polymer synthesis appears to be highly promising in terms of both utility and sustainability. Two simple arene monomers without any prefunctionalization can participate in the polymerization reaction via catalytic two-fold C–H bond activation. Mechanistic understanding of the process is essential to maximize its potential applications. Detailed mechanistic study of the successful Pd/Ag-cocatalyzed CDC polymerization of 3,3’-dihexyl-2,2’-bithiophene and 2,2’, 3,3’, 5,5’, 6,6’-octafluorobiphenyl were performed by Luscombe et al. (Image 1). Contrary to the Carothers equation, the second cross-coupling for the chain extension was found to be more efficient than the first cross coupling step and the homocoupling reaction. Different acceptor monomers are being screened with 2-alkylthiophenes and 2-alkylfurans for further understanding of rate acceleration phenomena in the chain extension step of CDC polymerization (Image 2). These results will be correlated with the results of respective polymerization reactions. All the developments in the ongoing mechanistic studies will be presented herein.
Oxidative molecular layer deposition of charged polymers for electrochemical applications

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Charged polymers such as polyethylenedioxythiophene (PEDOT), polypyrrole (PPy), and polyaniline (PAni) both conduct electricity and undergo redox reactions to store charge, making them appealing for applications in energy storage, electrochemical desalination, and chemical sensing. The work we report here focuses on experimental vapor-phase synthesis of thin-films of these charged polymers using gas-phase exposures of monomers and metal-chloride (e.g. MoCl\textsubscript{5}) oxidant in a process termed oxidative molecular layer deposition, or oMLD. This synthesis approach has benefits in (1) conformal formation of thin films of charged polymers on 3D surfaces, and (2) molecular control of polymer structure. Here, we report on our recent work studying oMLD using a range of different monomers. We report on insights we have gained into the oMLD growth mechanism from quartz crystal microbalance (QCM) measurements and density functional theory (DFT) calculations. We specifically identify the importance of a two-electron chemical oxidant with sufficient oxidation strength to oxidize both a surface and a gas-phase monomer to enable oMLD growth. We also identify that by controlling the dosing sequence of monomer precursors to form molecularly assembled copolymers, we gain control over various aspects of the electrochemical properties of these charged polymers that provide enhancements in charge capacity over homopolymer structures. Together, these contributions help establish a foundation to inform the development of further oMLD chemistries, offering a wide landscape of opportunities for the synthesis of thin films of charged polymers with molecular structure control.

If $E_{0}^{Ox} > [E_{0}^{A} \& E_{0}^{B}]$
Amphiphilic main-chain poly(fullerene xylene)s

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Main-chain fullerene-based polymers are still relatively rare. However, because they combine the properties of fullerene, such as exceptional electron acceptance capability and semiconductivity, with those of polymers such as good solubility and excellent film-forming characteristics, they are gaining particular interest for their use as interlayers in photovoltaics and organic electronics. They exhibit many of the properties of fullerenes, combined with the ability to be formed as a regular thin film. For examples, recent work by other groups has demonstrated their use as interlayers in perovskite solar cells to give efficiencies around 23% and good stabilities, and in our work that they might find use in ammonia sensors.

The methodology used to make these polymers can impact extremely heavily on its final physico-chemical properties. Therefore in this work, by way of introduction, we review the different known methods of preparing main-chain poly(fullerene)s and how those methods can modify the polymer’s behaviour in application. We further look to new methods for reacting with the chain-ends of these materials to expand their properties, especially by combining them with poly(ethylene glycol) to give amphiphilic materials. It is expected that these new materials might be of interest for ‘green’ processing of interlayers and drug delivery systems.
Optimized synthesis of poly(9,9-dioctylfluorene) via modified Grignard metathesis method

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Grignard metathesis (GRIM) method is well-known to synthesis regioregular poly(3-hexylthiophene) (P3HT) with controlled molecular weights, narrow polydispersity indices (PDIs), and known end-groups. However, applying the GRIM method to the synthesis of other conjugated polymers has not been well-established yet. In general, the syntheses of other conjugated polymers are performed through metal-catalyzed polycondensation reactions based on Yamamoto, Suzuki, or Stille coupling reactions, which usually require harsh reaction conditions and result in polymers with uncontrolled molecular weights, broad PDIs and unknown end-groups. In this work, the synthesis of Poly(9,9-dioctylfluorene) (PFO), a high-performance backbone-conjugated blue-light emitting polymer, via GRIM method was systematically investigated. By using different organomagnesium reagents instead of the traditional Grignard reagent used for P3HT, which didn't work for PFO, we proved that GRIM is also applicable for the synthesis of PFO from the commercially available monomer (9,9-dioctyl-2,7-dibromofluorene) with narrow PDIs (less than 1.5) and relatively high molecular weights (M_n ~15,000). The organomagnesium reagents we tried included “turbo-Grignard” reagents (LiCl plus a Grignard reagent) and organomagnesium ate complexes. Besides, we also studied the kinetic of the GRIM polymerization of PFO, which could indicate chain-growth nature of the polymerization, and the presence of chain termination. The end group study and device performance are still in progress.

Scheme 1. Synthesis of Poly(9,9-dioctylfluorene) by using di-sec-butyl magnesium lithium chloride (sBu₂MgLiCl) (a) and tri-n-butyl magnesium lithium (nBu₃MgLi) (b) for Bromine-Magnesium exchange during Grignard Metathesis Polymerization.
Chalcogenophene heteroatom control of conjugated polymer microstructure and mixed-conducting properties

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Conjugated polymeric mixed ionic-electronic conductors are an exciting class of materials for electrical energy conversion and storage, bioelectronics, neuromorphic computing, and more. Ionic and electronic coupling and transport enable a range of functionalities (charge storage, sensing/stimulation, amplification, electrochromism, actuation). One route to improve conjugated polymer properties is heteroatom substitution. While well studied in polymer photovoltaics and field effect transistors this route is less investigated for polymeric mixed conductors. We report the synthesis of characterization of a series of alternating copolymers of glycolated bithiophene and unsubstituted chalcogenophene (furan, thiophene, selenophene, tellurophene) subunits. While heteroatom substitution induced expected changes in optoelectronic properties (optical bandgap, HOMO/LUMO levels), the largest effects were observed in microstructure and mixed-conducting properties. GIWAXS revealed a semicrystalline microstructure (side-chain lamellae and π-π stack ordering) shifting from a face-on to edge-on orientation moving from furan to thiophene to selenophene copolymers. The tellurophene copolymer presented a distinct highly crystalline and highly oriented case with significant ordering along the conjugated backbone. Mixed conducting properties were investigated in organic electrochemical transistor (OECT) test beds. Between furan, thiophene, selenophene copolymers, the thiophene copolymer showed the best electronic transport (highest electronic mobility and volumetric capacitance, and lowest threshold voltage) of the three. The selenophene copolymer OECT transconductance frequency cut-off was very low indicating an ionic transport bottleneck. Again, the tellurophene copolymer presented a unique case, with high carrier mobility (nearly triple the thiophene copolymer), and anomalously high transconductance frequency cut-off, reflecting enhanced ionic and electronic transport. Further, the tellurophene copolymer OECT subthreshold swing (44 mV/dec) was lower than the expected thermodynamic limit (60 mV/dec) indicating a unique electrochemical DOS (i.e. redox states contributing to electronic charge transport) compared to the rest of the copolymer series, and mixed conducting conjugated polymers in general.
Hydroxide conducting anion exchange membranes (AEMs) have been materials of interest for use in electrochemical devices such as alkaline fuel cells and water electrolyzers. These membranes are comprised of a polymer backbone with covalently tethered cations; ammonium have been the cation of choice in due to their ease of synthesis and high conductivity. Despite these advantages, ammonium cations are susceptible to degradation in harsh alkaline conditions which has led to investigation of alternative cations based on main group elements. In particular, resonance-stabilized trisdialkylaminosulfoxoniums are a class of main group cations that have recently been explored in small-molecule studies and demonstrate promising long-term stability under caustic conditions, but have there are no reports to date on strategies to append these cations to a polymer backbone. Herein, we investigate various approaches to incorporate these alkaline-stable cations onto polymer backbones. One promising method to prepare trisdialkylaminosulfoxonium-functionalized polymers involves the use of a sulfoximine precursor and subsequent alkylation with a norbornene alkyl-halide to afford a polymerizable monomer for direct polymerization of the cation. The sulfoximine can also be attached post-polymerization to a polymer bearing pendant alkyl-halides. Herein, we implement this approach to evaluate various synthetic methods to incorporate sulfoxoniums onto polynorbornene backbones toward a series of novel AEMs.

![Chemical Reaction Image]
(Oxa-)norbornene derived block copolymers for the preparation of functional nanogels with stimuli-responsive Immunodrug delivery properties

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The living ring-opening-metathesis-polymerization (ROMP) of exo-(7-oxa)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid pentafluorophenyl esters results in well-defined polymers that allow for block copolymerization with hydrophilic oligo(ethylene glycol)-containing (oxa-)norbornene-imides. The resulting polymers self-assemble into micelles with amine reactive cores. Such precursor micelles are subsequently crosslinked and hydrophilized. The crosslinking reagent, equipped with a ketal moiety, is used to introduce a pH-sensitive disassembly behavior upon acidification. Due to the hydrophilic nature of the polymer, the structures then fall apart in aqueous media. The hydrophilicity can further be finetuned by the polymer backbone (norbornene vs. oxo-norbornene). Additionally, the amine-reactive core enables a covalent conjugation of highly potent immunomodulatory drugs, thus, controlling their transient bioactivity.

Synthesis of (oxa-)norbornene derived block copolymers. Nanogels are then prepared via self assembly and subsequent crosslinking and hydrophilization of the micellar core.
Selective demicellization of poly(benzyl ether)-based surfactants via head-to-tail depolymerization

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The presented work details a molecular design for self-immolative micelles composed of poly(benzyl ether)-based amphiphiles. These micelles exhibit triggered demicellization through head-to-tail depolymerization. The amphiphilic copolymers are synthesized through living anionic polymerization by sequentially adding two different quinone methide monomers. The hydrophilic and hydrophobic blocks of the copolymers enable them to form polymeric micelles effectively under aqueous conditions. Upon reacting an end-capping unit in the hydrophobic block with a specific stimulus, depolymerization proceeds outward in a head-to-tail fashion without requiring additional treatment (as shown in Figure 1a). The micelles can be successfully loaded with hydrophobic drug cargo and release them on demand upon exposure to fluoride. However, the micelles exhibit structural limitations such as spontaneous demicellization at concentrations below the critical micelle concentration (CMC). To address this, the shells can be selectively cross-linked to create polymeric particles (as shown in Figure 1b). Loading drug molecules into shell cross-linked micelles was found to be tolerable below the CMC, and an enhanced catalytic activity was also achieved.

a) Description of stimuli-responsive micelles and demicellization via triggered depolymerization. b) Shell cross linking by post thiol–ene reaction
We show that tuning the kinetics of a dynamic hindered urea bond in polyurethanes to match competitive isocyanate hydrolysis results in the formation of new, unhindered urea bonds upon incubation of the material in water (Figure 1). This significantly increases thermomechanical performance of the pristine material on demand. Most notably, strains at break could be increased up to 10x while elongations at break remained equal or even increased compared to the pristine material, which led us to term the effect “self-reinforcement”. We have elucidated the mechanism of self-reinforcement in small molecule studies and investigated its matrix-dependent effects on material properties of both, thermoplastic and thermoset materials.

Self-strengthening materials provide a unique opportunity to reconcile the contradicting properties of mechanical performance vs processability and highly porous design of final parts, which is particularly important for highly porous biomedical scaffolds. Here we show the application of self-reinforcing thermoplastic poly(urethane urea) for electrospun biodegradable vascular grafts. Notably, biodegradability of such scaffolds is enhanced compared to reference grafts despite their superior mechanical performance.
Antimicrobial resistance (AMR) is a silent pandemic caused by multi-drug-resistant ESKAPE pathogens. These microorganisms and their mounting resistance to common antimicrobials are the reason for increased morbidity and mortality rates globally. New generations of antimicrobials are needed to overcome AMR. Plant secondary metabolites are potential future solutions but need to be standardized. Since ancient times, plant extracts, medicinal plants and herbs are used by many cultures against ailments. Iodine is another well-known microbicide, which finds application in form of povidone iodine in many consumer products. We study formulations based on plant extracts and iodine complexed in the polymer polyvinylpyrrolidone (PVP). Such formulations can be solutions during future pandemics in the event of disinfectant shortages, because they literally can be found in almost every household. They present a sustainable solution based on natural ingredients, which can be used against AMR. In this study, we combined Aloe Vera barbadensis Miller (AV) gel with Green Tea extract (GTE), iodine and PVP in form of a AV-PVP-GTE-I2 complex. We studied the antimicrobial properties by using disc diffusion methods on agar plates against 10 reference microorganisms in comparison to common antibiotics. The formulations were impregnated into sutures and bandages to test their effects in preventing surgical site- and wound infections, respectively. The formulations were analyzed by Raman, UV-Vis, FT-IR, x-ray diffraction (XRD), microstructural analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results confirm the composition of the novel formulations AV-PVP-GTE-I2. The formulation strongly inhibits Candida albicans threefolds better than the antibiotic nystatin and can be used as an antifungal agent. Gram-positive and Gram-negative pathogens were also immediately susceptible to AV-PVP-GTE-I2. These promising findings underscore the potential of our sustainable formulation as disinfecting spray, as well as antimicrobial agent against surgical site- and wound infections.
Poly(2-ethylthio-2-oxazine): A versatile polymer platform for post polymerization modification reactions

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In recent years, poly(2-oxazine)s have gained interest for its use in biomedical applications. The additional methylene group in the main chain gives the polymer a slightly lower hydrophilicity and higher backbone flexibility, resulting in a lower glass transition temperature, compared to poly(2-oxazoline)s. These different properties results in improved antifouling properties and improved drug delivery. Also in gene delivery, the use of poly(2-oxazine)s can be advantageous. By controlled side chain hydrolysis of copolymers of 2-oxazoline and 2-oxazine, resulting in polyethylenimine-co-polypropylenimine, will improve the transfection efficiency, due to the increase in hydrophobicity and decrease in the charge density. A slight downside is that these properties are affected by the 2-substituent chosen, so it can be difficult to fine-tune the properties.

In this study, we synthesized 2-ethylthio-2-oxazine, inspired by a previously reported analogous 2-ethylthio-2-oxazoline. The resulting poly(2-ethylthio-2-oxazine) has a thiocarbamate as side function, which after oxidation can easily undergo nucleophilic substitution. Therefore, poly(2-ethyl-2-oxazine) emerges as a versatile polymer that can easily be transformed and used for many different applications. Utilizing this we explored two different routes: selective hydrolysis and introducing super-hydrophilic side-chain substituents. For the first route, selective hydrolysis, it bases around the thiocarbamate function that is not affected in acidic hydrolysis. This provides selective control over side-chain hydrolysis for copolymers of 2-ethylthio-2-oxazine with other cyclic imino ethers, which can be interesting for gene delivery applications. The second route is mainly explored for drug delivery and antifouling applications. The post polymerization modification of the thiocarbamate can be done with hydrophilic reagents resulting in super-hydrophilic polymers.
Antimicrobial resistance (AMR) is recognised as one of the greatest threats to human health worldwide, as such, there is a direct need for a wide variety of novel antimicrobial materials. Developing antimicrobial surfaces brings advantages in various aspects of life and will have great improvement in biomedical application and clinical industry. Of particular interest are polymer coatings which can endow the existing surfaces with suitable antimicrobial properties by utilising multiple bactericidal pathways thus preventing further AMR evolution.

Here we report a facile surface functionalisation with synthetic α-amino acid N-carboxyanhydride (NCA) derived polypeptides through surface-initiated ring-opening polymerization (SI-ROP) from solid substrates. Silicon wafer has been chosen to be engineered, due to the simplicity of modification, and the functionalisation chemistry can be translated to titanium surfaces, and thus for medical and dental implant technology. Surface functionalization with polypeptides was performed via grafting-from approach which is expected to give a dense polypeptide on the surface.

Polypeptides grafted surfaces with various amino acid sequences have been fabricated and demonstrate excellent antimicrobial activity against Gram-positive bacteria while having no cytotoxicity. The antimicrobial properties of these materials will be presented highlighting their potential application as a new class of antibacterial surface coatings.
pH-Responsive swelling of poly(methacrylic acid) multilayer hydrogels through controlling polyacid chain conformations

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Stimuli-sensitive nanostructured multilayer hydrogels obtained from layer-by-layer (LbL) polymer films have shown precise control over network composition, thickness, crosslink density, and fast and reversible stimuli-triggered hydrogel volume changes. These properties are crucial for biomedical applications, including drug and gene delivery, tissue engineering, and cell interactions. We showed that for chemically crosslinked PMAA multilayer hydrogels obtained from hydrogen-bonded multilayer templates, the internal hydrogel structure ranges from well-stratified to highly intermixed depending on the LbL assembly method. We also showed that crosslinking enhanced chain interdiffusion, which became more pronounced with increasing molecular weight of the sacrificial binder, poly(N-vinylpyrrolidone). Herein, we explored the effect of the polymer architecture and the chain conformation on the properties of PMAA hydrogels. We synthesized well-defined poly(tert-butylmethacrylate-co-N-(tert-butoxycarbonylaminopropyl)methacrylamide) copolymers (M_w of ~45 kDa and 80 kDa, polydispersity ≤ 1.35) RAFT copolymerization with different content of amino group (PMAA-NH_2 from 2.1 to 6.2 mol.%), Figure 1. The controlled polymerization was confirmed using ^1^H NMR and GPC analysis, and a gradient distribution of monomers characterizes the copolymers. The effects of pH-sensitive PMAA-NH_2 chain conformation on forming water-insoluble intramolecular complexes were studied and subsequently used for PMAA hydrogel fabrication via spin-assisted LbL. The effects of crosslink density and deposition conditions on the properties of the hydrogels were studied through in-situ ellipsometry and AFM techniques. This work opens opportunities for developing thin hydrogels with precisely tuned morphology, pH-triggered swelling, and hydration.
Synthesis of disubstituted γ-amide ε-caprolactone monomers for the amphiphilic diblock copolymers in drug delivery applications

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Polycaprolactones (PCLs) are essential aliphatic polyesters for drug delivery due to their biodegradability, biocompatibility, and synthetic versatility. Introducing different substituents at γ-position of ε-caprolactone (ε-CL) monomers can easily tune the properties of synthetic polymers. Most studies involve single substituent at the γ-position of ε-CL monomers due to ease of functionalization. This is a drawback since the side chain significantly affects the polymer's properties. Disubstituted γ-amide ε-CL monomers can double the density of substituents on a single polymer chain, which directly affects the properties of polymeric micelles, such as drug load capacity (DLC) and thermodynamic stability.

Our research aims to synthesize disubstituted amphiphilic block copolymers (AmBCs) from the novel disubstituted γ-amide ε-CL monomers and investigate their properties. The amide functionality allows two substituents to generate both hydrophobic and hydrophilic monomers. The hydrophobic substituents comprise aryl functional groups to explore the DLC via π-π stacking and hydrogen bonding with the hydrophobic drug molecule, Doxorubicin (DOX), and the release of the drug. The chosen hydrophilic substituent contains thermoresponsive tri(ethylene glycol), which can increase the micelles' thermodynamic stability. AmBCs were prepared by ring-opening polymerization (ROP) of each monomer using Triazabicyclodecene (TBD) catalysts to generate living polymerization behavior. Self-assembly, thermoresponsive behavior, and DLC of the AmBCs were analyzed. The in vitro biocompatibility and cellular uptake of the AmBCs will be thoroughly investigated for breast cancer treatment using MCF-7 cells.

Schematic representation of amphiphilic diblock copolymers and their self-assembly behavior.
Poly (glycerol ester)-based polyplex nanoparticles for safe and effective gene delivery

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Polyplex nanoparticles are widely used in molecular biology research as polymer-based gene delivery systems, with nanoparticle stability, cellular uptake, and transfection efficiency being significantly affected by the molecular weight, hydrophilicity, hydrophobicity, and charge density of the polymer. Balancing these factors is crucial for developing safe and effective gene delivery systems. Poly (glycerol esters) (PGEs) are a versatile class of biomaterials suitable for various biomedical applications due to their tunable physical properties and biocompatibility. PGEs were synthesized through polycondensation, using a variety of different length diacids with glycerol to form the PGE. Depending on the synthetic route and reaction conditions the microstructure can vary, thus changing further reaction kinetics and transfection rates. The resulting PGEs were then modified with various functional groups, including cationic, hydrophobic, and hydrophilic moieties, enabling the formation of nanoparticles with various nucleic acids. Nuclear magnetic resonance, size exclusion chromatography, and amine titration were used to characterize the molecular weights, dispersities, branching, and charge densities of the PGEs. The tunable properties of the PGEs were found to have significant impacts on the transfection efficacy with both non-adherent and adherent cell lines.
Towards enediyne substituted polycaprolactones in an attempt to generate Calicheamicin-like anticancer activity

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Enediynes are the warhead in Calicheamicin, one of the most potent small molecular anticancer drugs. However, enediynes are not selective and can be toxic to normal healthy cells. To address this issue, we have developed a new approach involving functionalizing enediynes to micellar nanoformulations that selectively target cancer cells. Specifically, we synthesized enediyne-substituted polycaprolactones that can self-assemble to form polymeric micelles. These micelles have a hydrophobic block comprised of maleimide-derived enediynes (MDE) functionalized PCL, and a hydrophilic block consisting of thermoresponsive tri(ethylene) glycol (ME3). When these micelles are exposed to elevated temperatures, they collapse, revealing the reactive MDE group, which inhibits tumor cell growth.

The developed nanoformulations show fluorescent properties due to the inherent fluorescence of the MDE system and were used to compare their efficiency with doxorubicin (DOX) and DOX-loaded micelles. The MDE functionalized nanoformulations induced DNA cleavage and exhibited cytotoxicity towards MDA-MB-231 breast cancer cells by producing diradical generation through Myers-Saito Cyclization. An electrophoretic mobility shift assay was performed to examine the DNA binding affinity of the nanoformulations, which revealed their ability to bind to the DNA backbone. By creating MDE functionalized nanoformulations, we developed the first enediyne-based biodegradable anticancer agent that specifically targets cancer cells.
Quadruple Hydrogen Bonded Silicone-based Polymer Blends

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Polysiloxanes are high value polymers that exhibit properties which are unmatched by organic polymers due in large part to the unique behavior of the Si-O bond. However, siloxanes are typically not miscible with most organic polymers. Blending polymers is a versatile and cost-effective method to control material properties but blends tend to suffer from macrophase separation leading to brittle material. Here, we present a compatibilization strategy for silicone-organic blends using complimentary quadruple hydrogen bonding end groups capable of heterodimerization. 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (Napy) functionalized polymers were prepared and the effectiveness of UPy-Napy heterodimerization characterized by, ¹H-NMR, optical photothermal infrared spectroscopy (O-PTIR), and optical microscopy.
Bottom-up design of functional polymer monoliths for effective adsorption of endocrine disruptors

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This presentation discusses the molecular design of functional fibrous polymer monoliths through a bottom-up approach to create self-assembled conjugated porous polymers (Figure 1). These resulting monoliths boast high structural stability and compressibility, thanks to their intrinsic fibrous structures similar to those of sea sponges. The versatility of the materials allows for further functionalization with a range of shapes and structures enabled by the diverse monomer structures and synthesis methods employed. For instance, fiber networks can be created using selected monomers and employed as functional hybrid scaffolds, supporting the formation of ZIF-8 nanocrystals. These nanocrystals catalyze the thiol-epoxy reaction and coat the fiber strands with a molecularly imprinted epoxy layer, making them selectively adsorbent for diethylstilbestrol. Additionally, the presentation demonstrates the fabrication of fibrous monoliths through charge transfer complexation. Here, electron donor and acceptor molecules are used to create fibrous monoliths, and the removal of one component creates effective recognition sites for bisphenol A.

Figure 1. (a) Schematic diagram of the formation of functional fibrous monoliths via a bottom-up approach. (b) Design of hierarchical functional monoliths for selective molecular recognition of diethylstilbestrol. (c) Formation of functional fibrous monoliths containing binding sites for adsorption of endocrine disruptors through the introduction of charge transfer complex.
Responsive nanotubes from asymmetric cyclic peptide-polymer conjugates

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Tubular nanomaterials are omnipresent in nature, with applications varying from structural to biological. Nature has evolved a variety of designs, from helical structures such as the natural antibiotic gramicidin A to proteins assembled like a barrel stave structure as in the cholera toxin. Inspired by these self-assembly strategies, our project is exploring the use of self-assembling cyclic peptides (CPs), which supramolecular stacking leads to nanotubes of defined inner diameter and guided functionality. CPs stack into supramolecular cyclic peptide nanotubes (SCPNs), driven by antiparallel β-sheet hydrogen bonding. Conjugating polymers of controlled size and functionality onto cyclic peptides enables the construction of nanotubes with well-defined functionalities and properties. Our group previously reported Janus cyclic peptide-polymer nanotubes with dual functionality through the attachment of two different phase-separating polymers onto the cyclic peptide cores, which provided a new strategy in the synthesis of transmembrane channel mimics[1]. We have also harnessed these structures to develop novel structures called tubisomes[2], based on asymmetric cyclic peptide polymer conjugates, based on one hydrophobic and one hydrophilic polymer conjugate per peptide. These conjugates assembled in hierarchical structures, forming single CP nanotubes first, which then self-assemble into tubisomes via hydrophobic interactions.

Herein, we focus our study on responsive asymmetric cyclic peptide-polymer conjugates by the attachment of a series of responsive polymers such as tertiary amine-based (meth)acrylates and acrylamide monomers on one side of the CP, and a hydrophilic polymer on the other side of the CP. We have designed a family of responsive asymmetric cyclic peptide-polymer conjugates and established their applications as transmembrane channels, gene delivery and drug delivery.
Templating trapped entanglements in polymer networks using coordination complexes

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Trapped entanglements play a key role in making soft materials tough. Polymer networks containing similar entities such as rotaxanes and catenanes have exhibited increased material toughness in comparison with covalently cross-linked networks, which is attributed to the ability of the chains/rings to slide against one another. However, the connection between the topology of trapped entanglements and toughness of polymer networks remains underexplored. An approach has been developed for installing entanglements with controlled topology in polymer networks. Copper-coordinated supramolecular complexes were utilized as entanglement templates that were cross-linked with polyethylene glycol (PEG) in organic solvent to form gels with veiled entanglements; removal of the copper then unveils the trapped entanglements. The chemical and mechanical properties of these gels versus control gels that had identical covalent networks were compared. However, the sliding mechanism is difficult to probe using common spectroscopic techniques. 2D neutron scattering was also applied to examine strain evolution of both the gels containing entanglements and control gels under uniaxial loading, and was corroborated with the mechanical data. This work will enable the design of materials with tunable properties.
Trainability in soft materials can be defined as the material's ability to utilize external environmental stresses such as mechanical load to impart useful functional responses via adaptable reconfiguration of the constituent units. Liquid crystal elastomers (LCEs) are lightly crosslinked polymer networks with covalently bonded liquid crystalline units (mesogens), which combine the mechanical properties of an elastomer with the anisotropy of small molecule liquid crystals. Dynamic LCEs are suitable as trainable systems on account of their ability to rearrange their mesogenic units in response to mechanical deformation. The presence of the dynamic covalent bonds in the LCEs imparts reconfigurability and adaptability to the network in response to such an external stimulus. In this project, a range of hydrogen-bond donor catalysts was explored to promote both the formation and dynamic exchange of aza-Michael bonds. With this knowledge, a series of aza-Michael LCEs were prepared and the dynamic exchange behavior of the aza-Michael adducts within the LCEs were examined by performing stress relaxation and creep measurements. Furthermore, it was possible to ‘switch on’ and ‘switch off’ the thermally-induced reprogramming of these LCEs by post-synthetically imbibing the catalyst via swelling or washing the catalyst out via soxhlet extraction. The ability to activate/deactivate the dynamic exchange in our LCEs allow us to induce programmability via training or maintain the network stability as desired.
Using a hybrid monomer to bridge the gap between silicones and traditional organic polymers

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Ubiquitous in daily life, silicones possess desirable material properties that arise from the unique character of their Si–O bonds. However, the nature of these bonds also renders silicones incompatible with most traditional organic polymers, necessitating improvements in current compatibilization strategies. Here, we examine the fundamental interactions of a novel silicone-containing methacrylate monomer with polydimethylsiloxane and poly(methyl methacrylate). Well-defined block, random, and block-random copolymer libraries of these three building blocks were synthesized and characterized. Specifically, to elucidate the effect of varying hybrid monomer content on the material properties of these copolymers, differential scanning calorimetry, small-angle X-ray scattering, and rheology were employed.
Branching anionic polymerization of cyanoacrylate without suppressing its high reactivity: A practical approach

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Cyanoacrylate constitutes a large portion of the adhesive market, owing to its capability to easily polymerize into a strongly adhering film. Such reactivity of cyanoacrylate, however, presents a double-edged sword. While it enables a practical and efficient polymerization method, the monomers typically polymerize rapidly into linear chains with broadly distributed molecular weights, indicating complications toward forming other polymer topologies and achieving control over the reaction. Previous efforts depended upon facilitating radical polymerization by deliberately suppressing the monomer reactivity, thereby losing the practical features of cyanoacrylate. We expanded the toolbox of polymerizing cyanoacrylate by developing a method of branching anionic polymerization that exhibits the practicality required for its utility as an adhesive material. We introduced a synthetic procedure, wherein cyanoacrylate is copolymerized with a comonomer that, after a polymerization-induced chain transfer, is converted into a branching junction. We demonstrate that the method promotes a rapid branching process and control of the molecular weight and branching density. Ongoing investigations based on these results suggest opportunities for obtaining properties that remain untapped by traditional adhesives.
Ordered mesoporous carbons (OMCs) exhibit utility in a vast range of applications including energy storage, adsorption/separations, drug delivery, and heterogeneous catalysis. However, conventional synthetic methods for OMCs prevent their large scale production due to inherent costs, complexity, and limited pore sizes. Recently, the synthesis of OMCs from commodity thermoplastic elastomers through a majority phase selective sulfonation-induced crosslinking reaction has been demonstrated as a simple fabrication method with potential for scaled processes. The crosslinking reaction, which enables the conversion of the majority phase into a carbon matrix, results in distinct sulfonation and crosslinking reactions which occur simultaneously within the nanostructured polymer and dictate the pore texture of the final product. This work deconvolutes the contribution of each reaction on the nanostructural changes of the precursor during nonequilibrium processing through altering reaction kinetics. This is achieved by varying processing temperatures or precursor identities to isolate the contributions from distinct sulfonation and crosslinking reactions. In turn, these results can assist in the rational design of precursors and processing methods for the use of thermoplastic elastomers in the synthesis of OMCs.
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Novel poly(vinylpyridine N-oxide)-based block copolymers with highly immiscible segments

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Block copolymers exhibiting a high Flory–Huggins interaction parameter (high $\chi$) have attracted considerable attention because of their potential in forming microphase-separated domains with very small feature sizes (<10 nm) useful for next-generation lithography. Here, we report the synthesis, characterization, and self-assembly of poly(styrene)-block-poly(2-vinylpyridine N-oxide) (PS-b-P2VPNO) and poly(styrene)-block-poly(4-vinylpyridine N-oxide) (PS-b-P4VPNO) block copolymers. These PS-b-PVPNOs were obtained from the oxidations of their precursors, poly(styrene)-block-poly(2-vinylpyridine) (PS-b-P2VP) and poly(styrene)-block-poly(4-vinylpyridine) (PS-b-P4VP), respectively. The PS-b-PVPNOs exhibit enhanced block incompatibility as revealed by ordered cylindrical and lamellar structures in the sub-10 nm scale from copolymers with low molecular weight. For several samples, the respective non-oxidized precursor copolymers remained disordered. This highlights how the facile oxidation and respective increase in the dipole-moment of the vinylpyridine N-oxide segments lead to an increased immiscibility with polystyrene. The morphologies and periodicities of the ordered structures were determined by small-angle X-ray scattering, while atomic-force microscopy was used to image the self-assembly in thin films. Our results demonstrate that PVPNO-based block copolymers are versatile candidates for nanopatterned structures with small feature sizes critical for the future microelectronics industry and beyond.
Direct synthesis of ultra-highly branched polyethylene materials via controlled chain walking polymerization

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Polyethylene (PE) is the most widely used commodity resin with versatile advantages, including facile processing, low-cost production and excellent mechanical properties. The type and amount of branching are the most important factors determining the macroscopic physical and chemical properties of PE materials. Recently, the chain-walking polymerization process can produce linear, branched, and even hyperbranched PEs from a sole ethylene feedstock without requiring high-cost α-olefin comonomers. In this report, a family of α-diimine Ni(II) and Pd(II) catalysts with a dibenzobarrelene backbone and axial flexible cycloalkyl substituents has been designed and synthesized. Unexpectedly, the cyclohexyl Ni(II) catalyst generated ultra-highly branched polyethylenes with stable branching density unaffected by changes in polymerization conditions. The resulting ultra-highly branched polyethylenes also known ultra-low density polyethylene (PE-ULD) were the newest and most recently commercialized member of polyethylene family, primarily used as a modifier for blending with other resins.
Fused macrocycle-cage molecule for nanoporous membranes

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Polymer membranes have drawn increasingly more attention due to their broad applications in water purification and molecular separation. However, it remains challenging to get polymeric membranes with high selectivity and permeance simultaneously. Making high-performance polymer membranes requires precise control of nanoporous structures with atomic precision. Macrocycles and molecular cages are ideal building blocks for making membranes because they have well-defined, intrinsic nanopores, and tend to have specific affinity to different molecules via host-guest interaction. Here I will present the design and synthesis of a new nanoporous molecule made by fusing three macrocycles and one molecular cage together. This molecule was synthesized by imine condensation between a dialdehyde linker and a molecular cage, yielding a unique three-dimensional structure. By converting imide into amine, we can polymerize this structure with 1,3,5-benzenetricarboxylic chloride and build a polyamide membrane with high mechanical strength and pore density. I will show the applications of this polymer membrane for molecular separation.
Direct arylation polycondensation of β-fluorinated bithiophenes to polythiophenes: Effect of side chains in C–Br monomers

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This study synthesized six polythiophenes (PThs) using direct arylation polycondensation (DArP). The C–H monomers employed were β-fluorinated bithiophenes, including 4,4'-difluoro-2,2'-bithiophene (2FBT) and 3,3',4,4'-tetrafluoro-2,2'-bithiophene (4FBT). The C–Br monomers employed were 5,5'-dibromo-2,2'-bithiophenes DCBT-2Br, DABT-2Br, and DTBT-2Br that carry alkoxy carbonyl, alkyl and alkylthienyl side chains at 4,4'-positions, respectively. Both 2FBT and 4FBT are highly reactive for DArP. Successful syntheses of high molecular weight (Mₙ) PThs without any observable defects were achieved using 2FBT/DCBT-2Br, 2FBT/DABT-2Br, 2FBT/DTBT-2Br and 4FBT/DTBT-2Br monomer pairs. However, DArPs of 4FBT with DCBT-2Br and DABT-2Br resulted in C–H/C–H homo-coupling defects along with lower Mₙs. The formation of the defects was found to follow the C–Br reduction provoked C–H/C–H homo-coupling mechanism, which is also responsible for the depressed Mₙs. Detailed theoretical calculations revealed that the side reaction was caused by the poor selectivity between the cis- and trans-forms of transition states in concerted metalation-deprotonation (CMD) processes of 4FBT/DCBT-2Br and 4FBT/DABT-2Br monomer pairs. The findings of this research indicate that relying solely on a C–H monomer with high reactivity and regioselectivity is inadequate to achieve well-defined conjugated polymers through DArP. This study highlighted the importance of the C–Br monomer structure in influencing the catalytic cycles of DArP.
Elasticity modulation of hydrogen bond-tethered near-amorphous conjugated polymers

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Intrinsic stretchable CPs are particularly promising in flexible electronics due to their potential for low-cost, large-area printing, and high-density device processing. Although non-covalent crosslinking was widely accepted for enhancing the mechanical properties of CPs, the comprehensive understanding of the influence of non-covalent crosslinking bonding strength on mechanical properties, especially elasticity, is still lacking. This work incorporated various strengths of hydrogen bonds as non-covalent crosslinking in side chains of high molecular weight indacenodithiophene-based polymers to further unravel the bonding strength-elasticity relationship (Figure 1). CPs with different functional groups led to quite different mechanical properties. Large steric hindrance and flexible functional groups without non-covalent crosslinking sites had a typical plasticizing effect but no obvious influence on electrical and mechanical properties. While weak hydrogen bond forming groups of small steric hindrance was introduced, the elasticity of the CPs was gradually enhanced, along with slightly lowered charge mobilities, particularly in the case of high hydrogen bond density. Further improving the crosslinking bonding strength and rigidity of groups, an apparent increase in elasticity (plastic deformation onset >40%) along with a decrease in charge mobility and ductility with crosslinking density could be observed. After systematically studying the structure-property correlations, we observed that non-covalent crosslinking between high-density, weak strength and low-density, high strength (the orange region in Figure 1) has the potential for the enhancement of elasticity of CPs without drastically sacrificing their stretchability and mobility. This work demonstrated that the rational incorporation of non-covalent crosslinking may offer an opportunity for the preparation of high-performance intrinsically stretchable semiconductors.
RAFT synthesis of polymers for regulating fluid loss in water and oil-based drilling fluids

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This study presents the synthesis and characterization of a class of polymers that can be utilized as a fluid loss control agent in either water or oil-based drilling fluids. The polymer was designed using hydrophilic and lyophilic monomer functionalities to create blocks with a tunable hydrophilic-lyophilic balance (HLB), which was optimized using a synthetic molecular approach. Then the synthesized block copolymer was crosslinked to form a star-like architecture.

The star polymers were synthesized using Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization. The structure properties of the polymers were characterized using various techniques including FTIR, NMR, GPC and SEM. The thermal stability of the polymer was also investigated with TGA-DSC.

Performance of these polymers were tested as a fluid loss control additive for non-aqueous fluids (NAFs) as well as aqueous fluids used in high-temperature drilling operations. The results showed that the star polymer exhibited high performance in reducing fluid loss and generating a thin filter cake.

The study demonstrates the potential of using star block polymers for fluid loss control in water and oil-based drilling fluids, which could lead to improved drilling efficiency and reduced environmental impact. Furthermore, photopolymerization utilizing UV lights can also yield the star polymer and necessitates less energy expenditure compared to thermal methods. The results in this study offer valuable perspectives for creating novel and enhanced additives for drilling fluids, which can promote sustainability in the drilling sector. Lastly, the limitations of scaling up the polymer synthesis using photochemistry are discussed.
Impact of mathematical models on the accuracy of analysis of high molecular weight polymers by multi-angle light scattering

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Comprehensive characterization of the materials has a crucial role in achieving a sustainable future development. Multi-detector separation chromatographic techniques such as size exclusion chromatography (SEC) are widely utilized methods for polymer characterization. In this context, the use of multi-angle light scattering (MALS) detection allows fundamental relationships between intra- and interparticle characteristics of the material to be captured and quantified and offers valuable information on the molecular weight distribution, as well as details on chain conformation and structure.

The effects of various data processing parameters on the accuracy of computed results were investigated in the analysis of high molecular weight polymers chosen as case studies. Thus, benefits and drawbacks of different fitting algorithms for determination of the mass distribution from light scattering - Berry, Zimm, and Debye - were compared, with various angular intervals used for the data extrapolation. Good correlation between mathematical formalisms and experimental data is imperative for robust and reliable analysis, especially in the case of large molecules.
New insights into coacervation: self-assembly of zwitterionic polysulfobetaine for multifunctional applications

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Self-assembling through coacervation is a simple process where oppositely charged polymers are brought together in an aqueous solution. This process involves a liquid-liquid phase separation that can be controlled by external factors such as pH, temperature, salt, or polarity. It has gained attention for various applications in the biomedical, coating, adhesives, personal care, and encapsulation fields. Here, we present our research on zwitterionic polysulfobetaine with a tertiary amide spacer that can self-assemble spontaneously to create coacervate microdroplets. By incorporating a hydrophobic backbone and a non-polar tertiary amide spacer between ionic groups, we have achieved a unique self-assembly process that forms coacervates as a single component without any additives, similar to mussel foot protein and tropoelastin. We also discuss how the polysulfobetaine can form reversible coacervates in the presence of salt and temperatures and how the spherically hydrated coacervates can physically entrap hydrophobic actives and trigger release upon physiological salt conditions. Our finding suggests that this robust and straightforward polysulfobetaine coacervating microcapsule, with its multifunctional properties, presents an exciting alternative to complex coacervation involving multiple components.

Spontaneous self-coacervation of zwitterionic polysulfobetaine
Polyethylene (PE) based food packaging film: Recyclable, unitary material composition, manufacturing processes, methods, and characteristics

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Due to the food easily deteriorating in the external environment, packaging materials and containers are used to maintain or extend the expiration date. Materials such as paper, polymer, metal, and glass are used to package foods. But the film materials using polymer resins have disadvantages in that they have lower external environmental barrier properties than other materials. Additionally, various polymer resins are blended to satisfy moisture (H₂O) and oxygen (O₂) gas barrier properties, which are required physical properties for food storage. For this reason, recycle of multi-material films can be especially difficult. In this study, polymer processing and test analysis were performed to improve the reusing of packaging materials. We used polyethylene (PE) resin as unitary material composition, and films were produced through a melt extrusion process. After the fabrication of samples, we analyzed the physical properties. By laminating the polyethylene film with multiple thin films, it can be manufactured thinner than a general polymer film in terms of film thickness, which increases flexibility. And it showed stable maintenance gas barrier characteristics even after physical deformation. The water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) decreased as the mechanical extensibility of the polymer film increased. Finally, we plan to use this study for future research on BOPE film materials.

Environmental issues of common packaging materials and advantages of BOPE packaging materials

Extrusion process and conditions
Aqueous solution properties of linear and star poly(2-hydroxyethyl acrylate)-based polymers: from RAFT-PISA or solution RAFT polymerization

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In this work, linear and star PHEA polymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in dimethylformamide (DMF) at 70 °C, using a RAFT agent trithiocarbonate-type. PHEA polymers were used to prepare block copolymers mediated by two strategies of synthesis (Figure 1). Subsequently, aqueous solution properties were studied.

The first strategy is “RAFT-PISA”, cholic acid-derived monomer (CAE) was used in the chain extension of linear PHEA homopolymer (l-PHEA) by polymerization-induced self-assembly (PISA) in ethanol/water mixture at 70 °C. Following this strategy were obtained nano-objects as spheres (diameters: 114 to 124 nm) and vesicles (diameters: 92 to 163 nm and membrane thickness: 29 to 36 nm) at a solid content of 8% and 11% (for ethanol/water 45:55, v/v), respectively.

The second strategy is “solution RAFT polymerization”. Firstly, aqueous solution properties of star PHEA homopolymers (s-PHEA) with dodecyl and carboxylic acid end-groups were studied. PHEA homopolymers with dodecyl end-group are not water-soluble when degree polymerization (DP) is 7 per arm. PHEA polymers with DP of 33 per arm can be dispersed in distilled water, forming large aggregates with $D_H$ of 1051 nm, but when DP is raised at 85 per arm, PHEA polymers were water dispersible forming stable aggregates with $D_H$ of 525 nm. On the other hand, PHEA homopolymers with carboxylic acid end-group were totally water-soluble. Next, s-PHEA-TTC homopolymers were chain-extended with N-isopropyl acrylamide (NIPAM) in DMF by RAFT. The aqueous solution properties of s-PHEA-b-PNIPAM were similar to its corresponding PHEA polymer. In addition, lower critical solution temperature (LCST) was estimated for PHEA-b-PNIPAM copolymers. Even if the molecular weight of the PHEA or PNIPAM block is modified, LCST was 32 °C and 34 °C for the block copolymers from dodecyl and carboxylic acid end-group, respectively.
Substituted Poly(para)phenylenes: Where is the Journey going?

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Poly(para)phenylenes (PPPs) were one of the most prominent and desired classes of conjugated polymers, during the 1990s and early 2000s. Even though they have been heavily investigated for different applications, they are now carving out a niche existence. We believe that this partial decline of interest has come from the obstacle of synthesizing high-molecular weight, processable, and defect-free (functional) PPPs as well as the limited performance in preliminary application studies.

Besides the utilization of substituted PPPs as emissive layer in organic light-emitting devices (OLED), they also possess promising properties for the application as ion-conducting solid-state electrolytes in all-solid-state batteries and proton-exchange fuel-cells. Other promising applications fields of substituted PPPs comprise sensing, catalysis as well as theranostics.

Recently, data mining and AI have taken the masses by storm by streamlining daily tasks but also for solving complex scientific problems. For example, data mining and machine learning were successfully used in synthetic chemistry to screen for synthetic optimizations and new catalyst designs. This progress will continue further and will undoubtedly find utility in the creation and optimization of new routes towards innovative functional polymers structures which are currently the largest hurdles for implementing new technologies into industrial applications.

As we have now gained a more profound understanding of these applications as well as optimized synthesis routes towards high-molecular weight PPPs, data mining and AI would be the next step bringing PPP-research back to the 21st century. On the upcoming ACS meeting in San Francisco, I would like to talk about recent PPP-synthesis approaches as well as their future prospects in innovative applications.
Tandem ring-opening and ring-closing metathesis polymerization of cyclopentenes containing terminal alkyne

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Tandem olefin metathesis is a metathesis reaction in which more than one olefin transformations simultaneously occurring in a single step reaction.¹ In this work, we studied one-pot tandem metathesis polymerization of a series of 1-propargyl-1′-carboxylate ester monomers derived from 3-cyclopentene using ruthenium-alkylidene based metathesis initiator (Scheme 1). A detailed DFT calculations and end group analysis using ¹H NMR experiments have been performed to investigate the catalytic mechanism of the metathesis reaction. The energy profile obtained from DFT analysis provides two pathways for the polymerization of monomers having both cycloalkene and alkyne functionalities. The most stable coordination of monomer was found to be via a π-coordination to the triple bond, which is oriented perpendicularly to the ruthenium-alkylidene bond. Both cycloalkene- and alkyne-initiated polymerizations were found to be feasible pathways. However, the alkyne-initiated polymerization mechanism was found to be the preferred pathway and the slightly lower rate-determining step barrier. In addition, the synthesis of the model compound supported our proposed polymerization mechanism as well as the position of the styrene end-group on the polymer chain.² Details of all these results will be presented.

Scheme 1. Tandem ring-opening and ring-closing metathesis polymerization of cyclopentene containing terminal alkyne
Cataracts turn the human ocular lens cloudy or opaque, and eventually, impaired vision will interfere with daily activities. The NIH National Eye Institute and WHO have identified cataracts as a cause of vision loss in one of six Americans over the age of 40, and notably, the risk of cataract formation increases exponentially with age. Surgery is needed to treat cataracts and usually includes two parts: removal of the clouded lens using phacoemulsification techniques and implantation of an intraocular lens (IOL). During the surgery, ophthalmic viscosurgical devices (OVDs, viscoelastic polymers) are used to protect the corneal endothelium from ultrasonic vibration and to keep the capsular bag inflated to implant the IOL. Therefore, a dispersive OVD (with high coatability) in the first step and a highly cohesive OVD (entangled and removed from the eye as a single mass) in the last step are needed. The dispersive OVD tends to remain in the eye within the corneal concavity, can clog the eye’s drainage system, and cause a spike in intraocular pressure (IOP). These IOP spikes can damage the optic nerve and result in vision loss and blindness after cataract surgery. It has been difficult to track down the remaining OVDs since all commercial OVDs are clear and colorless. Our work is to design and synthesize optically clear and fluorescent OVDs under visible light for cataract surgery. By detecting fluorescent OVDs in the anterior chamber and the capsular bag, the remaining OVDs can be completely aspirated after the surgery to avoid any postoperative complications. We tether a fluorescent dye (Cy3 and fluorescein) to a chain transfer agent and synthesize the polymers through RAFT polymerization using OEGMA-based macromonomers and yield fluorescent polymeric viscoelastics.
POLY 3907047

ROMP of a nitroso-Diels-Alder adduct leads to amino-and hydroxyl-functionalized "polyolefins"

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Recent research from our laboratory described the use of a nitroso-Diels-Alder (NDA) reaction to prepare new monomers for ring opening metathesis polymerization (ROMP) reactions. The resulting materials could then undergo hydrogenation and reductive cleavage of the N-O bond to provide amino and hydroxyl group-functionalized polymers. This poster describes the extension of this work toward the preparation of polar group-functionalized "polyolefins". This was achieved by the polymerization of an NDA-derived monomer with cyclooctene. Following hydrogenations, these polymers were subjected to reductive cleavage, leading to new polar group-modified saturated polymers.
Effect of oligo (ethylene oxide) functionalization on the phase behavior of two bicontinuous cubic lyotropic liquid crystal monomer platforms

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Bicontinuous cubic (Q) lyotropic liquid crystal (LLC) monomer systems are polymerizable amphiphiles that self-organize into ordered assemblies with 3D-interconnected nanopores that, upon cross-linking, create an organic material capable of molecular-size-separation. The cross-linkable gemini (i.e., joined 2-head/2-tail) and fishhook (i.e., 1-head + sidearm/1-tail) ionic LLC monomer platforms, originally developed by our research group, form a Q phase upon addition of a polar solvent, and can then be photo-cross-linked into 3D polymer networks. The high density of polar headgroups within the hydrophilic nanopores makes these Q-phase networks highly desirable materials for the incorporation of functionality into the headgroup of the amphiphilic monomer. To date, there is only one reported example of a functional Q-phase monomer system and a Q-phase network in the literature. Herein, we describe the design and synthesis of new oligo(ethylene oxide) derivatives of the gemini and fishhook ionic LLC monomer platforms to study the effect of structure and function modification on both the overall LLC phase behavior, and ability to retain the Q phase. This work will present methods to design and synthesize new functional Q-phase LLC monomer derivatives as well as discuss possible applications of these novel functional monomers. Incorporating ethylene oxide groups into these Q-phase LLC monomer designs has the potential for adding enhanced ion conductivity and anti-fouling properties to the final polymer material for membrane applications, while retaining the unique advantages provided by the formation of a Q-phase network.
Synthesis of a catenane via the exchange reactions of bis(hindered amino)disulfide linkages and its polymerization

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A catenane is known as a molecule consisting of two or more interlocked macrocycles, showing characteristic rotational motion. Derived from its unique topology and supramolecular interaction between two or more macrocycles, polymeric materials with catenated structure have flexibility, stimuli responsiveness, and unique energy dissipation. To access such materials in an easy way, we need a more universal and simple cyclization method that can introduce various functional groups and molecular structures.

We have selectively isolated macrocyclic compounds which have bis(2,2,6,6-tetramethylpiperidin-1-yl) disulfide (BiTEMPS) structures recently. The disulfides of BiTEMPS units can exchange with one another by heating around 100 °C. We can convert linear precursors containing BiTEMPS in their repeating unit or at both ends to the corresponding entropically favorable macrocycles spontaneously upon heating. The high functional tolerance of BiTEMPS introduces various structures into macrocycles.

In this study, we obtained a catenane from a rotaxane with BiTEMPS units at both ends. This approach requires only heating and produces a thermally dynamic catenane, achieving efficient synthesis of catenane structure. In addition, obtained catenane can be polymerized by just heating under concentrated conditions to produce polyrotaxanes or polycatenanes.

Figure. (a) This work. (b) Structure of [3]catenane. (c) Synthesis of [3]catenane. (d) ESI-TOF MS of [3]catenane.
POLY 3914789

Understanding the impact of vinyl and allyl species in the decrease of telogen content in transfer-dominated branching radical telomerisation

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The formation of hyperbranched polymers (HBPs) via conventional free-radical strategies has received much attention in polymer science. Transfer-dominated Branching Radical Telomerisation (TBRT) is a novel polymer technology employed for the synthesis of complex high molecular weight HBPs via conventional chain-growth chemistries whilst yielding architectures with step-growth characteristics. TBRT centres on the repeated telomerisation of multi-vinyl monomers (MVMs) in the presence of a molar excess of telogen in attempt to avoid termination and loss of radical species whilst avoiding propagation to DPₙ >2 to avoid infinite cross linking (gelation).

Alkyl thiols are commonly employed as telogens due to the presence of the weak S-H bond. Although the use of thiols gives arise to concerns over biological compatibility for medicinal applications along with their hazards, odour and difficult purification steps.

The concept of reactivity ratios was investigated to assess if vinyl acetate (VAc) and allyl phenyl ether (APE) can act as retarding agents and limit the propagation of a growing polymer chain by increasing the lifetime of the radicals present to promote further chain transfer.

The impact of these materials was studied for both traditional telomerisation and the TBRT mechanism. The effect on the DPₙ and molecular weight of the resulting polymer structures was monitored to see if they can provide a route for the reduction of telogen concentration in TBRT. TBRT mechanisms at a constant [MVM]₀/[Telogen]₀ ratio displayed a characteristic decrease in the molecular weight with an increase in the ratio of additive in the system (Fig. 1). These results consequently resulted in the ability to reduce telogen content without triggering gelation during TBRT.

Fig. 1: Comparative relationship between molecular weight and varying [Additive]₀/[EGDMA]₀ feedstock ratio for VAc (green) and APE (blue) with EGDMA employed as the MVM.
Understanding the influence of different chemical strategies on transfer-dominated branching radical telomerisation (TBRT) and the production of novel hyperbranched polymers

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Transfer-dominated Branching Radical Telomerisation (TBRT) is a new synthetic strategy for the preparation of high molecular weight branched polymers exhibiting step-growth characteristics but using conventional chain-growth free-radical chemistries. TBRT utilises the radical telomerisation of multivinyl monomers, or taxogens (MVTs) in the presence of an excess of telogen, commonly an aliphatic thiol, to facilitate the formation of fully-soluble hyper-branched polymers to >99% vinyl conversion. Additionally, copolymerisation offers access to physical properties often unattainable by homopolymerisation, and is achievable through the mixing of co-MVTs, co-telogens, or by introducing monofunctional co-monomers to the telomerisation.

A series of branched polymers incorporating variable telogen functionalities have been prepared via TBRT. Mayo experiments were performed to determine the chain transfer coefficients, $C_T$, of each telogen and the results correlated to observed differences in the formation of infinite cross-linked networks (gelation). Ultimately, by mixing telogens with significantly different $C_T$ at varied concentrations, the resulting branched polyesters showed composition dependent effects on branching behaviour during TBRT (Figure 1). This demonstrated the ability to control and prevent gelation by mixed telogen co-polymerisation.

The scope of the macrostructures generated by this approach is vast and understanding the factors that influence polymer properties is fundamental to the understanding of TBRT. A library of materials has been prepared in order to study the relationship between polymer composition and solubility. The resultant copolymers, demonstrating varying hydrophilicities, were assessed in a range of solvents and the solubilities subsequently quantified. The hyperbranched polymer structures produced by TBRT demonstrate readily tuneable physical properties that can be exploited to generate novel materials in an industrially applicable process.

Figure 1 Schematic representation of the functional variation in branched copolymers derived from mixed-telogen copolymerisation.
Due to its toughness and ability to degrade under physiological conditions, polycaprolactone (PCL) is a widely used material within the biomedical industry with a wide range of applications from drug delivery to the 3D printing of surgical implants. This has subsequently led to interest within Transfer-dominated Branching Radical Telomerisation (TBRT) and the opportunities that polycaprolactone dimethacrylate (PCLDMA) offer. TBRT follows free-radical chain-growth chemistries that allows the formation of high molecular weight branched polymers with properties that can be tuned through the careful management of the reaction conditions.

PCLDMA has been studied using a range of TBRT reaction conditions, from bulk reactions through to dilute solvent conditions. High molecular weight branched PCL has also been formed with the inclusion of epoxy functionality to allow curing to take place, using the addition of sebacic acid as a curing agent at temperatures of 150°C for 2.5 hours.

Figure 1: (a) TBRT reaction scheme for the epoxy functionalisation of PCLDMA with dodecanethiol as the chain transfer agent. (b) PCLDMA polymer cured on microscope slide at 150°C for 2.5 hours.
Vitamin E (tocopherol) is an essential antioxidant compound found in food, pharmaceutical, and personal care products used to stabilize formulations against the lipid peroxidative effects of free radicals. The utilization of this compound and its derivatives is of interest across a breadth of industries and research areas for its ability to extend the shelf-life of oil-based products. Furthermore, the hydrophobic, self-assembling properties of tocopherol are utilized for drug delivery in research settings to treat cancer and age-related memory disorders.

Polymers based on bioactive small molecules exploit the activity of the compound while offering the enhanced stability or controlled degradability intrinsic of polymeric macromolecules. In this study, we offer a polymeric biomaterial based on Vitamin E. We have investigated synthetic strategies to modify a Vitamin E derivative, tocopherol succinate, leading to the development of an acrylate-functionalized monomer which can undergo free-radical polymerization. The resulting polymeric macromolecule is investigated to determine molecular weight, degradation, and antioxidant behavior in a model environment. This study demonstrates the utility of poly(tocopherol) compounds to impart antioxidant activity in various applications.

Vitamin E succinate can be modified to create polymers with utility in scavenging free radicals. a) A facile synthetic route involves the functionalization of tocopherol succinate with hydroxyethyl acrylate using a Steglich esterification scheme. Upon purification, this monomer can be further polymerized using standard free-radical polymerization reagents. b) This material can be used to study polymer degradability and radical scavenging capabilities in a model environment.
Improving food and vaccine safety: A temperature-sensitive indicator for cold supply chains

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The cold supply chain is an indispensable part of our daily lives, particularly during the ongoing COVID-19 pandemic. Thermal exposure management is a critical concern for the supply chains of vaccines and perishable foods. With the rise of a contactless society, the demand for cold-chain transportation has increased, and it remains relatively safe today. But consumers remain concerned about the safety of their food and vaccine due to potential heat exposure during the consignment process.

This study introduces an innovative application for verifying the thermal exposure history of materials. The time-temperature indicator (TTI) developed in this work is a nano-/micro-fiber cluster based on thermoplastic urethane (TPU). Our TPU material features a self-healing characteristic through intermolecular hydrogen bonding and a metathesis reaction between disulfide groups. When fibers exposed to heat become active and interact with each other, they begin to fuse, causing the opaque non-woven mat to become a transparent film. This phenomenon is suitable for TTI applications due to its temperature sensitivity and irreversibility, making it difficult to manipulate intentionally.

The activation temperature range of the TTI can be adjusted by switching the composing monomer as a soft segment, which affects the glass transition temperature. Additionally, we found that the self-healing behavior can be controlled without altering the type of monomer. Our TPU is synthesized through a two-step reaction: 1) the reaction of diisocyanate with polyol and 2) the reaction of the product from step 1 with a chain extender. The injection rate of the diisocyanate solution and the degree of dilution of the polyol solution affect the viscosity of the TPU solution and thus the self-healing time at different temperatures.

Overall, our TTI offers a practical and effective solution for verifying the thermal exposure history of materials in the cold supply chain system, with the potential to improve food safety and vaccine efficacy for consumers. The facile method of TTI synthesis also enhances the availability of this technology.
Evaluation of biobased solvents for the synthesis of poly(2-oxazoline)s and poly(2-oxazine)s by cationic ring-opening polymerization

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The rising interest in poly(2-oxazoline)s and poly(2-oxazine)s, fueled by their multifaceted properties like biocompatibility, stealth behavior and thermoresponsivity, is bringing these polymers closer to industrial scale production, where process sustainability is becoming an increasing concern. Today, acetonitrile is a well-established solvent at the laboratory scale for the synthesis of these polymers due to the excellent control it provides over the polymerization process.

In the perspective of granting these polymers a further competitive advantage, we studied the polymerization of 2-ethyl-2-oxazoline, 2-ethyl-2-oxazine, and 2-phenyl-2-oxazoline in bio-derived, high boiling solvents like dimethyl isosorbide (DMI), representing the greener alternative to acetonitrile, maintaining the polymerization temperature (140 °C), initial monomer concentration (3 M or 4 M) and targeted degree of polymerization (DP = 60) constant. We confirmed the livingness of the polymerization of these monomers in DMI by kinetic measurements and a comparable level of chain transfer with acetonitrile by size exclusion chromatography measurements. In summary, DMI proved to be a promising bio-based solvent for the cationic polymerization of 2-oxazolines and 2-oxazines.
Homo- and co-cyclopolymer containing symmetrical motifs of (diallylammonio)diacetate

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Reaction of (H₂C=CH(CH₂)₂NCH₂CO₂Na with ClCH₂CO₂Na afforded zwitterionic-anionic (H₂C=CH(CH₂)₂N+(CH₂CO₂⁻)CH₂CO₂⁻Na⁺ (I) and cationic monomer [(H₂C=CH(CH₂)₂N⁺(CH₂CO₂H)₂ Cl⁻] (II). I and II underwent cyclopolymerization to give polyzwitterion-anion (PZA) III and polyzwitterion (PZ) IV, respectively. Monomer II/SO₂ and II/maleic acid pairs upon copolymerization led to zwitterionic poly[(II-HCl)-alt-SO₂] (PZS) V and poly[(II-HCl)-alt-maleic acid] (PZM) VI, respectively. III-VI having repeating units containing residues of iminodiacetic acid [NH(CH₂CO₂H)₂] have been tested as antiscalants and corrosion inhibitor. As an antiscalant, PZM VI at 1 ppm imparted 99% inhibition of CaSO₄ scale formation from a supersaturated solution of Ca²⁺ and SO₄²⁻ for a duration of 40 min, enough to safeguard desalination membranes from scale fouling. PZ IV (100 ppm) combined with KI (400 ppm) demonstrated a synergistic 93% corrosion inhibition of mild steel in 15% HCl for 6 h at 60 °C. The polymers may find applications in desalination as antiscalants and oil well acidization as corrosion inhibitors.
GCMS-HS and Py for polymer compatibility studies

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Gas chromatography mass spectrometry (GCMS) is a powerful capability that can be utilized to identify and verify complex compounds. Samples can take the form of a solid, liquid, or gas, making this a diverse instrumental technique. Paring GCMS with headspace (HS) and pyrolysis (PY), we are able minimize sample sizes and maximize instrument sensitivity. The combination of these techniques will be used to perform multiple material compatibility studies and identify degradation pathways of various polymers.
Preparation of novel nanosized polyelectrolyte brushes based on macromolecular photoinitiator

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Nanosized polyelectrolyte brushes are widely used in tumor imaging, targeted drug delivery, nanoreactor and other fields due to their small diameter, large specific surface area and sensitivity to the surrounding environment. The traditional spherical polyelectrolyte brushes use polystyrene (PS) with a diameter of ca. 100 nm as the core, which is covered with the photoinitiator 2-[p-(2-hydroxy-2-methyl-propio-phenone)]-ethylene glycol-methacrylate (HMEM), and then are grafted with polyelectrolyte chains. In this study, a macromolecular photoinitiator was prepared by emulsion polymerization and directly grafted acrylic acid (AA) on it to form nuclear-free polyelectrolyte brushes. The size of the non-nuclear brush is about 60 nm as determined by dynamic light scattering (DLS), small angle X-ray scattering (SAXS) and TEM, which is much smaller than traditional spherical poly(acrylic acid) brushes with PS core. By changing the ratio of photoinitiator to polyelectrolyte chain, the grafting density and brush thickness can be tuned, which laid a foundation for the application of nano-sized nuclear-free polyelectrolyte brushes. The columnar brushes were also prepared by solution polymerization using macromolecular photoinitiator and grafting polyelectrolytes.

Figure 1. Polymerization of photoinitiator and synthesis of polyelectrolyte brushes.
Visible-light-mediated controlled radical branching polymerization in water

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Synthesis of hyperbranched polymethacrylates were carried out by green-light-induced atom transfer radical polymerization (ATRP) under biologically relevant conditions in the open air. This is the first example of a controlled radical branching polymerization in water using inibramer chemistry using sodium 2-bromoacrylate (SBA) as a water-soluble inibramer. Well-defined branched polymethacrylates were obtained in less than 30 min with predetermined molecular weights (36 000-170 000), tunable degree of branching, and low dispersity values in one pot. Moreover, due to the high oxygen tolerance of EY/Cu-catalyzed ATRP, polymerizations were carried out under fully open-air conditions with stirring. This versatile approach exhibited spatial control and enabled the synthesis of hyperbranched polymer bioconjugates with well-defined polymer architecture.
Covalent adaptable networks (CANs) are dynamic crosslinked polymer networks that undergo bond exchange reactions under certain conditions, resulting in reversible transitions between thermoset-like rigidly crosslinked materials and viscous, flowing states more similar to thermoplastics. Guanidine-based CANs engage in a dynamic, dissociative exchange reaction at elevated temperatures above the glass transition. As a result, rheological properties of these CANs can be measured by exposure to temperatures between the glass transition and degradation, allowing for the quantification of material changes occurring due to activated dynamic reactions. $N,N',N''$-trisubstituted guanidine CANs were synthesized by combination of amine-containing crosslinker molecules and multifunctional oligomers possessing carbodiimide functionalities. Crosslink density was manipulated by variation in loading of difunctional and monofunctional amine crosslinkers. In order to quantify the effects of varied crosslink density on rheological properties of guanidine CANs, a series of stress relaxations was performed alongside frequency sweeps. The results of this work will be presented.
InsectERA: Converting cultured insect exuviae into valuable biopolymers

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Extracting valuable platform chemical from waste biomass is a crucial part of the path to developing a circular, sustainable materials economy. As a particular example, recent developments at the insect biorefinery - utilization of insect biomass - are herein discussed. The focus will be placed on the valorization of one of the most abundant, natural polysaccharides, chitin, a linear polymer composed of repeating β-(1,4)-N-acetylglucosamine units. Chitin can be extracted from solely black soldier fly (BSF) exuviae, currently considered the only waste in the fly life cycle, as it has no valuable application so far. The extraction of chitin from BSF exuviae is accomplished by demineralization followed by deproteinization and discoloration. The extracted chitin is then transformed into chitosan by deacetylation (73%), which is mostly used to produce biopolymers. Several biopolymers presenting different properties are achieved: from thin films, very malleable, to thicker ones, still malleable or fragile (0.01 - 0.39 N/mm²). In addition, a successful scaling up of the process is accomplished leading to an identical biopolymer, thus representing a potential industrial method to produce sustainable bioplastics.
Synthesis and characterization of thioether-functionalized poly(2-alkyl-2-oxazoline)s for ROS-responsive nanomaterials

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Self-assembling polymers have gained significant attention in recent years due to their ability to form various complex structures. Among these, poly(2-oxazoline)s (PAOx) have emerged as promising candidates for bio-inspired applications such as drug delivery and nanoreactors, owing to their synthetic versatility and ability to form amphiphilic block copolymers. However, amphiphilic polymers containing an oxidation-sensitive building block, such as a thioether moiety, are sensitive to the presence of oxidants like reactive oxygen species (ROS), which can be present in excessive amounts in diseases like cancer-related inflammation. In this study, we report on the synthesis and self-assembly of sulfur-containing poly(ethylene glycol)-block-poly(alkyl oxazoline) (PEG-b-PAOx) copolymers obtained through the reacylation of a polyethylene imine block (PEI) with a series of sulfur-containing carboxylic acids. Aqueous self-assembly of the block copolymers via nanoprecipitation was characterized and studied in depth by a combination of techniques [e.g., ^1^H NMR, size-exclusion chromatography (SEC), dynamic light scattering (DLS), transmission electron microscopy (TEM)]. The results of this study highlight the potential of PEG-b-PAOx copolymers for use in targeted drug delivery and other biomedical applications.
Photo Pisa-mediated synthesis of enzyme-loaded polymeric vesicles with tunable membrane permeability for intracellular cascade reactions

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Biomimetic polymeric vesicles, also known as polymersomes, have garnered significant attention due to their potential applications in drug delivery, diagnostics, and biocatalysis. The membrane permeability of these vesicles plays a crucial role in enabling controlled membrane transport and modulating internal functions that depend on substrate uptake and chemical signaling. However, the regulation of membrane permeability remains a challenge, particularly for the loading of enzymes and the cascade reactions between individual nanoreactors. In this study, we aimed to control the membrane permeability of polymeric vesicles for the loading of different enzymes. To validate the compartmentalization of enzymes within separate vesicles and their interaction in a multistep catalytic process, a model cascade reaction involving nanoreactors containing glucose oxidase (GO) or horseradish peroxidase (HRP) was used. The enzyme-loaded vesicles were prepared through aqueous photo polymerization-induced self-assembly (PISA) of hydroxypropyl methacrylate (HPMA), mediated by photo-iniferter chemistry, utilizing a PEG-modified macro chain transfer agent. Subsequently, we introduced \( N-(2,2,2\text{-Trifluoroethyl}) \) acrylamide to the polymeric chain as a comonomer by seeded photo-PISA. Different types of crosslinker were furthermore employed to adjust the membrane permeability of the vesicles. The self-assembly of the block copolymers was characterized using various techniques, including \(^1H\) NMR, size-exclusion chromatography (SEC), dynamic light scattering (DLS), and transmission electron microscopy (TEM). The results demonstrated that controlling the membrane permeability of polymeric vesicles is crucial for the loading of enzymes and cascade reactions and our synthetic approach provides a viable means of achieving this control.
Bifunctional initiator for ring-opening metathesis polymerization

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Linear block copolymers exhibit versatile and tunable properties, making them crucial for various applications, including biomedical and soft robotics. However, their preparation often involves complex procedures, limited by chemical reactivity and solubility challenges. This study presents a novel bifunctional ruthenium initiator (bifu-Ru) that streamlines the synthesis of linear ABA triblock copolymers by reducing monomer additions and displaying excellent functional group tolerance with different cyclic olefin monomers. The bifu-Ru was synthesized via ligand exchange between a bifunctional organic ligand and tricyclohexyl phosphine (PCy₃) on Grubbs second-generation catalyst (G2), forming a bis-ruthenium Hoveyda-Grubbs type catalyst. This initiator exhibits a unique symmetric polymerization chain growth mechanism from the middle-out, enabling the synthesis of linear ABA triblock copolymers with only two monomeric additions instead of the conventional three required by previous Grubbs catalysts. The bifu-Ru maintains excellent control over polymerization, producing polymers with well-defined structures and enhanced properties. Kinetic studies were conducted to characterize the bifu-Ru by determining conversion and molecular weight of the resulting polymers, demonstrating the initiator's ability to exert strict control over polymerization reactions under optimal conditions. These research findings underscore the potential of the bifu-Ru initiator as a powerful tool for developing next-generation linear block copolymers with tailored properties to meet the demands of emerging technologies, from protective gear to soft and tough biomedical devices.

ABA triblock copolymer synthesis with bifunctional ruthenium initiator.
Considering the huge increase in plastic waste resulting from difficulties in dealing with the end-of-life usage of polymeric materials, there is an urgent need for a new generation of polymers that can be recycled as thermoplastics but still retain the beneficial properties of crosslinked thermosets, mainly high chemical and temperature resistance, dimensional stability. Vitrimers are a recent type of polymeric materials that have the ability to retain their mechanical properties even after being recycled and reprocessed multiple times. This exceptional characteristic of vitrimers is attributed to the existence of reversible dynamic covalent bonds that can be broken and reconnected by external stimuli such as heat, light, or mechanical force. This unique property allows the material to be easily reshaped and recycled.

Herein, we developed novel bifunctional monomers based on biobased D-isosorbide for the synthesis of hard vitrimers. Isosorbide bis(acetylacetone) was synthesized and crosslinked with several multifunctional amines to obtain vinylogous urethane networks. These networks are readily processable/recyclable at higher temperatures (>150 °C). Prepared vitrimers were characterized by several techniques, including DSC, DMTA, and tensile testing. The physicochemical properties of the prepared networks depend on the structure of amines used for crosslinking.
Synthesis, characterization, property, and processing of polyvinyl alcohol bottlebrushes

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Polyvinyl alcohol (PVA) is a water-soluble, non-toxic, biocompatible material that has found a wide range of applications. Due to the challenges associated with the synthesis of polyvinyl acetate (PVAc), the precursor to PVA, the majority of the reported hydrogel materials derived from linear PVA, and materials based on PVA with architectures more complex than linear have been rarely explored. In this work, we developed a general and modular strategy to access PVA bottlebrush polymers and successfully fabricated the corresponding PVA bottlebrush hydrogels. These bottlebrush hydrogels possess distinct rheological properties and interesting processability compared to their linear counterparts.
Self-assembling multidomain peptide hydrogels with histidine functionalized cores

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Multidomain Peptides (MDPs) are a class of self-assembling peptides that rely on supramolecular interactions to create hydrogels from the formation of uniform nanofibers in aqueous solution. They are of interest due to their tunable physical properties, biocompatibility, injectability, and elasticity. MDP self-assembly relies on their ABA motif, where in the A domains contains a hydrophilic, charged amino acid termini that flanks the central B domain containing alternating hydrophilic and hydrophobic amino acids. This allows the peptides to assemble through the sequestering of central hydrophobic residues, as well as capitalizing on the hydrogen bonding between adjacent peptides to adopt a β-sheet conformation. Herein, we substitute histidine in the central B domain of MDPs, which characteristically controls hydrophobic and hydrogen bonding interactions between peptides, to create novel pH sensitive hydrogels. Creating MDPs with histidine substitutions in both canonically hydrophobic and hydrophilic residues allows for pH responsive activity in both the secondary structure self-assembly and fiber formation stages of hydrogel creation. Their structural similarity to enzymatic amyloid peptides also allows for the possibility of esterase abilities.
High sulfur incorporation into sulfur-based hydrogels via inverse vulcanization

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Approximately 70 million tons of elemental sulfur are produced as a byproduct of the petrochemical refinement industry every year; in response to this surplus, sulfur “waste” has garnered scientific interest as an inexpensive, abundant, and sustainable alternative to typical monomers used in polymer synthesis. This research utilizes elemental sulfur to create sulfur-based hydrogels, a novel type of polymer with unique properties suited to many material applications. These hydrogels were synthesized by combining polar monomers with sulfur and garlic essential oil via inverse vulcanization to create a three-dimensional mesh-like hydrogel structure incorporating high quantities of elemental sulfur and sulfide-rich garlic essential oil. Samples high in garlic essential oil swelled up to 645% by weight in pure water, and samples containing 45% elemental sulfur by mass swelled up to 221%. Additionally, these high-sulfur hydrogels retained interaction with water and exhibited limited leaching despite sulfur’s challenging hydrophobicity. Characterization methods including DSC, TGA, GPC, and H1NMR have been used to provide insight into the hydrogel structure. Ongoing efforts aim to incorporate higher sulfur content while maintaining minimal leeching and maximum swelling of these hydrogels.

Reaction scheme of inverse vulcanization of the hydrogel.
Evaluating poly(Anhydride-ester)s’ hydrolytic degradation & encapsulation characteristics for retinol release

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Controlled small molecule release systems represent a growing field that offers many advantages for a multitude of applications such as agriculture, drug delivery, and consumer products. Here, we describe recent developments of novel biodegradable and environmentally-safe salicylic acid-based poly(anhydride-ester)s (SAPAEs) for controlled release of small molecules upon hydrolytic degradation. Previously, our group has shown that SAPAE homopolymers can degrade in the span of months to release salicylic acid, a bioactive material that promotes bone growth, prevents biofilm formation, and shows anti-inflammatory responses in organisms. The degradation and salicylic acid release rate of these polymers can be modified by altering their chemical composition through co-polymerization with other linker molecules to increase the polymers’ hydrophilicity. Copolymerization allows for the incorporation of different linker molecules, creating a variation of ester bonds incorporated in the polymer in ratio to the amount of anhydride linkages. In this work, we present the synthesis of two copolymers through the incorporation of two aliphatic diacids: fumaric acid or adipic acid. This allows for tunability of SAPAEs, and faster degradation of copolymers compared to homopolymers. In addition, we demonstrate the preparation of SAPAE-based microspheres and assess their small molecule release and encapsulation properties of retinol at pH 5, 7, and 9. Our results indicate that SAPAEs function as an efficient delivery system for the encapsulation of small molecules of interest, such as retinol, and easily degrade to release it alongside salicylic acid at varying rates depending on the polymer composition.

\[ \text{SAA-Homopolymer} \]
\[ \text{SAA-co-FA, } x:y = 4:1, R = \]
\[ \text{SAA-co-AA, } x:y = 4:1, R = \]
Innovative glass fiber nonwoven reinforced polymer composites: Effects of addition of cellulose nanofibers on physical and mechanical properties

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Glass fibers are high-strength, low-elongation materials with excellent heat resistance and insulation properties. In particular, it is widely used as a heat-resistant material and electronic product material because of its excellent shape stability at high temperatures. Recently, as the demand for industrial nonwoven fabrics has steadily increased due to the advancement of industries such as aviation, electronics, and communications, interest in glass fiber nonwoven fabrics that are thinner and lighter and have excellent physical properties is increasing. Non-woven fabric manufacturing using glass fibers mainly uses a wet method that forms a web in water rather than a dry method. However, glass fibers do not disperse well in water and aggregate in water. In order to manufacture high-quality wet-laid nonwoven fabrics, it is essential to have a technology for evenly dispersing fibers in water so that they do not get entangled with each other and a technology for maintaining strong bonds between fibers by adding an appropriate binder. In this study, cellulose nanofibers were added to improve the dispersibility of glass fibers in water, and wet-laid nonwoven fabrics were manufactured using ultrafine glass fibers with a diameter of less than 3 microns. These webs were then used as reinforcement for making polymer composites. The effects of the addition of cellulose nanofibers on the dispersibility of glass fibers in water, the physical properties of non-woven glass fibers, and the mechanical properties of the final polymer composite were confirmed.

Figure 1. Schematic diagram of the process for manufacturing innovative wet-laid nonwovens.
Catenane formation of a cyclic poly(alkyl sorbate) via Lewis pair polymerization induced by an N-heterocyclic carbene and ring-closing without extreme dilution

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Molecules with mechanical bonds, such as catenanes and rotaxanes, have received a lot of attention in recent years due to their potential for a wide range of applications, including molecular machines. Generally, their specialized structures are synthesized by template synthesis using metal complexes or non-covalent interactions such as hydrogen bonding. However, that requires a tedious synthetic process, such as the introduction of the molecular framework necessary for complex formation. Furthermore, ring-closing reactions require the use of high diluted conditions to suppress intermolecular reactions.

In our laboratory, we have reported a method for the synthesis of cyclic vinyl polymers by ring-closing reactions that avoid high diluted conditions. In this study, we attempted to use this synthetic procedure to synthesize catenanes without complicated synthetic processes and without requiring high diluted conditions.

We report here the formation of catenane by two-step polymerization of ethyl sorbate (ES). In this case, after complete monomer (ES) consumption ([ES]₀/[NHC₄Bu]₀=100/1), a second addition of ES monomer ([ES]₀/[NHC₄Bu]₀=20/1 or 100/1) resulted in the formation of catenanes. Catenane formation was proved by transmission electron microscopy (TEM) observation after thiol-ene click grafting with 1-dodecanethiol. The characterization was performed by size exclusion chromatography (SEC), dynamic light scattering (DLS), and nuclear overhauser effect spectroscopy (NOESY).
Polymerization of cyclic ketene acetics in aqueous media: The competition between radical ring opening and hydrolysis

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Cyclic ketene acetals (CKAs), such as their well-studied representative 2-methylene-1,3-dioxepane (MDO), allow to introduce ester bonds as breakpoints into the C-C backbone of otherwise non-biodegradable polymers and have thus attracted both industry and academia by opening a way to more eco-friendly and biodegradable polymers. MDO and its derivatives have been intensely studied regarding their polymerization behavior with various comonomers both in solution and bulk, however there are only few examples regarding the use of CKAs in emulsion polymerization. As CKAs are prone to hydrolyze with water, forming hydrolysis products that cannot undergo polymerization, it is of key interest to investigate if successful emulsion polymerization is possible by comparing the time scales of polymerization and hydrolysis of CKA monomers.

Since degradable dispersions would be of great value for various applications like engineered fabrics, paper coating or degradable packaging, we aim to shed light on the competing kinetics of polymerization and hydrolysis of CKAs.
Design of novel water-soluble purely organic photocatalyst for aqueous PET-RAFT polymerization

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We report a design of novel water-soluble purely organic photocatalyst (PC) and its application to aqueous photoinduced electron/energy transfer-reversible addition fragmentation chain transfer (PET-RAFT) polymerization. Ultra-low concentrations of the designed PC (5 ppm to monomers) enabled an oxygen-tolerant (or oxygen-accelerated) PET-RAFT polymerization of a variety of acrylate and acrylamide monomers in water and buffer. In addition, using chain transfer agent-modified bovine serum albumin (BSA), protein-polymer conjugates (PPCs) were successfully synthesized via grafting-from polymerization method under mild reaction conditions (e.g., at room temperature and under green light irradiation (515 nm, around 10 mW/cm²) - notably in the absence of deoxygenation process or any additives such as sacrificial reducing agents including tertiary amines and ascorbic acid. Neutral, anionic, cationic, and zwitterionic polymers affected the enzymatic activity of the corresponding PPCs, indicating that enzymatic activity of protein could be tailored by the characteristics of conjugated polymers. As oxygen-tolerant aqueous PET-RAFT polymerization eliminates high-cost and time-consuming deoxygenation process, accordingly facile preparation of PPCs would expand their utility to a wide range of applications. We also anticipate this novel PC to be employed for a variety of photocatalysis processes in aqueous and/or biologically relevant media.

Novel water-soluble purely organic photocatalyst 3DP-MSDP-IPN was discovered and enabled the efficient synthesis of protein-polymer conjugates through a “grafting-from” PET-RAFT polymerization from protein initiator at ambient aqueous conditions without any additives.
Active esters and post-polymerization modification in metal-free ring-opening metathesis polymerization

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Polymers produced by ring-opening metathesis polymerization (ROMP) represent an important class of commodity polymers. Our group developed a metal-free variant of ROMP (MF-ROMP) that utilizes organic photocatalysts and initiators to produce ROMP polymers. A major challenge of MF-ROMP is limited functional group compatibility due to the highly oxidizing conditions and reactive radical cationic chain ends produced during polymerization. In this talk we will highlight our initial efforts at understanding ion-pairing effects in MF-ROMP. Then, we will discuss how these effects led us to discover that pentafluorophenyl esters are tolerated in MF-ROMP, and discuss our efforts to optimize polymerizations containing these monomers to date. Finally, we will discuss our attempts to conduct post-polymerization modification of these active ester containing polymers.

\[
\begin{align*}
\text{PMP} & = \text{p-OMe Phenyl} \\
R & = \text{H, or (CH}_2\text{)}_x\text{COOC}_6\text{F}_5
\end{align*}
\]
Synthesis and characterization of semi-fluorinated polymers for $^{19}$F MRI

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Magnetic resonance imaging (MRI) is one of the most extensively used non-invasive methods for visualization in medical applications. However, with the current use of hydrogen MRI, images are mostly suffering from the background noise of biological water in tissues. $^{19}$F MRI has an increasing interest for medical use with its potentials such as imaging without any fluorine background signal in the body, and having a very close resonance frequency to that of hydrogen, allows its imaging with currently used MR instruments just with a slight adjustment of radiofrequency coil. Despite all the potentials of $^{19}$F MRI, inadequate availability and hydrophobic characteristics of fluorine tracers do not allow its widespread use in the medical field.

With the use of semi-fluorinated polymers, properties can be adjusted according to desired use with the use of different monomers. In this aspect, our aim is comparing a range of semi-fluorinated polymers and selecting the best water-soluble polymer with highest signal intensity. For this purpose, we prepared a series of statistical RAFT copolymers of fluorine containing monomers and hydrophilic monomers. Resultant polymers have been analyzed with $^1$H NMR, $^{19}$F NMR, SEC and they have been compared according to their water solubility and fluorine MR signal intensity.
Synthesis and characterization of silicone based segmented polyurethane/ureas

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Segmented polyurethanes with traditional polyester soft segments are highly susceptible to hydrolysis of the backbone. Polyurethanes with silicone soft segments stand to increase the hydrolysis resistance compared to these traditional polyester soft segments due to the increased stability of Si-O linkages as compared to ester functionalities. In this study, polyurethanes made with polydimethylsiloxane (PDMS) soft segments are being investigated. We expect PDMS’s retention of flexibility and increased resistance to hydrolysis to improve the stability of the polyurethane polymer while retaining the desired mechanical properties.
Polyureas have a wide range of applications extending from construction and automotive manufacturing to drug delivery and tissue engineering. They are traditionally synthesized by step-growth polymerization of carbonylating agents and diamines, which limits both the $N$-functionality and attainable macromolecular architectures of resulting polyureas. Step-growth polymerization also inherently lacks good control of polymer mass, dispersity, and endgroups. We recently developed a synthetic pathway of $N$-functionalized polyureas through the chain-growth cationic ring-opening polymerization (CROP) of iminooxazolidines which has the potential to resolve the architectural limitations of traditionally synthesized polyureas. The iminooxazolidine monomer can be derived from widely available amines or isothiocyanates and aldehydes, and the CROP synthetic pathway allows for the independent tunability of each $N$-substituent. Spectroscopic analysis showed successful polymerization and modest dispersity, with kinetic studies indicating variable polymer molar mass associated with modified reaction times. Polymer molar mass was shown to increase in relation to larger monomer:initiator ratios, which is expected for the proposed CROP pathway. The tunable structures of polyureas derived from iminooxazolidines through the CROP pathway may allow for greater adaptability of polyureas for specific applications as well as more complex polymer architectures such as block polymers.
It's essential that materials designed to be administered into the human system are biocompatible and biodegradable, and the reception of such materials by the human tissue is important to achieve its purpose. Ring-opening polymerization of amino acid N-carboxy anhydrides was investigated with α-hydroxy-ω-amino polyethylene glycol (PEG) as macro initiator to synthesize amphiphilic block copolymers with varied chain lengths. The block copolymers are explored as delivery vehicles for drugs and imaging agents by processing them into micelles. The amphiphilic properties of the copolymer were investigated for physical entrapment of hydrophobic drugs and imaging agents. Further conjugation of folic acid to the block copolymer enhances the binding efficacy of the micelles to targeted cells, increasing drug concentration on the targeted site. Folate-conjugated PEGylated poly(L-Leucine) with varying leucine monomer ratios were synthesized and processed into micelles to deliver iron oxide nanoparticles. The imaging characteristics of the micelles were investigated. Iron oxide encapsulated micelles exhibit higher relaxivities at low iron oxide concentration. The monomer ratio of the amino acid block was observed to determine the micelles' properties, and relaxivities as a result of particle spacing.
Transamidation of poly(2-ethyl-2-oxazoline) to a random copolymer

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Poly(2-ethyl-2-oxazoline), (PEOX), is a water-soluble polymer that is stable at temperatures up to 380°C. PEOX is used in over twenty industries including adhesives, ceramics, printing, and electronics. Starting with commercially available poly(2-ethyl-2-oxazoline) and select fatty acids, PEOX is converted via transamidation to a random copolymer. This transamidation allows us to tune the water solubility properties of PEOX, creating new application opportunities. The starting fatty acid has an eighteen-carbon chain and by varying chain lengths and saturation, the random co-polymer can be tuned to achieve desired properties.
Polymerizable channel-like stacks derived from cyclic tetrameric diacetylenes

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A small series of cyclic diacetylenes has been synthesized and tested by scanning electron microscopy (SEM), single crystal X-ray diffraction, and atomic force microscopy (AFM) to examine their ability to form arrangements of discrete molecules in the solid state. Examining solid state structures clearly demonstrated propensity of diacetylene tetramers to form channel-like stacks which may undergo 1,4-addition polymerization resulted in very specific tubular ene-yne alternated polydiacetylene scaffolds (PDAs). Remarkably, cyclotetradiyne DA-4 monomer tends to produce two types of nano-tubular motifs (i.e., the channel-like arrangement with solvent matrix inside and unprecedented flattened nano-tube incorporated no solvent guest molecules) which is indicative of the weak C-H/π interactions dominating and directing supramolecular stacking in such simplistic diacetylene systems. Noteworthy, DA-4 molecules may be crystallized from organic solvents into birefringent branchy patterns revealed by Polarized Optical Microscopy (POM) and twisted ribbons of right and left helical sense as evidenced by SEM data. We hypothesize that all these secondary structures may arise from UV- or temperature induced ladder-type polymerization of the individual stacks discovered by X-ray studies. Overall, engineering the elongated motifs may open up new opportunities for the future applications such as a rational design of synthetic ion channels and carriers, synthesis of the covalent polymeric nanotubes, etc.
Temperature responsive diblock polymer spherical brushes as nanoreactors to prepare and load silver nano-catalysts

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Metal nanoparticles are widely used in catalysis. Spherical diblock polymer brushes, sodium polystyrene sulfonate-b-poly(N-isopropylacrylamide) (PSV@PSS-b-PNIPA) and PSV@PNIPA-b-PSS with reversed block sequence, on polystyrene core were prepared by surface initiated photoiniferter-mediated polymerization and used as nanoreactors to in-situ prepare and load silver nanoparticles (AgNPs). The block sequence caused the difference of conformation and further affected the catalytic performance. PSV@PNIPA-b-PSS@Ag was found to be able to control the amount of AgNPs exposed to external reactant of 4-nitrophenol at different temperatures to regulate the reaction rate due to the hydrogen bonds and further physical crosslinking between PNIPA and PSS.

Figure 1. Schematic illustration of PSV@PSS-b-PNIPA@Ag and PSV@PNIPA-b-PSS@Ag.
Expanding the applications of metal-free ring-opening metathesis polymerization through functional initiators and chain-transfer agents

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Metal-free ring-opening metathesis polymerization (MF-ROMP) is an efficient route to achieving high-value linear polymers equivalent to those made using metal-mediated ROMP. Because MF-ROMP eliminates the need for transition metal-based initiators by instead using an organic enol ether initiator activated by a pyrylium photocatalyst, the applications of polymers made using this technique can be expanded into areas previously inaccessible to ROMP-based polymers, including biomedical and electronic applications where residual transition metals can be detrimental to the environment in which they are used. However, the low functional-group tolerance of MF-ROMP has made synthesis of structurally useful polymers challenging. In this research we will explore how the orthogonality of MF-ROMP towards various functional groups can allow for the synthesis of completely metal-free heterotelechelic polymers that can be used to make interesting and useful materials.
Epoxy resin formulation and study using ammonium carbamates as latent curing and blowing agent

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Capture of CO₂ by amines to form ammonium carbamates in which the active amine groups are blocked by CO₂ is a simple and economical approach for making environmental-friendly latent foaming and curing agents for epoxy resins. The ammonium carbamates with their dual functionalities, decompose when subjected to heat above 90°C, releasing CO₂ as blowing agent and amines as curing agent, to form epoxy foams as high-performance materials. The objective of this project is to evaluate the use of polymeric amines, such as polyethyleneimine (PEI), in comparison to small molecule amines, for forming the corresponding carbamate latent curing and foaming agents. In this presentation, we will summarize all epoxy foam formulations along with their properties. The thermoset epoxy foam prepared using ammonium carbamates have low density, good mechanical properties, thermal stability, and are comparable with the epoxy foams prepared by other techniques. Furthermore, we demonstrate the approaches to adjust the resin viscosity during curing to control the resin mobility which can be important for various applications.

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\text{NH}_2\text{RNH}_2 + \text{CO}_2 \overset{\oplus}{\longrightarrow} \text{H}_3\text{N}\text{RNHCO}_\oplus \overset{\text{Curing with epoxy resin}}{\longrightarrow} \text{Epoxy Foam}
\]

Latent blowing and curing agent
Toughening elastomers by entangling the crosslinkers

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Toughening polymer materials often accompanies a decrease in stretchability. Entangling the crosslinkers in elastomers may overcome the trade-off because it helps dissipate energy when the material is experiencing forces. Herein, we made acrylic elastomers using free radical polymerization, with a tetraacrylate-functionalized metal-ligand coordination complex as the crosslinker. The complex templates an entanglement, which is unveiled through a post-polymerization demetalation. We observe that the elastomers bearing the entangled crosslinkers are tougher, with a stretchability comparable to those without installed entanglements. Molecular dynamics simulations suggest that the entangled crosslinkers are less stretched in mechanical tests compared to the control materials, where the entanglements were not templated through coordination. In conclusion, with a twist of the topology, we overcome the trade-off between toughness and stretchability. This strategy is applicable to elastomers made of commercial monomers, including acrylates, methacrylates, styrene, and acrylamides.
Biobased aliphatic polyesters from renewable resources: Synthesis, properties and performance

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Of late, the glittering concept of ‘sustainability’ to design environment-friendly and biobased polymer materials has attracted immense attention within the domain of polymer science. Among them, bio-based polyesters have made great progress in the past but there are challenges and prospects for future development due to their tunable properties. In this work, an efficient, original synthesis of poly (alkylene sebacate) via two-step melt polycondensation of biobased dimethyl sebacate (derived from waste plastic) and different diols at relatively high temperatures (200-240 degree temperature) in presence of a catalyst was achieved. The molar compositions of the substrates and the effects of diols (increase in chain length) structure on the polyester properties were investigated. The structure-property relationship, molecular weight, and thermal properties (melting and crystallization behavior) of biobased polyesters were evaluated by FT-IR, NMR, GPC, and DSC analysis, respectively. The average molecular weights (Mw) of the polyester were obtained in the range of 15,000 to 56,000 g/mol. The equilibrium melting temperature \( T_m \) of the different poly (alkylene sebacate) was found between 70-80 degree temperature. Moreover, the enthalpy of fusion of polyesters was calculated in the range of 75 to 86 J/g using DSC analysis. The percentage crystallinity values for synthesized polyesters ranged between 54 to 62 %, thus confirming the semi-crystalline nature of polyester. Finally, polyester films were fabricated with tunable mechanical properties. With rising awareness for biodegradable materials, we feel that this kind of biobased polyester holds a great potential to be used as future materials in various packaging and medical applications.

Biobased Aliphatic Polyesters from Renewable Resources: Synthesis, Properties and Performance

Abstract Image
Investigating hydrophobic and hydrophilic poly glycerol esters for non-viral delivery

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Polyplex materials are widely used in biology as a polymer-based gene delivery system, with their stability, cellular uptake, and transfection efficiency being significantly affected by factors such as hydrophobicity and charge density. Balancing these factors is crucial for developing safe and effective gene delivery systems. Polyglycerol esters (PGEs) are a versatile class of biomaterials suitable for various biomedical applications due to their tunable mechanical properties and biocompatibility. PGEs are typically synthesized through polycondensation, using a variety of different length diacids with glycerol. The resulting polyglycerol esters can be modified with various functional groups, including cationic, hydrophobic, and hydrophilic moieties, enabling the formation of nanoparticles with various nucleic acids. The hydrophobicity and hydrophilicity of the functional groups on PGEs play an important role in the stability and cellular uptake of the resulting polyplex material. Hydrophobic functional groups tend to cluster together in aqueous environments, leading to aggregation of the resulting nanoparticles. Hydrophilic functional groups tend to be more compatible with biological systems, promoting the stability and cellular uptake of the nanoparticles. Nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), and amine titrations were performed to obtain the molecular weights, dispersities, and charge densities of the polymers. These characteristics of the polymer has led to the development of stable and effective polyplex materials for gene delivery applications.
Polyester-based non-viral vectors for gene therapy: Characterization and optimization of poly (glycerol ester) polymers

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Gene therapy shows promise for treating inherited and acquired diseases previously bereft of treatment and one of the key design inputs for developing a successful gene therapy involves the transfection techniques used to deliver the genetic payload to the target cells. Previous research with viral transfection reagents demonstrates potential dangers involved with viral vectors. Non-viral vectors such as lipid or polymer-based systems have been developed to alleviate the dangers with viral vectors. Cationic polyesters present a potentially useful class of polymers for designing transfection agents owing to their scalability, biocompatibility, and versatility in design. In the present work, a family of poly (glycerol ester) (PGE) polyesters are investigated where several aliphatic diacids are used to determine the effects of diacid length on nanoparticle formation and nucleic acid binding. Gel-Permeation Chromatography (GPC) is used to determine molecular weight, Nuclear Magnetic Resonance (NMR) is used to determine degree of branching, Fourier-Transform Infrared Spectroscopy (FTIR) is used to compare functional chemistry. After preparing a family of base polymers, further chemistry can be performed to modify the polymers and decorate them with either cationic, hydrophilic, or hydrophobic groups. These modifications are used to tune the ability of the PGE to bind nucleic acids, which was determined by both a gel electrophoresis retardation assay as well as a PicoGreen nucleic acid binding assay.
Group 14 radical coinitiators of photopolymerizations with alkyl and perfluoroalkylhalides

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Unlike conventional styrene or acrylate monomers that propagate with comparatively more stable radicals, initiation of fluoromonomers like vinylidene fluoride (CH$_2$=CF$_2$, VDF) requires very reactive primary alkyl radicals, available from alkyl, semi- and perfluoroalkyl R-X halides in the presence of strong photoactivators such as Mn$_2$(CO)$_{10}$. Interestingly, photolysis of related R$_4$Mt, R$_3$Mt-Y or R$_6$Mt$_2$ group 14 dimers (R = alkyl, aryl, Y = halide, etc., Mt = Si, Ge, Sn, Pb), provides a mixture of R$^\bullet$ and MtR$_3$$^\bullet$ radicals that can directly initiate alkenes polymerizations without the need for R-X coinitiators. Conversely, since such species are also strong halide abstractors, it also relevant to assess them in R-X derived initiations. In the current study, a series of regular alkyl, semi- and perfluorinated R-X halides was evaluated by $^1$H/$^{19}$F NMR and GPC studies in the initiation of VDF and of conventional monomers (St, MMA, VAc, dienes) to reveal that upon increasing the R-X chain transfer constant, initiation and termination is progressively accomplished by a combination of radicals derived from R$'$_6Mt$_2$ or R$_4$Mt (R$'^\bullet$, R$'$_3Mt$^\bullet$), solvent (S$^\bullet$), and R-X (R$^\bullet$), thus ranging from e.g. R$'$_3Mt/S/R-PVDF-H to highly functionalized R-PVDF-X.
Grafting well-defined polymers onto poly(vinylidene fluoride) via thiol-ene click reactions

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Poly(vinylidene fluoride) (PVDF) is a commercially available fluoropolymer, second in market value only to polytetrafluoroethylene. PVDF displays great thermal and chemical stability, making it a popular material in coatings, membranes, and lithium-ion battery fillers. Pristine PVDF lacks specific functionality, as such, there has been great interest in functionalizing PVDF by synthesizing graft copolymers. These materials have been used in advanced applications such as wearable nanogenerators and solid polymer electrolytes in batteries.

Many authors have reported using PVDF as a backbone for “grafting-from” using atom transfer radical polymerization (ATRP). However, the mechanism of this functionalization is unclear. Homolytic cleavage of the carbon-fluorine bond (BDE ~480 kJ/mol) to generate the initiating radical is difficult, if not impossible. Additionally, PVDF is subject to side reactions with the basic, amine-like ligands commonly used in ATRP in the form of dehydrofluorination. All these factors affect the reactivity of PVDF and result in poorly defined graft copolymers.

Because of the lack of mechanistic insight, we propose an alternative method- grafting onto PVDF. PVDF that has undergone dehydrofluorination will possess unsaturated sites on the backbone that can react with thiol-terminated polymers in a thiol-ene click reaction. Thiol-terminated polymers can be easily synthesized using various controlled radical polymerization techniques like ATRP and reversible addition-fragmentation chain-transfer (RAFT) polymerization. These polymers are uniform and well-defined, and the molecular weight can be determined prior to grafting. This information can then be used to calculate grafting density and efficiency. Herein, we systematically investigate how different starting materials and thiol-ene click reaction mechanisms affect the grafting efficiency of grafting onto PVDF-based materials.
General Topics: New concepts in polymer characterization

Factors affecting the ethylene-vinyl acetate copolymer crystallinity in islatravir implants - Zhu, Xiaolong (Oral Preferred)

3D characterization of extended defects in block copolymers using slice and view focused ion beam/scanning electron microscopy - Thomas, Edwin (Oral Only)

Clicking viral particles into polymeric hydrogels for sustained immunotherapy - Leganes, Jorge (Oral Preferred)

Copolymerization of ethylene and 1,4-pentadiene using a group IV single-site catalyst: Multi-faceted NMR characterization and reaction mechanism - Hou, Jianbo (Oral Only)

Surface modified dendrimer for slow release of active ingredients - Trashi, Orikeda (Oral Preferred)

Determining partial scattering functions of multicomponent polymer thin films with contrast-variation resonant soft X-ray scattering - Murphy, Julia (Oral Only)

Molecular orientation within hierarchical high-Chi block copolymers by polarized resonant soft X-ray scattering (P-RSoXS) - Patel, Bijal (Oral Only)

Hydrodynamic Chromatography an efficient tool to quickly determine particle size distributions in the sub-micron range - Lohmann, Derek (Oral Preferred)

Virtual chemistry lab: Improving polymer materials using state-of-the-art molecular models - Sweere, Teun (Oral Only)

Structure-dynamics relationships in high performance nylon fibers via x-ray scattering - Kearney, Logan (Oral Preferred)

Evolution and characterization microstructure in a single isotactic polypropylene spherulite. synchrotron microfocus X-ray scattering measurements - Kloczkowski, Andrzej (Oral Only)

Unveiling the mechanical properties of optically clear adhesives with a novel transfer method - Yang, Chanhee (Poster Preferred)

Porous Se@SiO2 nanospheres inhibit calcium oxalate kidney stone formation by oxidation resistance - Yang, Boyu (Oral Preferred)

Theoretical analysis of vulcanized polymer model properties using molecular dynamics simulation and machine learning - Yoshida, Kohei (Poster Only)

Rigid phenylene ethynylene trimer-based degradable block copolymers for siRNA delivery - Sarker, Md Golam Sabbir Sarker (Poster Only)
General Topics: New concepts in polymer characterization

Gelatin and poly(ethylene glycol) core-shell nanogels for their use as an Alzheimer disease drug carrier - Ruiz Galindo, Oscar (Poster Preferred)

Determination of electrical measurement of carbon fiber reinforced plastics under load - Yim, Yoon-Ji (Poster Only)

Stimuli responsive reversible self-folding bilayer thin films - Edirisinghe, Dimuthu (Poster Only)

Application of dual thermo-responsive block copolymers in size-tunable strategy toward improved retention in tumor tissues - Pal, Juthi (Poster Preferred)

Unusual inward growth of hexagonal nanosheets by the self-assembly of a homopolymer - Fan, Yirong (Poster Preferred)

BODIPY-based initiators for photo-induced polymerization - Zhang, Yuanwei (Poster Preferred)

Modeling random scission in polyethylene melts using energy conserving dissipative particle dynamics - Anik, Arefin Mustafa (Oral Only)
Factors affecting the ethylene-vinyl acetate copolymer crystallinity in islatravir implants

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Islatravir, a highly potent nucleoside reverse transcriptase translocation inhibitor, has great potential to be formulated as ethylene-vinyl acetate (EVA) polymer-based implants via hot melt extrusion. Microstructures of the implant revealed by X-ray computed tomography suggest drug release primarily depends on the open channels that are formed in the polymer matrix. Therefore, the measurement and quantification of EVA crystallinity is of great importance. Herein, we describe the systematic analysis of factors affecting the EVA crystallinity in islatravir implants. Differential scanning calorimetry (DSC) study on EVA melting enthalpy and solid-state NMR revealed API loading promoted EVA crystallization. DSC also revealed BaSO4 loading decreased EVA crystallinity. Dynamic mechanical analysis showed the storage modules of the implant is positively correlated to drug loading. After γ-irradiation, the crystallinity of EVA in implants became less prone to annealing on storage. Furthermore, DSC analysis on thin implant slices prepared by ultramicrotome indicated that the surface layer of the implant was more crystalline than the core. These findings provide insights for understanding the factors affecting crystallinity, mechanical properties, physicochemical properties and the stabilities of the EVA polymer matrix within the islatravir implant.
3D characterization of extended defects in block copolymers using slice and view focused ion beam/scanning electron microscopy

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Transmission electron microscopy tomography employs very thin samples of only 1-2 unit cells in thickness and thus, reconstructions are typically limited to regions of < 100 unit cells. On the other hand, 3D slice and view scanning electron microscopy (SVSEM) reconstructions can image volumes containing ~ 10^4 unit cells allowing detailed characterization of various types of extended defects such as dislocations and grain boundaries. Moreover, order-order phase transitions can be studied. We study diblock copolymers comprised of polystyrene (PS) and polydimethyl siloxane (PDMS) blocks and the greyscale SEM images can be readily binarized into bright regions corresponding to the PDMS domains (due to enhanced generation of secondary electrons by the Si atoms) with dark PS regions. Segmentation and registration of many such images after serial imaging and focused ion beam slicing allows high fidelity 3D visualization. The large volume reconstruction can then be interrogated to locate, characterize and quantify the various defects and distortions that are present. For example, we investigated the double gyroid (DG) to double diamond (DD) phase transformation using SVSEM and were able to unambiguously determine the transformational pathway and the 3D nature of the nanoscale structures across the phase boundary. Malleable mesoatoms are useful as the basic building blocks that undergo cooperative interactions within a narrow transition zone (TZ). Mesoatoms smoothly deform from trihedral DG to tetrahedral DD preserving network topology. The TZ contains “intermediate mesoatoms” distinguishable by their variable shapes as the numbers, lengths, and directions of the struts that connect a given mesoatom to its neighbors evolve. Another type of grain boundary is a twin, where the structures on either side are in mirror symmetry. Twin boundaries are a low energy defect and SVSEM has key to identify (422) twin boundaries in DG and (222) twins in DD.

Order-order phase transformation of double gyroid to double diamond in a tubular block copolymer showing the coherent but nonperiodic transition zone.
Clicking viral particles into polymeric hydrogels for sustained immunotherapy

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In recent times, the use of viral nanoparticles has led to advancements of scientific knowledge and development of novel materials with wide-ranging applications, especially for diagnostic and therapeutic purposes. Plant-viruses and plant-based virus nanoparticles (VLPs) in particular, have been broadly applied in medicine, notably for the development of vaccines targeting chronic diseases and cancer, without the danger of animal pathogen contamination.[1] A notable example is the application of a VLP in situ vaccination that has shown success in the treatment of canine cancer patients.[2] There remain challenges with the administration of such vaccines and immunotherapies; in most cases when treating cancer or other chronic diseases, repeat administration is needed.[3] To overcome this, we propose the formulation of VLP hydrogels, or 3D crosslinked polymeric networks, to formulate VLP vaccine depots for sustained efficacy.

Accordingly, the aim of this work is to incorporate VLPs into a 3D polymer network by means of covalent bond formation using bio-orthogonal click chemistry, which will ultimately result in the long-term release of the viral cargo due to the strong covalent nature of these bonds. Due to the remarkable multivalency of the surface proteins in these viral platforms, the nanoparticles were first functionalized with terminal alkyne groups by targeting the surface-exposed lysines (lys) (up to 720 surface-exposed lys per virus particle), which resulted in highly functional VLP crosslinkers. The modified VLPs were then incorporated into the network of a hydrogel containing azido pendant groups through copper-free click reaction, rendering the virus-loaded hydrogels (VLHG), where both chemical and viral crosslinkers coexist. These slow-release VLHG formulations are expected to prolong the therapeutic antitumor effect of the free VLPs, which constitutes an important goal in reducing the number of necessary administrations and enable translation into in situ applied therapeutics.
Copolymerization of ethylene and 1,4-pentadiene using a group IV single-site catalyst: Multi-faceted NMR characterization and reaction mechanism

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Fundamental understanding of the underlying mechanism associated with the catalytic reaction is essential for new catalyst design and development. We present our work on copolymerization of ethylene and 1,4-pentadiene using a Group IV single-site catalyst to understand the insertion mode of 1,4-pentadiene. Polymer microstructure was subjected to structural characterization using quantitative NMR spectroscopy, diffusometry, two-dimensional correlation spectroscopy and selective refocused insensitive nuclei enhanced by polarization transfer (Sel-RINEPT). Selective pulse based ¹³C NMR spectroscopy has been developed to suppress experimental artifacts, such as decoupling side band, which often become problematic with sensitive cryogenic probe to affect the interpretation of small peaks. Such a capability can be also built into the single pulse as well as the polarization transfer, such as RINEPT. The multimodal NMR characterization allows to effectively differentiate chain end and backbone signal, filtrate irrelevant spectral information and provide site specific information to achieve unambiguous structural elucidation. Detailed molecular structure characterization provides critical insights to advance the understanding of the reaction mechanism. As a result, it reveals that pentadiene has been primarily converted to cis- and trans- dialkyl substituted cyclohexane moieties along the polymer backbone over the course of polymerization. The analysis also confirms that unreacted pendant allyl groups (a result of 1,2-insertion) remain at a concentration that is significantly lower than the dominate cyclic structures. When compared to literature result, some discrepancy in structural assignment has been identified and the result will be discussed.

Figure 1. Novel NMR characterization unraveled reaction mechanism for the formation of cyclic structures (bottom). The lack of 4-(C) and 8- (G) membered ring structure and the dominance of 1,3-dialkyl substituted cyclohexane (F) indicate that 1,4-pentadiene first adds into growing polymer chain via 1,2-insertion (B), followed by ethylene insertion (structure D), which is then followed by 1,2-insertion of the second diene vinyl group (F).
Surface modified dendrimer for slow release of active ingredients

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Active ingredients are widely used compound to treat skin texture, prevent skin dehydration, stimulate collagen production. Despite their good properties, it comes with unpleasant side effects such as irritation, peeling, and redness of the skin at high concentrations. Designing a nanocarrier for hydrophobic and photosensitive ingredients that allows controlled release over time is of great importance in skincare products. Polyamidoamine (PAMAM) dendrimers are polymeric nanocarriers that can be designed on a specific nano-sized scale with high functionality that allows the conjugation of multiple molecules. Herein, we developed a PAMAM dendrimers with a hydrophobic core, modified on the surface by polyoxazolines to enhance their water solubility and reduce the potential toxicity. In order to increase the skin penetration, nanocarrier is further grafted by collagen stimulating peptide. This system is cleavable by skin enzymes hence slowly release the encapsulated active ingredient over the course of time. The nanocarrier was characterized by DLS, TEM, and SEC. Preliminary cell viability data showed that the nanocarrier has no significant cytotoxicity on human adult fibroblasts. The in vitro release study has shown the overall system has slow release of the active ingredient up to 12h.
Determining partial scattering functions of multicomponent polymer thin films with contrast-variation resonant soft X-ray scattering

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Triblock copolymer thin films exhibit a complex phase diagram with a wide range of diverse morphologies dependent on the specific composition and energetic interactions between components. The resulting morphological features are generally difficult to distinguish through microscopy and other conventional characterization methods. Contrast variation small angle neutron scattering (CV-SANS) offers a method to probe the individual contributions of each block, but is limited to bulk films (> 1 mm) and the required deuterium labeling has the potential to alter the interfacial interactions. Here, we develop contrast variation resonant soft X-ray scattering (CV-RSoXS) as a label-free method for structural characterization, for disambiguating the phases of a model triblock copolymer thin film, poly(1,4-isoprene)-block-polystyrene-block-poly(2-vinyl pyridine), which exhibits a rich array of morphologies including core-shell cylinders or spheres, alternating cylinders or spheres, and lamellae. In CV-RSoXS, scattering contrast arises due to the distinct K-edge energies of the functional groups for each component material. Tuning the intrinsic bond-specific energies allows us to resolve the individual contributions of each block, analogous to CV-SANS. With this approach, we decompose the overall energy-dependent scattering into energy-independent partial scattering profiles, relying on each material's distinct complex indices of refraction. We further refine the energy selection utilizing clustering algorithms and model the morphology of the film by forward-simulating the X-ray scattering patterns. CV-RSoXS offers future potential to resolve the partial scattering of a broad range of multicomponent (three or more) systems that are currently inaccessible through scattering or other traditional characterization methods.
Molecular orientation within hierarchical high-Chi block copolymers by polarized resonant soft X-ray scattering (P-RSoXS)

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Block copolymers (BCP) comprising covalently linked, chemically dissimilar chain segments are valued for their ability to form well-controlled microphase-separated nanostructures at predictable length scales. High-χ block copolymers (BCP) exhibit an enhanced driving force for microphase separation and offer an attractive route towards further downscaling of pitch for microelectronics patterning. As these systems push towards smaller domains (via low degree of polymerization and large chemical incompatibility), there is also strong potential for perturbed, non-gaussian, chain conformations to exist. Here, we apply the new structural characterization tool of polarized resonant soft X-ray scattering (P-RSoXS) to probe bond orientation and clarify the intra-domain structure at a level impossible to achieve using conventional hard X-ray, neutron, and electron-based scattering/imaging techniques.

We present a detailed structural investigation of a block copolymer system comprising a poly(styrene) A-block and perfluorinated glycidyl methacrylate-derived B-block. Upon thermal annealing, a hierarchical structure forms, with a distinct length scale for A/B microphase separation (L₀ ≈ 20 nm) and a sub-lattice contribution with periodicity as small as ≈ 3 nm. Through near-edge absorption fine structure (NEXAFS) and polarized resonant soft X-ray scattering (P-RSoXS) measurements, we probe the differing molecular orientation of distinct chemical moieties. Through fitting of the experimental spectra to computational scattering simulations, we develop a rich description of the extent and nanoscale spatial variation of composition and orientation.
Hydrodynamic Chromatography an efficient tool to quickly determine particle size distributions in the sub-micron range

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Hydrodynamic chromatography (HDC) is a size-based separation method allowing for the determination of particle size distributions in the range of 20 – 1,000 nm. This extends the separation range of the classic size exclusion chromatography to larger moieties.

The principle of HDC is based on the distribution of particles in the flow streams of parabolic flow profiles occurring in narrow capillaries. Small particles can access all flow streams, while larger particles can only access the velocities close to the center of the capillary. Consequently, larger particles elute before smaller ones, similar to the separation order in size exclusion chromatography.

A disadvantage of using single capillaries is that they may easily block. This risk is reduced by HDC in packed columns, where the interstitial volume can be regarded as a bundle of capillaries.

Using suitable standards, the retention time can be correlated to the particle size, allowing for the determination of particle sizes and their distributions.

Using an appropriate column in a conventional GPC/SEC system allows a first crude estimate on particle sizes and their distribution. Improvements of the separation efficiency and more detailed information on the sample properties can be gained by using more sophisticated instrument control in combination with an efficient deconvolution software.

We will be presenting selected applications of HDC separations ranging from polymer emulsions to liposomes and will demonstrate the advantages of a new software module.
Virtual chemistry lab: Improving polymer materials using state-of-the-art molecular models

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Digitization, digitalization and digital transformation: companies are currently putting a lot of effort to store, analyze and use their data to improve business processes company-wide. Electronic lab notebooks, ELN’s, are implemented within different organizations to save and share the performed experiments and generated data efficiently. This availability of information offers great opportunities in the development of new products and the design of better material compositions using computational chemistry. Easily accessible in-house experimental results can be used to create and validate molecular models. Moreover, using the laws of thermodynamics, these generated molecular models can be used to predict properties of unexplored polymer formulations.

Working closely with our industrial partners, we have discovered the power of computational chemistry in characterizing polymer formulations, and subsequently improving their mechanical properties. The opportunities of molecular modeling are demonstrated by two industrial case studies.

Case study 1: Prediction of the permeability of various permeants through different packaging materials. Within the development of effective packaging products it is important to have a good understanding of the barrier properties against unwanted external substances and the leakage of internal substances.

Case study 2: Characterization and optimization of the mechanical properties of separator membranes. Coarse-grained models have been developed and validated for the calculation of stress-strain curves of polyethylene blends. Screening a wide variety of polyethylene formulations under different conditions using the digital models results in improved product properties and reduced time-to-market.

Visualization of six 100 kDa polyethylene (PE) chains in a semi-crystalline PE blend
Structure-dynamics relationships in high performance nylon fibers via x-ray scattering

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Nylon is an important engineering polymer used in a wide variety of applications and possesses a highly tunable set of physical properties which are primarily determined by the selection of a polyamide subunits. One such application is found in the deployment of nylon as fibers where extensive deformation in the melt leads to a highly aligned microstructure. Nylon fibers have found utilization as a highly desired fiber material in textiles due to its combination of toughness, dyeability and high luster. High performance nylon fiber formulations have been used as tire cord to enable the function of tires in extreme conditions common in Formula 1 racing. In these applications, a precise understanding of the interdependencies of entropically driven shrinkage and the rubber interphase is essential to predict fluctuations in the bulk tire geometry and thereby tire performance. In this work, we utilize one of the first implementations of a gallium jet x-ray source, available at ORNL, producing world leading peak brilliance coupled state-of-the-art detector sensitivities which results in time resolved structural resolution (on the order of several seconds). The peak brilliance of this laboratory scale system and a tensile mode environmental stage is leveraged to resolve the characteristic structural changes which act as precursors to the onset of creep and stress relaxation behavior. In addition to dynamic experiments, we demonstrate the capability of this optical configuration to resolve isolated single fibers to accurately determine the thermally induced fluctuations in crystallite system orientation. Connecting the polyamide repeat unit chemistry and as-spun fiber morphology to thermally induced relaxation dynamics will provide useful insight to the function of these fibers in high value applications.
Evolution and characterization microstructure in a single isotactic polypropylene spherulite. Synchrotron microfocus X-ray scattering measurements

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Isotactic-polypropylene (iPP), one of the frequently used polymers in industrial processing and scientific research, is used as a model material in this review. The precise location of the X-ray beam in the spherulite is realized through the use of carbon fibers. The results show that the mother lamellae in the spherulite are aligned mainly along the radius, and the daughter lamellae are inclined 80.75° with respect to the radius. The lamellar and chain arrangements in a single spherulite are quantitatively investigated by synchrotron microfocus wide-angle X-ray scattering. The crystallinity in the spherulite is in the range of 46% to 56%, which is rarely influenced by crystallization. The ratio between the subsidiary daughter lamellae and the dominant mother lamellae is 0.18 when iPP crystallizes at 138°C and it decreases to 0.11 as the crystallization temperature is decreased to 130°C. The b-axis and c-axis in the crystal are oriented perpendicular to the radius direction, and the a-axis is aligned in the radius direction. In addition, the results of this study prove the possibility of detecting the microstructure in a single isotactic polypropylene spherulite by synchrotron microfocus X-ray scattering. In this study, the structural evolution is monitored by in-situ synchrotron X-ray scattering. The interests in this brief overview are briefly focused on the topic of microstructure characterization in a single iPP spherulite by synchrotron microfocus wide-angle X-ray scattering measurements.
Unveiling the mechanical properties of optically clear adhesives with a novel transfer method

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In this research, we performed direct tensile testing of optically clear adhesive (OCA) using a novel transfer method on a water surface. OCA is a crucial material in flexible electronics, photovoltaic modules, and medical devices due to its excellent interlayer adhesion and optical transparency. In particular, in the case of flexible displays, OCA improves the mechanical reliability of the device by inducing multiple neutral planes in the layer structure, which reduces strain in brittle layers. Therefore, to enhance the mechanical reliability of electronic devices, it is essential to precisely evaluate the mechanical properties of OCA. However, due to its low modulus and sticky properties, conventional testing methods are challenging to apply. To overcome this, we employed polystyrene sulfonate (PSS) film as a sacrificial layer to transfer the OCA to the water surface, which allowed the OCA to be free-standing on the water surface which is a suitable state for measuring its mechanical properties. Polystyrene sulfonate dissolves well in water and has no chemical reaction to OCA, making it an appropriate sacrificial layer. With the polystyrene sulfonate sacrificial layer, we transferred OCA to the water surface without any damage or deformation. We captured the exact strain value of the test specimen using the digital image correlation (DIC) method by tracking randomly sprayed patterns on it. Young’s modulus and Poisson’s ratio of the OCA were also successfully calculated from the stress-strain curve for the tensile test performed on the water surface. Additionally, we observed the viscoelastic properties of OCA by observing the variation in the stress-strain curve slope with different loading rates. The measured properties of OCA can be utilized for the accurate mechanical reliability analysis of various systems that include OCA. This research not only provides a better understanding of the mechanical properties of OCA but also offers a new approach to the mechanical analysis of extremely soft and sticky materials.
POLY 3903828

Porous Se@SiO2 nanospheres inhibit calcium oxalate kidney stone formation by oxidation resistance

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Porous Se@SiO2 nanospheres inhibit calcium oxalate kidney stone formation by oxidation resistance
Theoretical analysis of vulcanized polymer model properties using molecular dynamics simulation and machine learning

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The performance trade-offs of rubber materials are a major barrier to their development. Therefore, to overcome these limitations, there is a strong need to understand the mechanisms related to the effects of polymer structure on the physical properties of rubber materials. Molecular dynamics (MD) simulations are an effective method to address these challenges, which are difficult to accomplish using experimental approaches. Although there have been many studies analyzing the relationship between monomer structure and polymer properties, few studies have focused on the contribution of polymer dynamics to the analysis of physical properties. Therefore, to analyze the relationship between the structure and physical properties of vulcanized natural rubber, molecular dynamics simulations were performed to calculate the dynamic structural features and physical properties. Using machine learning, the effects of changes in polymer structure (e.g., sulfur cross-linking) on physical properties were analyzed, and the structural parameters involved in the properties were extracted. The thermal conductivity and elastic modulus, which showed a trade-off relationship, were targeted in this study.

The results of the analysis suggested that the two physical properties are affected by different parameters. Furthermore, based on the analysis results, polymer models with a new range of properties were created by controlling the structural parameters involved in each property. It was shown that the analysis combining MD and linear regression is a useful method for understanding the mechanism by which the structure of a polymer model is involved in its physical properties.

(a) Main explanatory variables and their regression coefficients obtained from ridge regression with stress–strain as the objective variable (b) Comparison of the physical properties of previous models with the newly created polymer model. Blue represents the conventional models with a sulfur stocking value of 80 or higher. Red represents the newly created model (sulfur preparation value = 80).
Rigid phenylene ethynylene trimer-based degradable block copolymers for siRNA delivery

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Owing to their intrinsic fluorescence properties and good cellular entry, p-electron conjugated polymers (CPs) have been used for intracellular labeling, sensing, and delivery of biological substances. By balancing the rigid and hydrophobic backbone with hydrophilic and charged side chains, nucleic acids and proteins were successfully complexed with CPs and delivered to live cells. Previously, our group demonstrated a target gene knockdown in mucus-covered epithelial cells using poly(phenylene ethynylene) containing carbamoylated guanidine (CG) side chains. The neutral CG group with an enhanced number of hydrogen bonding donors allows stable nanoparticle formation with small interfering RNA (siRNA) and penetration through the negatively charged mucus layer. Although we demonstrated target gene knockdown in normal human bronchial epithelium expressing mucus, we hypothesized that further tuning of positive charge density, flexibility, and degradability along the backbone while maintaining the CG side chains would enhance overall delivery efficiency due to improved complexation, cellular entry, and intracellular availability of siRNA. In this presentation, the synthesis of a series of rigid-flexible block copolymers using dynamic covalent chemistry between dialdehyde-containing phenylene ethynylene trimers (PETs) and disulfide bond-containing diamines followed by reductive amination (Fig. 1) will be presented. Loading capacity, mucus penetration, and target gene knockdown efficiency of PET-based degradable polymers will be measured using model cell lines.

Tuning of positive charge density, backbone flexibility of rigid-flexible block copolymers for siRNA delivery
Gelatin and poly(ethylene glycol) core-shell nanogels for their use as an Alzheimer disease drug carrier

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Alzheimer's disease is difficult to treat because drugs need to be able to pass the blood-brain barrier without being subject to the hepatic first metabolic step, also drug carriers design to target the disease need to have very specific characteristics to pass the blood-brain barrier and deliver the drug to the brain.

In this work we describe the synthesis of a gelatin and poly(ethylene glycol) core-shell nanogel that is able to pass the blood-brain barrier, that is biocompatible and biodegradable. These nanogels were synthesized by means of soap-less emulsion polymerization, which is a method that does not require a surfactant agent, rather poly(ethylene glycol) is used as the particle stabilizer and at the same time serves as the biocompatible and biodegradable shell of the nanoparticle. For this, both macromonomers were first modified with methacrylic anhydride to produce methacrylated derivatives of both gelatin and poly(ethylene glycol), in order to introduce double bond functionalization and make it possible to crosslink them together.

Nanogels were chemically characterized, they were shown to be biocompatible in biological essays, a model drug was loaded into them, and their pharmacokinetics was determined.
Determination of electrical measurement of carbon fiber reinforced plastics under load

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Structural health monitoring includes non-destructive inspection systems that incorporate sensors into structures to enable periodic or continuous inspection. Instead of relying on separate complex processes and methods such as dismantling structures and manual inspections, the result data allows operators to understand the damage status of structures in real-time, enabling diagnosis of damage types, locations, sizes, and structural integrity. This structural health monitoring technology is emerging as a more important technology to secure the safety against aging of large structures such as buildings, bridges, and aircraft. Damage to a structure appears as a change in material properties such as strength, rigidity, or electrical resistance. If the electrical conductivity of the material itself is used, changes in the internal electrical resistance of the material can be observed due to micro damage caused by external loads. Carbon-based materials are being used as materials for large structures instead of steel due to their lightweight and excellent mechanical, thermal and electrical properties. Among them, carbon fiber is a well-known electrical conductor. Therefore, the principle of change in electrical resistance caused by damage to carbon fiber can be applied and utilized in the detection/evaluation of various damages and defects of fiber-reinforced polymers (CFRPs). In this case, the carbon fiber becomes the reinforcing fiber of CFRPs, and the sensor itself detects the damage signal. Therefore, the damage detection method of CFRP is possible by attaching electrodes to the surface of the composite structure without a special manufacturing process. Therefore, this method has the advantage that it can be applied to structures already in use without a decrease in strength. In this study, a study on the damage detection evaluation method of composite materials using the electrical resistance measurement method was conducted by observing the electrical behavior of CFRPs under mechanical load.

Figure 1. Schematic diagram of electrical measurements of carbon fiber reinforced plastics under load.
The development of stimuli-responsive, self-folding materials is important in designing various smart, functional materials and actuators. Polymer-based self-folding materials are interesting due to their unique mechanical properties and chemical properties that can be modified to obtain sensitivity toward a broad range of stimuli. Well-adhered polymer bilayers are an interesting approach to designing self-folding structures. One polymer layer should be inactive or comparatively less active toward the particular stimulus to obtain the reversible folding and unfolding caused by swelling/dwelling or expansion/shrinking of the one polymer layer compared to the other one. The development of reversible self-folding polymer bilayers that are sensitive to chemical changes in the environment is presented in this project. Different polymer combinations of Polystyrene (PS), Poly(butyl methacrylate) (PBMA) dissolved in toluene, Poly(4-vinyl pyridine) (P4VP) dissolved in ethanol (EtOH), and Polyvinylpyrrolidone (PVPyr) dissolved in water have been used to develop polymer bilayers. Polymer bi-layer behavior after exposure to different chemical environments has been studied via UV-Vis spectroscopy and Raman spectroscopy.
Application of dual thermo-responsive block copolymers in size-tunable strategy toward improved retention in tumor tissues

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Size-tunable strategies are very promising in eliminating the limitations associated with fixed-size nanoparticle-based drug delivery. For example, small-sized nanoparticles, although advantageous for accumulation in tumor tissues, suffer from poor retention thereby decreasing the overall therapeutic efficacy. Post-accumulation size expansion by aggregation strategies can remove this limitation. Various stimuli can be used to design such smart nanoparticles that aggregates post accumulation. In this direction, we have explored the potential of dual thermo-responsive polymer nanoparticles. We have synthesized N-Vinyl-2-pyrrolidone (NVP) and substituted NVP (sub-NVP) based polymers with precisely controlled lower critical solution temperatures (LCSTs). RAFT polymerization was used to synthesize the polymers with narrow polydispersity. The minimal compositional alteration of the thermo-responsive blocks enabled the control of LCSTs within the physiological range. The LCSTs were tuned by varying the ratio of NVP and sub-NVP, where the first LCST value was kept below 37 °C to promote drug loading and the second LCST value was around 41-43 °C to ensure mild hyperthermia-induced drug release. The composition of the core and the corona-forming blocks were varied by different sub-NVP monomers and their combinations. The drug loading and release were found to be highly dependent on the hydrophobicity of the nanoparticle core and the hydrophilicity of the corona. The release of the anticancer drug Doxorubicin (DOX) was monitored at two different temperatures (37 °C and 43 °C). The polymeric nanoparticles showed aggregation-induced emission upon covalent attachment of TPE (AIEgen) to the polymers. TPE acted as a FRET pair with DOX, which further helped us in real-time monitoring of drug release. These polymeric nanoparticles were also subjected to different in vitro cell studies such as, toxicity, cellular uptake, thermos-responsive drug release and real-time tracking of FRET.
Unusual inward growth of hexagonal nanosheets by the self-assembly of a homopolymer

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Unrevealing the nucleation and growth of nanocrystals is very important for understanding the relationship between structure and properties. In particular, the crystallization behavior of polymers is complicated and has attracted extensive attention of scientists. Generally speaking, the crystallization starts from the nucleus and continues to epitaxial growth. However, in this study we discover an interesting phenomenon of inward growth of a crystalline homopolymer to form hexagonal nanosheets. The amphiphilic homopolymer poly(3-(4-(phenyldiazenyl)phenoxy)propyl methacrylate) (PAzoPMA) with azobenzene pendants is synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization, which can self-assemble into various morphologies including nanowires, hexagonal nanosheets, giant compound micelles in different alcohols (ethanol, isopropanol and n-butanol) by solvothermal method. Notably, we find that the hexagonal nanosheets are crystalline other than the amorphous state. Therefore, we monitor the growth process of the hexagonal nanosheets at different annealing time, and find that the hexagonal nanorings with hollow structure are formed at the very beginning of annealing. With the increase of annealing time, the homopolymer attaches at the internal surface of the hexagonal nanorings and the inner wall of the nanorings begins to grow inward gradually to form a thin film that fully covers the bottom of the hexagonal nanorings. As the annealing time continues to extend, the thin layer at the bottom further grows along the side of the hexagonal nanorings to form hexagonal nanosheets with a uniform thickness, eventually. Overall, we find an unusual crystal growth mode from the outside to inside of polymers for the facile preparation of hexagonal nanosheets, which may bring new insight for understanding the crystallization behavior of polymers.

Figure 1 TEM and AFM images of hexagonal nanosheets formed by the inward growth of PAzoPMA.
BODIPY-based initiators for photo-induced polymerization

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Photopolymerization is a highly efficient and green process in the field of material science with a wide range of applications in coatings, inks, adhesives, and biomedical devices. Functional systems that can be mediated by an external stimulus such as light are crucial as they can aid in polymerization and control the procedure with high spatiotemporal resolution. The thiol–ene Michael addition is a powerful “click” reaction utilized broadly in polymer chemistry, but the report of photo-triggered thiol-ene Michael polymerization is rare. Herein, we designed, synthesized, and evaluated BODIPY-based highly reactive and effective catalyst protecting a strong base tetramethyl guanidine (TMG) for light-induced activation of thiol-ene Michael addition reactions.

The visible-light sensitive photobase generators are prepared in four step synthesis process starting with 2,4–dimethyl pyrrole and acetoxyacetyl chloride and resulting in a BODIPY-based photo base generator (PBG) protecting TMG. Our studies showed that the BODIPY-based PBG exhibits strong photophysical properties as well as a high potential for increased photolysis efficiency due to the heavy atom effect. Moreover, this “photo-click” reaction enables controlled polymer network formation in thiol-Michael polymerizations which can be further utilized for surface patterning, 3D printing, film development, and biological applications such as pH balancing.

Visible–light initiated mechanism for photo-initiated thiol-ene Michael addition polymerization.
Modeling random scission in polyethylene melts using energy conserving dissipative particle dynamics

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Understanding thermal degradation of polyolefins on the mesoscale can result in development of more efficient strategies for recycling and upcycling of a range of thermoplastics. Herein we develop a mesoscale framework to model random scission at high temperatures in polyethylene melts. We use the energy conserving dissipative particle dynamics (eDPD) approach. To prevent unphysical topological crossings of bonded polymer chains in standard DPD, we utilize mSRP (modified Segmental Repulsive Potential) formulation, which captures the effects of entanglements in polymers melts. We model bond breaking as a stochastic process by setting a probability of bond breaking. We first systematically characterize the fragmentation process, specifically time evolution of distribution of molecular weight and dispersity of chain fragments at a range of high temperatures. Fig. 1a shows an initial equilibrated melt within the box and a schematic of the random scission mechanism used in our mesoscale simulations of thermal degradation in polyethylene melt. We track the weight fraction distribution of chain fragments, during the random scission (Fig. 1b), where denotes a fraction of bonds broken, and is the number fraction of chains with monomers during the random scission. Our results show that both and during random scission can be approximated by the most probable distribution, also known as Flory-Schulz distribution (solid line in Fig. 1b). We then focus on characterizing the random scission process during temperature ramp. A constant heat flux is added to each bead to increase the temperature with the constant rate; the probability of bond breaking is correspondingly modified dependent on local temperature. We characterize the time evolution of molecular weight distribution of chain fragments and their dispersion dependent on the rate of temperature increase. The eDPD/mSRP approach developed herein constitutes first mesoscale framework that allows one to account for diffusion of all the species (original chains and their fragments) and heat transfer along with the random chain scission.
General Topics: Ultrahigh molecular weight and network polymers

Ultrastong and multifunctional polymeric gels with hyperconnective nanofiber networks - Xu, Lizhi (Oral Preferred)

Understanding the effect of zwitterion incorporation on 2DP materials quality - Oanta, Alexander (Oral Preferred)

Macroscopic properties of polyacrylate gels across an ion-induced volume transition - Mussel, Matan (Oral Only)

Polydopamine polyelectrolyte hydrogel with antibacterial activity - O'Connor, Naphtali (Oral Only)

Versatile synthesis of PDMS-g-PMMA with tunable grafting density and molecular weight - D'Ambra, Colton (Oral Preferred)

Crystallinity and perfection in ethylene vitrimers probed by time-domain NMR, calorimetry and X-ray scattering - Saalwaechter, Kay (Oral Only)

Understanding factors influencing the network topology rearrangements of vitrimers utilising transfer-dominated branching radical telomerisation (TBRT) copolymers - Wright, Stephen (Oral Preferred)

Rheological isotope effects in dynamic covalent networks - Chapman, Steven (Oral Only)

Liquid deposition modeling of polybenzoxazine and graphite nanocomposite - Chiou, Kevin (Oral Preferred)

Leveraging supramolecular chemistry to template entanglements in polymer networks - Kruse, Benjamin (Oral Only)

Structural characteristics of catechol-modified tetra-arm poly(ethylene glycol) networks - Ryu, Jungju (Oral Only)

Polymer networks of poly(ε-caprolactone) (PCL) and epoxidized soybean oil (ESO) with nanoscale morphology - Madbouly, Samy (Oral Only)

Synthesis of graft (co)polymer with a high degree of branching based on nucleophilic substitution reaction between polyhalohydrocarbon and macromolecular living anion - Lin, Vichao | Tang, Tao (Oral Only)

Understanding of partially fluorinated electrolyte for LiNi0.5Mn1.5O4 with sulfurized carbon anode from polyacrylonitrile for lithium-ion battery - Berhe, Gebregziabher (Oral Preferred)

Microgels adapt to guest molecules: Superchaotropic nano-ion binding - Richtering, Walter (Oral Only)
General Topics: Ultrahigh molecular weight and network polymers

Spatial control over mechanical properties of polymer networks from single resin feedstocks - Allen, Marshall (Oral Preferred)

Self-assembled, crosslinked, and nanostructured block copolymer organogels - Werner, Joerg (Oral Only)

Programmable mechanochromic response in direct ink written chiral photonic elastomers - Choi, Jihye (Oral Preferred)

Introduction of -NSS- and -NS- bonds in advancing chemical, auxochromic and thermal properties in phenylenediamine polymers - Rathnayake Wickremasinghe, Shanari (Oral Only)

Towards the use of nanocaged Rose Bengal to enhance photo-induced collagen crosslinking - Aguirre Soto, Hector Alan (Oral Only)

Additive manufacturing with silicone by Heating at a Patterned Photothermal Interface (HAPPI) - Lee, Chang-Uk (Oral Only)

Reconstructible and programmable polymer gels with photothermal responsive properties and homogeneous network structure - Gao, Guohao (Poster Only)

Synthesis of stereoregular cyclic poly(alkyl sorbate) initiated by strong base - Ide, Yuto (Poster Only)

Thioaminals as degradable cross-links in polymer networks via exchange with thiols - Sanchez, Cassandra (Poster Only)

New chemistry for revealing latent acrylates and its implementation in controllable polymer systems - Niemet, Claire (Poster Only)

Construction of discrete poly(rac-lactide) networks composed of precisely-controlled network precursors via SuFEx and SPAAC click chemistry - Koo, Mo Beom (Poster Only)

Solute diffusion in glycopolymer-based hydrogels for potential transcuticular drug delivery - Wang, Xianjun (Poster Only)

Biopolymer matrix for smart food packaging technology - Kedir, Welela (Poster Preferred)
Ultrastong and multifunctional polymeric gels with hyperconnective nanofiber networks

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3D fibrillar networks represent an essential structural feature in natural load-bearing soft tissues, providing an excellent combination of mechanical strength, flexibility, porosity and biological functionalities. Inspired by natural soft tissues, we utilize synthetic polymers to construct self-assembled 3D nanofiber networks, providing a biomimetic materials platform for applications in bio-integrated systems. In this presentation, I will introduce our recently developed hydrogels and aerogels involving hyperconnective network of aramid nanofibers. The reconfigurable interactions between stiff and soft components in the composites lead to unique microstructural features that are responsible for their outstanding mechanical properties. Theoretical models were developed to further explain general strengthening mechanisms for materials involving 3D fibrillar networks. This biomimetic materials platform may enable advanced applications in medical implants, tissue engineering, wearable electronics, and other device technologies.
Understanding the effect of zwitterion incorporation on 2DP materials quality

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We report the first study on the effect of zwitterion loading on the stacking behavior of two-dimensional polymers (2DPs). These porous polymers hold potential for a variety of applications that rely on the presence of accessible channels that arise from the ordered stacking of the polymer sheets. Therefore, understanding how structural features affect stacking order is of the utmost importance, and there is an underlying assumption that the long-range order will be only minimally affected by side chains that occupy the pores. Here we explicitly evaluate this assumption and find it to be unreliable. Instead, these findings demonstrate that specific side chain structures and loadings might be used to control 2DP stacking and/or exfoliation in the future.

Numerous methods involving installing motifs of varying sizes and/or charge states have been employed to understand how 2DP functionality directs the overall stacking order. Installing zwitterionic moieties within the 2DP pores, which can yield a high ion density within these nanometer-scale channels, has yet to be thoroughly explored. Here we incorporate zwitterionic groups into 2DP pores with high yields and variable loadings and demonstrate that zwitterion loading has a destabilizing effect on the apparent crystallinity and porosity of the 2DP. The stacking order was found to diminish above certain zwitterion loading threshold values for the two different 2DP systems examined. These results demonstrate that alkyl chains stabilize the stacking interactions of layered 2DPs, and that interlayer interactions and resulting stacking order can be manipulated by including variable amounts of zwitterions.
Macroscopic properties of polyacrylate gels across an ion-induced volume transition

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Introduction of high valence counterions into polyelectrolyte gels results in a reversible volume transition in many synthetic and biopolymer systems. In this talk we summarize results obtained from systematic investigations of macroscopic properties of polyacrylate gels across an ion-induced volume transition. These include the degree of swelling in different ionic environments, elastic modulus, NMR parameters, electric potential difference, and ion partitioning. Our purpose is to illustrate the richness of the phenomenon, and to provide insights into possible properties of biological polyelectrolytes such as DNA, pectin, and mucus, which are more challenging to measure at their native physiological environment.
Polydopamine polyelectrolyte hydrogel with antibacterial activity

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Polydopamine (PDA) has attracted considerable attention as a surface material for its ease of modification, adhesiveness, and biocompatibility. A polydopamine polyelectrolyte hydrogel was developed by ionic crosslinking dextran sulfate with a copolymer of polyethylene imine and polydopamine. Polydopamine inclusion was confirmed by changes in hydrogel color and morphology. The PDA hydrogels were demonstrated to be biocompatible, showing comparable cell viability with PBS buffer up 48 hours after treatment. PDA containing gels also showed comparable levels of irritation biomarkers interleukins IL-8 and IL1-α to PBS buffer. Polydopamine was used to produce silver nanoparticles in situ, generating nanoparticles in the range of 25 nm to about 200 nm. The silver nanoparticle containing hydrogels had wide ranging antibacterial activity being effective against P. aeruginosa, K. pneumoniae, E. coli and S. aureus, the four most prevalent bacterial infections in chronic and septic wounds.
Versatile synthesis of PDMS-g-PMMA with tunable grafting density and molecular weight

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A versatile synthetic platform is reported that yields high molecular weight graft copolymers through a combination of click chemistry and controlled free radical polymerization. Macroinitiators are synthesized from commercially available siloxane copolymers with tunable grafting densities and accurate control over side chain molecular weight. Optimized polymerization conditions show minimal radical-radical coupling with degradation of the siloxane backbone further confirming control over growth of the side chains.

Graphical representation of the versatile synthesis of graft copolymers with tunable grafting density and controlled molecular weight.
Crystallinity and perfection in ethylene vitrimers probed by time-domain NMR, calorimetry and X-ray scattering

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Vitrimer networks, a new class of reconfigurable polymer networks based upon dynamic bonds, are considered a sustainable alternative to conventional thermosets. A potential partial crystallization can aid in further improving the mechanical properties, yet a balance with the degree of crosslinking (that normally impedes crystallization) has to be considered. Here, we focus on a recently developed class of "ethylene vitrimers" made from (α,ω)-diamino alkanes and boric acid. The samples were known to exhibit polymorphic crystal structures, which we now show to be distinguishable by proton NMR via their dipolar line width, enabling simple time-domain experiments based upon the related differences in transverse ($T_2$) relaxation. We can thus obtain absolute degrees of crystallinity in excess of 90%, which thus has to include the boric acid crosslinks. We can follow the kinetics of crystallization and crystal-crystal transformations in real time and elucidate the conditions under which the polymorphs form and interconvert, with a focus on recrystallization after full and partial melting. DSC experiments are used to clarify an unexpected superheating effect, which challenges the determination of actual melting points. We further identify a strong memory effect in isothermal (re)crystallization. Implications of the dynamic nature of the vitrimers in relation to the kinetics of crystallization are discussed.
Understanding factors influencing the network topology rearrangements of vitrimers utilising transfer-dominated branching radical telomerisation (TBRT) copolymers

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The chemical structure of polymers has a direct impact upon their thermomechanical and thermorheological properties. Hydrogen bonds and steric effects have been incorporated into a vast array of polymer systems to tune these characteristics. In the emergent field of vitrimer research slight attention has been given to the structure-property relationship, specifically the tuning of tensile strength and topology freezing temperature (Tv). Utilising a catalyst free approach, a series of covalent adaptable networks (CANs) have been synthesised to form hydroxyl rich hyperbranched architectures with distinct topologies. Transfer-dominated branching radical telomerisation (TBRT) is a polymerisation strategy used to form branched polymers. Utilising ester and urethane containing MVTs and a range of sterically hindered telogens, a sequence of epoxy functional copolymers have been synthesised with divergent physical properties related to the glass transition temperature (Tg) and viscosity. Upon curing, a series of CANs with transesterification and transcarbamoylation capabilities have been prepared. Incorporation of higher ratios of the urethane functionality has facilitated manipulation of Tv by over 20 °C and activation energy (Ea) by 50 KJ/mol. Exploiting different telogens it has been established how the network flexibility directly impacts tensile strength. Increased substitution of the telogen has been shown to increase the ultimate tensile strength and decrease elongation at fracture both by a factor of 10.

Such insights provide opportunities to manufacture fully reprocessable CANs with shape memory behaviour and tuneable properties related to dynamic bond exchange. The potential of the TBRT platform for the industrial translation of high-performance polymers will be discussed.

Figure 1 a) The tensile strength of pristine and recycled dog bone mould. b) Stress relaxation of urethane copolymer with Arrhenius plot.
Rheological isotope effects in dynamic covalent networks

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Among the most sensitive and prevalent tools for probing reaction mechanisms is the kinetic isotope effect (KIE). This effect originates from the differences in vibrational energy between isotopically labeled molecules. The most common KIE involves substituting a deuterium for a proton because this substitution results in the largest change in vibrational energy between isotopologues. When this change in energy perturbs bond formation either before or during the rate-determining step of a reaction, a KIE can be measured by the relative rates of reaction between isotopologues. Recently, our lab has developed dynamic covalent cross-linkers for hydrogels that relax stress through an associative thiol conjugate addition–elimination mechanism. The structure of the cross-linker markedly affects the rate of thiol exchange. We hypothesized that isotope effects can influence the rate of thiol exchange and therefore influence the viscoelasticity of the dynamic networks. With small-molecule kinetics, we show that exchange with hydrogenous vs deuterated thiols provides an inverse KIE: the deuterated thiol (R–SD) in D₂O exchanges faster than the thiol (R–SH) in H₂O. This is further reflected in the different rates of stress relaxation of analogous hydrogels swollen with either D₂O or H₂O. We are further studying this effect computationally with the goal of providing fundamental physical organic understanding of how isotope effects manifest in dynamic polymer networks.
Liquid deposition modeling of polybenzoxazine and graphite nanocomposite

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Direct 3D printing of graphite reinforced polybenzoxazine nanocomposite was performed using liquid deposition modeling. Polybenzoxazine is a class of thermoset typically polymerized with heat, and benzoxazine monomer typically liquefies before ring-opening polymerization. While the monomers can be 3D printed, the thermal ring-opening polymerization would destroy the printed structure. A solution to polymerize polybenzoxazine nanocomposites without losing shape was found in combining the use of a graphite scaffold and using a temporary powder mold during the polymerization process. By printing a polybenzoxazine nanocomposite precursor with over 30wt% graphite, the mixture can retain its shape during printing at room temperature. The printed structure is then embedded into a powder bath to help stabilize the mixture during the thermal crosslinking process. The end result is an arbitrarily shaped, 3D printed polybenzoxazine reinforced with high content of graphite flakes.
Leveraging supramolecular chemistry to template entanglements in polymer networks

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The existence of entanglements—mechanical connections among polymer chains—has been appreciated since 1940. A growing body of evidence suggests that entanglements trapped in polymer networks have been correlated with strength, toughness, and fracture energy enhancement. Despite the ubiquity of polymer entanglements, the topology-property relationships of entanglements remain ill-defined. By merging the fields of supramolecular topology with polymer network chemistry and physics, we investigate the role of trapped entanglements within polymer networks in regards to network toughness and fracture energy. Entanglements are templated within networks via ligands coordinated to a metal center that are subsequently clicked to polyethylene glycol chains. The entanglements are preserved upon removal of the metal center, creating a topological bond. Comparing the mechanical properties of these networks with non-templated networks illuminates the role of templated entanglements in polymer networks.
Structural characteristics of catechol-modified tetra-arm poly(ethylene glycol) networks

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The internal structures of tetra-arm poly(ethylene glycol) networks were investigated to understand the influences of crosslinking types on finite polymer units. The end groups of poly(ethylene glycol) were modified with catechol moieties that provide bis- and tris-complexation with iron(III) ions depending on pH levels. Here, we observed that the crosslinking types establish the internal structures assembled with regular polymer units. The structural aspects were explored using light scattering, small-angle X-ray scattering, and neutron scattering techniques. The scattering features at the low q evaluated the presence of inhomogeneities in the networks according to bis- and tris complexation types. The correlation length parameter values (ξ) correspond to the star polymer sizes containing catechol-based crosslinking units, which exhibited shadow effects under the neutron contrast variation methods. For the networks by bis-complexation, ξ decreased with ξ ~ c-0.33 in the networks, indicating elastic ball-like behavior. Therefore, the results show that the uniform tetra-arm polymer networks can be formed consecutively by linear bindings of the iron(III) based-catechol connections. It suggests that the coordinatively bonded star polymer networks can provide a strategy to develop novel polymer architecture.
Polymer networks of poly(ε-caprolactone) (PCL) and epoxidized soybean oil (ESO) with nanoscale morphology

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Semi-interpenetrating polymer networks of poly(ε-caprolactone) (PCL) and epoxidized soybean oil (ESO) with nanoscale morphology have been successfully synthesized using a relatively new in situ cationic polymerization and compatibilization in homogeneous solution. Miscible blends with single glass relaxation process (a-relaxation process from DMA measurements) have been observed for blends with PCL concentration of ≤ 10 wt.%. Highly interconnected, co-continuous nanoscale morphologies were observed using TEM for blends with high concentrations of ESO (≥ 60 wt.%). Blends with lower concentration of ESO, showed dispersed nanoscale particles of approximately 500 nm in PCL matrix. Partially miscible blends with PCL-rich and ESO-rich phases were evaluated from the shift in the glass relaxation processes of each component in the blends relative to the pure polymer components. The a-relaxation process of the PCL-rich phase shifted to higher temperatures indicating partially miscibility of the blend components. The crystallization behavior of PCL in the blends was investigated using DSC and x-ray scattering techniques. The melting and crystallization temperature as well as heat of fusion and degree of crystallinity of PCL in the blends were found to be decreased linearly with increasing the concentration of ESO. The blends showed also excellent shape-memory effect based on the program temperature (melting temperature of PCL) and the fixing segments (ESO crosslinked structure). Furthermore, all the blends particularly with high concentration of PCL have biocompatibility and might be useful for biomedical applications. The current versatile, low-cost, and relatively new strategy for synthesizing nanoscale morphology of semi-interpenetrating polymer networks structures with shape-memory effect and biocompatibility should be widely applicable for new polymer systems.
Synthesis of graft (co)polymer with a high degree of branching based on nucleophilic substitution reaction between polyhalohydrocarbon and macromolecular living anion

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"Graft onto" method based on controlled living polymerization techniques was considered as a modular approach in the preparation of graft (co)polymers. By this method, side chains and backbones are predesigned as building blocks for coupling reaction to desired graft polymers. In this work, a new method based on macromolecular nucleophilic substitution reaction between polyhalohydrocarbon and living polymer lithium (side chains) is used to synthesize graft (co)polymers. Details are as follows:

Firstly, A series of graft (co)polymers were synthesized through the reaction between iodinated 1,2-polybutadiene (PB-I, backbone) and living polymer lithium (side chains), shown as Scheme 1. The coupling reaction between PB-I and living polymers can finish within minutes at room temperature, high conversion (up to 92%) could be obtained by effectively avoiding side reaction of dimerization when living polymers were capped with 1,1-diphenylethylene. Graft copolymers could also be synthesized with side chains of multi-component polymers, such as block polymer (polystyrene-b-polybutadiene) and even mixed polymers (polystyrene and polybutadiene) as hetero chains.

To further synthesize comb-like polymers using the above method, a backbone with pendent double bond, such as poly(4-(vinylphenyl)-1-butene) ((PVSt)), was used as precursor. At the same time, a series of model comb-like polymers (PSVS-g-PS and PSVS-g-PE) with high branching degree were synthesized by nucleophilic substitution reaction between iodinated copolymer of styrene (St) with 4-(vinylphenyl)-1-butene (VSt) (PSVSI, backbone) and living polystyrene lithium (PSLi, side chain) shown as Scheme 2.

Synthesis of PS based graft (co)polymers based on “Graft onto” method.
Understanding of partially fluorinated electrolyte for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with sulfurized carbon anode from polyacrylonitrile for lithium-ion battery

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A new lithium-ion battery is configured by coupling sulfurized carbon anode and high voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) cathode. The anode is derived from sulfurized polyacrylonitrile (S-C(PAN)). Severe capacity fading usually becomes unavoidable due to the oxidative decomposition of solvents, primarily when a conventional carbonate electrolyte with 1 M lithium hexafluorophosphate (LiPF$_6$) is employed. Fluoroethylene carbonate (FEC), ethyl methyl carbonate (EMC), and 1, 1, 2, 2-Tetrafluoroethyl-2, 2, 3, 3-tetrafluoropropyl ether (TTE) are formulated as the best electrolyte (3:2:5 in vol. ratio) for this new high-voltage lithium-ion battery to mitigate this capacity fading and improve the adaptability of the S-C(PAN) and LNMO. The discharge capacity of full cell made with 1 M lithium hexafluorophosphate (LiPF$_6$) in FEC/EMC/TTE (3:2:5) electrolyte reaches 688 mAh g$^{-1}$ at a rate of 2 C, while 19 mAh g$^{-1}$ for the control electrolyte. X-ray photoelectron spectroscopy (XPS) results confirm that the fluorinated electrolyte stabilizes both surfaces of S-C(PAN) and LNMO in the full cell effectively. Compared to the control electrolyte, the developed electrolyte enhances the cyclic stability and rate capability of both half cells (Li//S-C(PAN and Li//LiNi$_{0.5}$Mn$_{1.5}$O$_4$) and S-C(PAN)//LiNi$_{0.5}$Mn$_{1.5}$O$_4$ full cells.
Microgels adapt to guest molecules: Superchaotropic nano-ion binding

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Microgels are polymer networks with colloidal dimensions that are swollen in a good solvent. Since microgels are soft systems, they adapt their structure to the incorporation of guests. It is therefore interesting to study the impact of model guest molecules on microgels. Nanometer-sized anions (nano-ions), such as dodecaborates and Keggin polyoxometalates (POMs) have recently emerged as potent inorganic additives for aqueous non-ionic soft matter systems. Their unique combination of sizes around one nanometer and ionic charges typically from -1 to -6, place nano-ions at the boundary between classical ions and charged colloids, which results in fascinating solution properties and nano-ions were termed superchaotropic ions in extension to the well-known Hofmeister series.

In this contribution we report on the interaction of a superchaotropic Keggin polyoxometalate with PNIPAM microgels. Scattering experiments reveal that in the swollen state below the VPTT, the addition of SiW causes first a swelling of the microgel with a subsequent deswelling. The binding of superchaotropic SiW is found to exceed the effects of classical salts by several orders of magnitude.

Such nonmonotonic swelling/deswelling of microgels with SiW-concentration appears as a general response of non-ionic PNIPAM-microgels to superchaotropic ion binding. However, it is distinctly different from linear macromolecules.

Binding of nano-ions to microgels
Spatial control over mechanical properties of polymer networks from single resin feedstocks

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Synthetic platforms allowing for spatially localized mechanical properties of soft polymeric materials are a critical challenge in the development of next-generation manufacturing. To this end the synthesis of an orthogonally initiated interpenetrating polymer network system is presented. The kinetics and initiation of each network are independently controlled, allowing for tuning of final network morphology and/or crosslinking density. The effect of differences in morphology on fracture toughness and modulus are investigated, with final properties ranging over three orders of magnitude. The use of light as a stimulus allows for spatial patterning of mechanical properties within a chemically uniform sample. Macroscopic, multi-mechanical structures are produced, and emergent mechanical properties are explored. Mechanically patterned materials could be employed as soft actuators, structure for stretchable electronic devices, or specialized medical devices.

**Mechanical Patterning**

\[\lambda = 1\]  \[\lambda = 1.4\]

Selective Strain
Self-assembled, crosslinked, and nanostructured block copolymer organogels

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The self-assembly of block copolymers into a variety of ordered morphologies on the sub-100 nm scale has been and remains a topic of interest from fundamental polymer physics to scalable nanomaterial fabrication. Interestingly, despite decades of block copolymer research, very little is known about the behavior of self-assembled block copolymers upon exposure to good or non-selective solvents if individual blocks are crosslinked. In this talk, we will discuss our recent results on the swelling behavior of self-assembled and crosslinked block copolymer bulk films with 100s of microns in thickness. Specifically, we designed our polymers with the block that forms the 3D continuous matrix to be selectively crosslinkable to a tunable degree, another block that is amenable to chemical modifications after synthesis, self-assembly, and crosslinking, as well as a neutral block in the case of triblock terpolymers to tailor swelling interactions. The molecular design of our block copolymer system with post-self-assembly crosslinking of the matrix-forming block enables the formation of organo-gels with any kinds of solvents, including good and non-selective ones, without disassembly of the bulk film but with controllable extent of swelling. We present results on the composition- and crosslink-dependent degree of swelling of these block copolymer organogels, as well as the retention of the morphological nano-periodicity including co-continuous gyroid and anisotropic cylindrical structures. Surprisingly, even at low crosslinking degree and swelling up to 500%, the ordered self-assembled nanostructure and its periodicity is maintained as confirmed by small-angle X-ray scattering. Furthermore, we find that in bulk block copolymer materials, even morphologies without a 3D continuous matrix retain their nanostructure upon crosslinking and swelling in non-selective solvents. Our research demonstrates that appropriately designed block copolymers can form homogenously swollen polymer networks with chemically distinct nanophases representing a novel class of ordered organogels.
Programmable mechanochromic response in direct ink written chiral photonic elastomers

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In this study, we develop a new method to develop cholesteric liquid crystal (CLC) phase-based chiral photonic elastomers through UV-assisted direct ink writing (DIW). The helical axis of the DIW-processed CLC elastomers (CLCEs) was slanted by about 40 degrees along the printing direction, which led to blue- or red-shifting of the reflected structural color of the CLCEs depending on the printing direction and the viewing angle. Interestingly, the mechanochromic behavior of the CLCEs was considerably altered by the printing direction due to the change in the slant angle of the helical axis. By harnessing both the chiroptical and mechanochromic properties of CLCEs, the potential of our CLCE as a novel strain sensor was demonstrated, which could be useful for creating an interesting anti-counterfeiting device.

Photographic images of CLCE film showing “PNU” letters as it is stretched.
Introduction of -NSS- and -NS- bonds in advancing chemical, auxochromic and thermal properties in phenylenediamine polymers

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The synthesis of polymers with heteroatoms of sulfur and nitrogen along their backbones have recently been investigated due their potential interesting chemical and physical properties. In these classes of polymers, those containing sulfur-nitrogen bonds have understudied despite the ease of synthesis of these bonds and the highly conjugated polymers that can be synthesized. In this study, a sulfur transfer reagent (S₂Cl₂) was reacted with aryl diamines to introduced -NSS- (diaminodisulfides) and -NS- (diaminosulfides) functional groups that led to highly crosslinked, colorful polymers. Poly NSS were synthesized using five different aryl amine monomers (p-phenylene diamine; 2,3,5,6-tetramethyl phenylene diamine; 1,5-diamino naphthalene; 4,4’-diaminodiphenyl sulfone; and 4,4’-oxydianiline). Due to conjugation through the aromatic rings and the NSS functional groups, the polymers possessed a wide range of colors (red, orange, green, yellow, and blue). The polymers were analyzed by size exclusion chromatography-multiangle laser light angle scattering, UV-Vis spectroscopy, elemental analysis, thermogravimetric analysis, and nuclear magnetic resonance spectroscopy. Thermally stable (200-250 °C), highly crosslinked polymers with molecular weights ranging from 10⁴-10⁶ g/mol were obtained. Their ability to be used as sensors and as 3D printable polymers were investigated. Poly NS were synthesized using S₂Cl₂ in DMF which rapidly led to the formation of SCl₂ and resulting polymers with the NS functional group. These polymers were also brightly colored and highly conjugated. This presentation will describe the synthesis and characterization of these polymers and selected applications.

Colourful NSS polymers
Towards the use of nanocaged Rose Bengal to enhance photo-induced collagen crosslinking

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Photosensitized crosslinking of proteins in tissues has many medical applications including sealing wounds, strengthening tissues, and beneficially altering tissue properties. Rose Bengal (RB) is used most frequently as the photosensitizer but is not as efficient as would be desired for broad utilization in medicine. Aggregation of RB, at the high concentrations used for medical treatments, decreases the yield of singlet oxygen, which mediates collagen crosslinking. We hypothesized that nanocages that sequester RB would inhibit self-association, increasing photosensitization efficiency. We tested cucurbituril and cyclodextrin nanocages, demonstrating that hydroxypropyl-functionalized cyclodextrins are most effective in inhibiting RB aggregation. For these RB/cyclodextrin solutions, we investigated the effect of nanocaging on the photobleaching and oxygen consumption kinetics under 530 nm LED light in aqueous phosphate-buffered solutions. At 100 μM RB, the initial oxygen consumption rates increased by 58% and 80% compared with uncaged RB for the β and γ (2-hydroxypropyl) cyclodextrins, respectively. For 1 mM RB, the enhancement in these rates was much greater, about 200% and 300%, respectively. In addition, at 1 mM RB these two cyclodextrins increased the RB photobleaching rate by ~20% and ~75%. These results suggest that nanocages can minimize RB aggregation and may lead to higher-efficiency photo-medical therapies.
Direct additive manufacturing (AM) of commercial silicones is an unmet need with high demand. We report a new technology, heating at a patterned photothermal interface (HAPPI), which achieves AM of commercial thermoset resins without any chemical modifications. HAPPI integrates desirable aspects of stereolithography with the thermally driven chemical modalities of commercial silicone formulations. In this way, HAPPI combines the geometric advantages of vat photopolymerization with the materials properties of, for example, injection molded silicones. We describe the realization of the new technology, HAPPI printing using a commercial Sylgard 184 polydimethylsiloxane resin, comparative analyses of material properties, and demonstration of HAPPI in targeted applications.
Reconstructible and programmable polymer gels with photothermal responsive properties and homogeneous network structure

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The development of controlled/living polymerization techniques has provided various syntheses for fabricating complicated polymeric architecture with controlled sizes and functionalities. For example, star polymers are linear polymer chains amalgamated at a central point with numerous functional end groups. They represent a variant of linear polymer and thus have been appealing to scientists to seek high-order architectures with unique properties due to the compact three-dimensional structure and high arm density. A vast range of star polymer structures, such as block copolymers, can be synthesized through controlled polymerization. Here, we demonstrate a synthesized star-shaped diblock copolymer with narrow molecular weight distribution. First, a diblock copolymer composed of N-isopropylacrylamide (NIPAm) and N-ethylacrylamide (NEAA) was synthesized by single electron transfer living radical polymerization using a four-branched halogenated initiator, named pentaerythritol tetra(2-chloropropionate). In the block copolymer preparation, the disappearance of the halogen end group in tertiary acrylamides is much higher than in secondary acrylamides and occurs during polymerization. Hence, to reach a high degree of functionality, NEAA was selected as a suitable monomer for the second block, and ended group transformation from the halogen group to the azido group was implemented directly as a one-pot synthesis without further isolation. After introducing N-propargyl-9-anthracene-carboxamide through the click reaction, a four-branched star-shaped diblock copolymer ended with the photoresponsive groups obtained. The polymer gel consisting of the diblock copolymers of NIPAm and NEAA has a faster thermo-response to a broader range of temperature stimuli. Moreover, the anthracene derivative's high-efficiency photodimerization and photocleavage can be achieved under 395nm and 254nm light.
Synthesis of stereoregular cyclic poly(alkyl sorbate) initiated by strong base

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Since the stereoregularity affects thermal and mechanical properties of polymer materials, stereospecific polymerization is necessary. However, there are few examples of stereospecific polymerization of cyclic polymers because it is difficult to synthesize them. Cyclic polymers have attracted attention in recent years because of their unique properties, such as higher glass-transition temperature ($T_g$), lower intrinsic viscosity ($\eta$) due to the lack of chain ends. Therefore, this study aims at the synthesis of stereoregular cyclic polymer without extreme dilution.

Lewis pair polymerization of ($E,E$)-ethyl sorbate (ES) was executed in toluene at $-20^\circ C$ by diisopropylamide (LDA), strong base, in the presence of methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD), a bulky organoaluminum reagent, as catalyst. In order to confirm the topology of resulting polymer, we used transmission electron microscopy (TEM) and afterwards cyclic polymer was observed. Since LDA is strong base, this is basic initiation pathway and subsequent ring-closure occurred.

Next, we worked on controlling the stereoregularity of cyclic polymers. Polymerizations were carried out at $-40^\circ C$ in the absence and presence of ($-)$-sparteine. Then, poly(ES)s were obtained under both of experimental conditions. We hydrogenated internal double bonds of poly(ES)s and determined stereoregularities by using $^{13}$C NMR. As a result, both of obtained polymers were about 90% of threo diastereoselectivity. Furthermore, when the reaction temperature was lowered to $-60^\circ C$, disyndiotacticity increased up to 83%. On the other hand, the remarkable difference in stereoregularity due to the addition of sparteine wasn’t observed. Finally, cyclic polymers synthesized at $-60^\circ C$ with addition of sparteine were observed directly by TEM. As the result, stereoregular, threo(93%)-disyndiotactic(83%), cyclic poly(ES) was synthesized without extreme dilution in one pot.

Lewis pair polymerization of ethyl sorbate (ES) in the presence of ($-)$-sparteine
Thioaminals as degradable cross-links in polymer networks via exchange with thiols

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Thioaminals are a functional group where a carbon atom is bonded to one nitrogen and one sulfur atom. These groups can undergo exchange with thiols, resulting in a new thioaminal. When thioaminals are incorporated into polymer networks, the thiol-thioaminal exchange reaction allows the thioaminal to serve as a degradable link, resulting in a degradable crosslinked network. We’ve shown that polymer networks containing various thioaminal crosslinks can be degraded by reaction with a number of different thiols, and that timescale for these reactions varies with different functional groups on both thiol and thioaminal. Moving forward from that, we’re investigating the effect of varying functional groups on the equilibrium and kinetics of the thiol-thioaminal reaction through small molecule studies. Understanding the effect of different functional groups on thiol and thioaminal will allow us to apply the knowledge to thioaminal polymer networks; create networks that can be tuned to desired properties through the thioaminal functional group; and synthesize networks that can be degraded at desired rates, temperatures, and extents based on the thiol used to exchange.

![Thioaminal exchange reaction scheme](image1)

![Thioaminal crosslinked polymer network degradation scheme](image2)
New chemistry for revealing latent acrylates and its implementation in controllable polymer systems

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Acrylate materials are widely used in polymer science due to their high reactivity and synthetic versatility. However, this can also be a disadvantage because acrylate functionalities need extensive care to stabilize. Additionally, these materials cannot typically be degraded, thus adding to the existing plastic waste issue. This work explores a chemistry which reveals latent acrylates within a polymer network, allowing the user to control when the acrylates appear. A small molecule system was first developed, in which a mercaptopropionate was added to allyl glycidyl ether to form a thioether with an epoxide functionality. It was found that when this material was heated at 125°C, acrylates were exposed via a mechanism not widely explored in the literature. To further probe the mechanism of the reaction, the reaction products and yield were examined using a variety of catalysts and reaction conditions. This chemistry was then explored for applications in controllable and degradable networks by using a multi-functional thiol.
Construction of discrete poly(rac-lactide) networks composed of precisely-controlled network precursors via SuFEx and SPAAC click chemistry

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Synthesis of homogeneous polymer networks with the homogeneity have been desired to enhance the mechanical and physicochemical properties for their practical applications. In this work, we prepared homogeneous polymer networks composed of tetra-arm discrete poly(rac-lactide) polymers via SuFEx and SPAAC click chemistry. Both coupling chemistry enabled the efficient crosslinking reactions between precisely defined network precursors. The preparation of homogeneous polymer networks was identified via swelling measurements and also, the network disassembly experiment revealed that there was low level of the defects, derived from the unreacted functionalities, in the polymer networks.
Ticks as vectors of pathogens can cause serious illnesses in humans and severe economic damage to livestock production. Using broad-spectrum insecticides for tick control is not a permanent solution because they are highly toxic environmental pollutants and have reduced effectiveness over time due to long-term drug resistance. Gene-modification technology, such as RNA interference, has shown great success in the laboratory and is a promising alternative to control tick-borne diseases in the future. The modified genetic fragment can intervene in harmful bacterial colonization inside the tick or weaken the attachment between the tick and its host. However, traditional gene delivery methods, such as soaking ticks in a dsRNA solution, are tedious and only applicable in the laboratory. Our approach is to use a bio-adhesive hydrogel as a drug delivery vehicle to passively increase the drug retention time on the tick cuticle to support transcuticular dsRNA delivery in the tick’s native environment. For this research, glycopolymers were synthesized via free radical polymerization in water to form the hydrogel matrix. We focused on how the commoner ratio and stereochemistry of the pendant saccharide unit affects the structural water in the hydrogel and diffusion behavior of the model compound to support the future sustained release of dsRNA.
Biopolymer matrix for smart food packaging technology

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Food packaging innovations focused on the inclusion of these active ingredients in polymer matrices with the goal of prolonging food shelf life. The use of non-biodegradable materials in numerous packaging applications has currently increased environmental degradation. The food packaging sector is increasingly looking for lightweight biodegradable packaging to reduce material use, waste, and transportation costs. Nevertheless, widespread use of these bio-based plastics is hampered by one or more of their intrinsic shortcomings, which include poor process ability, brittleness, hydrophilicity, poor moisture and gas barrier, poorer compatibility, and poor electrical, thermal, and physical qualities. The incorporation of additives such as essential oils and bioactive metabolites improves biological activity. The effective development of new bioactive packages for food preservation is enabled by the encapsulation of natural antimicrobial antioxidant agents, such as essential oils, using modern nanotechnology techniques. These novel strategies are piquing the interest of the food sector and scientific community worldwide. As a result, this study covers the most prevalent biopolymer utilized as bio-based plastics and gives an overview of current improvements in the selection and application of bioactive metabolites, as well as their effect on material performance and bioactivity. In addition, we describe bioactive plastic synthesis methods from biopolymer composites that increase the overall performance of bio-based plastics. But the evaluation provides additional guidance to subsequent researchers on the utilization of bio-based plastic as food packaging. In addition, we describe bioactive plastic synthesis methods from biopolymer composites that increase the overall performance of bio-based plastics. But the evaluation provides additional guidance to subsequent researchers on the utilization of bio-based plastic as food packaging. The most recent applications of biopolymers, as well as the ongoing challenges and future prospects for bio-based plastics, are also discussed.
Henkel Outstanding Graduate Research Award in Polymer Science and Engineering
Honoring Christopher DelRe

Harnessing enzymes to engineer catalytic soft materials - DelRe, Christopher (Oral Only)

Solid-state biocatalysis: Time matters - Xu, Ting (Oral Only)

Transporting gases in microporous water - Mason, Jarad (Oral Only)

Peptide-based complex supramolecular systems - Ulijn, Rein (Oral Only)

Stabilizing proteins using polymeric nanomaterials for enhanced enzyme performance and sustainable material applications - Hall, Aaron (Oral Only)

Electrostatics at the interfaces of complex materials - Jimenez Angeles, Felipe (Oral Only)
Harnessing enzymes to engineer catalytic soft materials

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Enzymes have advanced catalytic features that are unsurpassed by even their most sophisticated synthetic counterparts. However, their inherent instability in non-natural environments and complicated interactions with other macromolecules makes it difficult to harness enzymes as building blocks for soft materials. In this talk, I will show how advances in protein stabilization allow us to interface enzymes with synthetic polymers and control their catalytic behavior inside solid plastic matrices. When the plastic matrix is also a substrate for the enzyme, the reactivity of the enzyme-based material can be tuned with precise control. For instance, by engineering the interactions between embedded enzymes and the host polymer at the molecular level, it becomes possible to preserve enzymatic latency during the plastic's lifetime and then trigger its depolymerization into recyclable or metabolizable by-products. Features such as the enzyme's active site, the enzyme–protectant interactions, and the host polymer's hierarchical structure can all be tuned to control depolymerization rates, mechanisms, and by-products. By quantifying and manipulating how enzymes interact with synthetic polymers in the solid state, we open a new route to engineer polymeric materials that can be modified or depolymerized on-demand.
Solid-state biocatalysis: Time matters

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Being vetted through evolution, enzymes are high effective to catalyze reactions in their native environment. Recently advances in enzyme evolution led to new opportunities to program how enzyme behaves based on end needs. Rational design and manipulating enzymatic reactions within a solid matrix can lead to bioactive plastics. It is also fundamentally interesting when one has to deal with two classes of macromolecules. I will share our latest thoughts and recent progresses in this area. Specifically, I will discuss the interplay of multiple parallel processes across multiple time and length scales.
Transporting gases in microporous water

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The efficient transport of gas molecules through aqueous fluids is essential to sustain life, but the low solubility of nearly all gases in water imposes fundamental limitations on many biomedical technologies that can be difficult to overcome. Owing to their high internal surface areas, microporous solids can concentrate gas molecules through adsorption to much higher densities than are present in a bulk gas phase or than can be dissolved within a liquid. The high gas capacities of microporous solids, however, are difficult to translate to the aqueous environments that are ubiquitous to biology because water typically floods the pore networks, precluding gas sorption. Here, I will describe the design, synthesis, and characterization of aqueous solutions of microporous nanocrystals that feature low viscosities, long-term colloidal stability, and permanently dry micropores even when surrounded by liquid water—the combination of which allows high densities of gas molecules, including oxygen, to be stored and released in physiological environments. Implications of this approach for overcoming gas transport challenges in fuel cells, electrocatalytic processes, and bioreactors will also be discussed.
We are interested in learning how peptides can be used to create functional materials and adaptive systems using bottom-up approaches. We use integrated computational and experimental approaches to search and map the peptide sequence space and create guiding principles for the formation of gels, soluble nanofilaments, liquid condensates and complex, sequence-adaptive liquids. The talk will provide updates on three ongoing research directions: (i) Design of peptide modalities that give rise to formation of fluorescent liquid condensates that are taken up by cells; (ii) Mechano-responsive peptide crystals; (iii) Experimental learning and memory using sequence-adaptive peptide mixtures. Overall, the research demonstrates that peptides, and mixtures of peptides, show significant potential as designable and tunable nanomaterials for a variety of applications in biomedicine and green nanotechnology.
Stabilizing proteins using polymeric nanomaterials for enhanced enzyme performance and sustainable material applications

Aaron M. Hall, aaronhall@berkeley.edu. Intropic Materials, Oakland, California, United States

Intropic Materials is commercializing an enzyme stabilization platform that enables the use of enzymes in non-aqueous solvents and soft materials. By rationally designing the energetic and chemical interactions between our polymeric nanomaterials and the enzyme of interest, we deliver enhanced enzyme performance across a broad range of acellular environments. This unlocks the ability to explore new synthetic routes to the production of commodity and specialty chemicals, as well as novel smart material applications.

Our first product is an additive that enables certain bioplastics to depolymerize from the inside out in a processive manner. The breakdown proceeds rapidly (days to weeks) under mild aqueous or compost conditions, and achieves near-complete degradation into small molecules without the formation of microplastics. This addresses a key design challenge for bioplastics, improves the end-product design space, and increases their market viability.

By combining natural and synthetic building blocks, Intropic Materials is building chemical and material innovations for a more sustainable world.
Electrostatics at the interfaces of complex materials

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Proteins, polymers, and nanomaterials are combined to create new complex materials for applications ranging from energy storage and production to therapeutics and bioinspired functions. In this talk, we discuss the role of electrostatic interactions, ionic correlations, and polarization on the assembly, structure, and properties of new soft complex materials.

Polyelectrolyte adsorption on a protein surface via electrostatic interactions.
Herman F. Mark Award in Honor of Robert Waymouth (Invited)

Modern approaches to functional polymeric materials - Hawker, Craig (Oral Only)

3D printing at scale to drive global sustainability goals - DeSimone, Joseph (Oral Only)

Organocatalytic polymerization: From chemistry to immunology - Waymouth, Robert (Oral Only)

Catalyst development for polymerization and CO$_2$ capture, storage and upcycling to high value materials - Hedrick, J (Oral Only)

Sugar plastics: Rich regiochemical and stereochemical diversities for sustainable, digestible polycarbonates derived from carbohydrates - Wooley, Karen (Oral Only)

Responsive and functional polymers for applications in diabetes - Maynard, Heather (Oral Only)

Functional and tunable polymers from natural products - Reineke, Theresa (Oral Only)

New routes to sustainable polymers - Coates, Geoffrey (Oral Only)
Modern approaches to functional polymeric materials

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

Scalable methodologies for synthesizing block copolymer libraries and recyclable 3D printed objects with spatially resolved mechanical and chemical properties will be discussed and the power of accelerated synthesis and purification strategies for the “bottom-up” fabrication of nanostructured systems with exceptional properties illustrated. In preparing these nanostructures, orthogonal functional group interconversions and efficient organic transformations combined with controlled polymerizations are critical.

Patterned dynamic/covalent hydrogel network
3D printing at scale to drive global sustainability goals

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Digital fabrication techniques based on additive manufacturing (AM) are poised to revolutionize manufacturing. AM is considered a central tenet for the full realization of the positive impact promised by Industry 4.0, including local-for-local manufacturing to mitigate supply-chain disruptions, flexible factories, on-demand inventory, design freedom, impossible geometries, digital traceability, and mass customization to name a few. We believe there are important economic, strategic, and innovation imperatives to translate AM from the present, mostly prototyping technology, to a manufacturing technology that can achieve high-volume production of remarkable new and sustainable products.

We envision a future wherein products:
A. are reimagined as ultra-lightweight, bio-inspired, latticed, “de-materialized” structures that reduce material consumption when produced, have lower CO₂ emissions in use (materials for electric vehicles), and degrade rapidly due to designed high surface area when recycled;
B. have the range of properties needed for broad applications AND are recyclable through the co-design of chemistries that enable a circular economy;
C. are economically produced through the introduction of new high-speed 3D and multi-material printing processes with the precision, resolution, repeatability, and throughput required for energy-efficient production;
D. are produced locally and “on-demand” to reduce the need to ship products long distances and to eliminate slow-moving inventory—e.g. spare parts—that are stored for years in climate-controlled warehouses.

I will describe a new 3D printing process that we pioneered called Continuous Liquid Interface Production (CLIP). CLIP embodies a convergence of advances in software, hardware, and materials to bring the digital revolution to polymer additive manufacturing. CLIP uses software-controlled chemistry to produce commercial quality parts rapidly and at scale. Compatible with a wide range of polymers, CLIP opens major opportunities for innovative products across diverse industries.

Latticed microneedles
We have developed a family of versatile organic catalysts for the living polymerization of lactone and carbonate monomers that have been integrated into efficient flow reactors for the programmed synthesis of block copolymer libraries. These synthetic methods spawned the development of a new concept for gene delivery based on a class of dynamic oligomeric cationic materials that are designed to self-assemble with polyanionic nucleotides to form coascervate nanoparticles. These Charge-Altering Releasable Transporters (CARTs) are structurally unique oligomers that operate through an unprecedented mechanism, serving initially as oligo(α-amino ester) cations that complex, protect and deliver mRNA, and then change physical properties through a degradative, charge-neutralizing intramolecular rearrangement, leading to intracellular release of functional mRNA and highly efficient protein expression, both in cell culture and in live mice. The key roles of the catalytic process, synthetic conditions and structure of the materials on the biological performance will be described.
Current strategies to reduce CO2 emissions are insufficient—both point-source and direct-air-capture (DAC) must be considered to mitigate excessive atmospheric CO2 concentrations. Given the urgency of climate change issues and the immense challenges of developing viable methodologies for CO2 conversion, we posit that understanding structure–property relationships of organic/inorganic molecular reactivity across multiple length scales will lead to the evolution of remarkably efficient transformations of CO2 and revolutionize chemistries to control the fate of this greenhouse gas. Thus, we sought to investigate families of superbases (SBs) that serve as CO2 mitigating agents. This talk will focus on describing the wide-scope reactivity of a family of modular SBs that can be exploited in a variety of chemical transformations of CO2 from dilute and pure gaseous sources as well as polymerizations. We found that the SBs can form zwitterionic complexes to activate CO2, which can be readily mineralized into metal carbonates. Importantly, the highly reactive nature of SBs renders them widely useful to upcycle CO2 into high value products.
Sugar plastics: Rich regiochemical and stereochemical diversities for sustainable, digestible polycarbonates derived from carbohydrates

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A primary interest in the Wooley laboratory is the production of functional polymers from renewable sources that are capable of reverting to those natural products once their purpose has been served. Building from Bob Waymouth’s fundamental contributions to organobase-catalyzed ring-opening polymerizations, this presentation will highlight the development of synthetic methodologies for the preparation of polycarbonates from carbohydrates. Detail will be provided from a series of rigorous investigations of the regiochemical complexities during ring-opening polymerizations, which also invoke in-situ structural metamorphoses to produce degradable polymers of diverse compositions and regiochemistries. Moreover, recent advances involving carbohydrate building blocks having stereochemical differences will also be discussed. Target materials are designed for potential applications in diverse areas, from energy, to medicine, to the environment. Examples will highlight contributions that polymer chemistry can make toward bulk technological materials that are capable of impacting global needs, such as water-food-energy-health, and the grand challenges that must be solved in the coming decade, while also emphasizing fundamental synthetic chemistry advances.
Responsive and functional polymers for applications in diabetes

Heather D. Maynard, maynard@chem.ucla.edu. Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California, United States

This talk will focus on polymer conjugates and polymeric nanoparticles to enhance the drug delivery of protein therapeutics for the treatment of diabetes. The rational design, synthesis, and preclinical evaluation of these materials will be discussed. Materials that respond to chemical triggers in vivo and reductive pH will be disclosed with a focus on therapeutics for diabetes. Polymers that contain groups that actively stabilize these therapeutics will also be revealed.

Responsive nanomaterials for delivery of diabetes medicines will be discussed. Image created by Ellie Puente (UCLA).
Natural products offer modern polymer chemistry and engineering numerous pathways for tailororable materials development. Renewable feedstocks provide a multitude of rich monomer functionality (i.e., high heteroatom content, stereochemistry, architecture), low toxicity/biological tolerability, and the potential for triggered degradation. Indeed, the chemical, physical, mechanical, and morphological properties of polymers containing sustainable and biologically-friendly monomers can be tuned based on chemistry, sequence, and composition to yield diverse function and properties. Herein, the design and development of tailored polymers from levoglucosan and quinine will be presented. Levoglucosan is a renewable chemical obtained in high yields from pyrolysis of cellulosic biomass, which offers rich functionality for polymerization, synthetic modification, and crosslinking. We report the facile synthesis and characterization of 1,6-alpha linked functional stereoregular polysaccharides from biomass-derived levoglucosan via cationic ring-opening polymerization. We have also report the utility of levoglucosan as a renewable platform chemical that enables access to tailored thermosets important in applications ranging from 3D printing to biomaterials. Likewise, we have shown that the cinchona alkaloid, quinine, can bind DNA through both electrostatic interactions with the phosphodiester backbone and intercalation through pi-stacking interactions with nucleobases. We have directly copolymerized quinine with HEA in a one-step free-radical polymerization reaction and demonstrated the exceptionally efficient delivery of plasmids to several human cell types, including keratinocytes, for which suitable transfection methods are limited. Overall, the design, development, and application of natural product-based polymers will be highlighted.
New routes to sustainable polymers

Geoffrey W. Coates, gc39@cornell.edu. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States

This lecture will focus on our research to transition from fossil fuels to renewable resources such as CO and CO2 for polymer synthesis, as well as the development of polymeric materials that exhibit lower post-use impact on the environment, such as biodegradable polymers.
Industrial Innovations in Polymer Science (Invited)

Innovation at BASF - Gupta, Rohini (Oral Only)

Use of multiple linear regression in the development of a process aid for PVC packaging with high melt strength and clarity - Petr, Michael (Oral Only)

From inventory to analysis: Enabling end-to-end data management in large chemical organizations - Tashman, Will (Oral Only)

Light weighting composites with 3D graphene - Boul, Peter (Oral Only)

Design, development, and delivery of programmable polymer nanoparticles for treating CMT disease with antisense oligonucleotides - Ting, Jeffrey (Oral Only)

Encoding complex polymer formulations into standardized data schema - Arora, Akash (Oral Only)

System for anomaly detection and performance analysis in high-dimensional streaming manufacturing data - Subramanian, Karthik (Oral Only)
Innovation at BASF

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At BASF, we create chemistry for a sustainable future by combining economic success with environmental protection and social responsibility. Innovation has always been the key to BASF’s success. Protecting our climate and making the best use of limited natural resources while supplying the fast-growing global population with food, energy and clean water are among the greatest challenges of our time. Innovations based on chemistry play a pivotal role in overcoming these. That is why we are working together with our customers on innovative processes, technologies, and products for a more sustainable future. In this seminar, we will focus on BASF’s journey of innovation, along with recent success stories that highlight our commitment to sustainability and digitalization. We will then take a deeper dive into the technical details of a successful academic collaboration focused on tunable molecular design strategies for commercially relevant adhesive polymers, which addresses sustainability challenges surrounding such polymers by enhancing their biodegradability, while retaining their functionality and efficacy. This project epitomizes how our global network of top universities, research institutes and companies, known as our Know-How Verbund, helps us develop targeted, marketable innovations, strengthen our portfolio with creative new solutions, and in this way, reach our growth targets.
Use of multiple linear regression in the development of a process aid for PVC packaging with high melt strength and clarity

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Process aids for clear poly(vinyl chloride) (PVC) offer a unique challenge because they need to provide both melt strength and clarity. In general, melt strength increases with the molecular weight due to increased chain entanglements, but clarity decreases or, rather, haze increases with molecular weight due to the increased difficulty of disentanglement and dispersion into the host PVC melt. However, a low T_g and high compatibility composition was shown to break out of this trade-off and produce higher molecular weight process aids with concomitant low haze because they soften earlier during processing to promote fusion and are able to disentangle more quickly and disperse into the PVC more easily. Accordingly, the design space for molecular weight, T_g, and composition was defined using Multiple Linear Regression to predict clarity given these input process aid variables.
From inventory to analysis: Enabling end-to-end data management in large chemical organizations

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All enterprise chemical companies want to have an abundance of "good, clean" experimental data to learn from. They want to share data more effectively, empower their scientists to learn from the wealth of information already generated by the organization, and utilize more advanced machine learning to accelerate development of new products. However, it is extremely difficult to get scientists to adopt new tools that aren't their finely-tuned spreadsheets, given the flexibility and the years of habits they've formed doing their research in the past 30 years. Furthermore, harmonizing data standards across global organizations where teams operate slightly differently from each other is a difficult task from an information capture and alignment perspective.

Uncountable provides an enterprise solution for chemistry-driven organizations that allows for flexible, detailed data capture from raw material inventories, to formulation and processing, and all testing in a single data system. By leveraging Uncountable, R&D teams are able to find and compare data instantaneously, no matter who created it. And with data captured in a structured and consistent matter, built-in ML tools have enable 30-40% reduction in experimentation to reach performance targets on individual projects.
Light weighting composites with 3D graphene

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LytR™ is a 3D graphene that has been tuned for optimal product performance as a filler and reinforcement for polyethylene. The graphene is produced through the microwave pyrolysis of methane to render a custom-tuned carbon material. Hydrogen is produced as a side product of this reaction. The graphene itself is embedded with functionality which enables adaptivity of the filler to the surrounding matrix polyethylene. The surface area of LytR™ is tuned with respect to the 3D graphene layer count and surface area to give the optimal product performance by insuring easy and effective dispersion on the polyethylene. The dispersibility is key to achieving product performance.

Light-weighting composites with LytR™ offers performance enhancements while achieving lower weight material of lower carbon footprint. Polyolefins are effectively fortified with 3DG through increases in flexural modulus, tensile strength, and impact strength. Performance enhancements of these kinds reduce the amount of polyethylene required for the manufacture of variety of different products. Because of the enhanced performance of polyethylene with LytR™, the product has been selected by Pelican, to reduce the weight of their line of cases by 40%. LytR™ also opens many new market opportunities in light weighting materials including cases, kayaks, agricultural tanks, and coolers.
Charcot-Marie-Tooth (CMT) disease is an inheritable, chronic genetic nerve disorder that affects nearly 3 million people worldwide and involves progressive nerve degradation, leading over time to symptoms that range from mild mobility issues to severe limb/muscle atrophy. The majority of CMT cases are caused by mutations within myelinating Schwann cells behind blood-nerve barriers in the peripheral nervous system. CMT1A for example is characterized by uncontrolled duplication of the peripheral myelin protein 22 (PMP22) gene. Antisense oligonucleotides (ASOs: small, single-stranded nucleic acids that are chemically modified to be complementary to mRNA targets) have recently emerged as potent therapeutics for reducing PMP22 expression in Schwann cells but, like most gene therapy approaches, are plagued by ineffective delivery and pose significant toxicity risks at high doses. In this work, we present an AI-driven platform that unifies motifs from high-throughput polymer synthesis, rapid biological screening of multiplexed polymer nanoparticles, and machine learning techniques to design CMT1A-relevant, fit-for-purpose delivery vehicles. We prepared 100+ polymers by systematically tuning multimonomeric microstructures and architectures from the vast molecular space. Key polyelectrolyte features (i.e., charge type, polymer length, non-electrostatic interactions) were evaluated to overcome challenges in ASO cargo complexation, binding, and colloidal stability. In vitro screening of polymer nanoparticle assemblies into cell-based models revealed distinct differences between polymers in the reduction of PMP22 mRNA levels, allowing us to down-select promising candidates for further in vivo characterization. Initial structure-property-performance data at all stages of materials development and assay characterization were used to train and develop an iterative machine learning/synthesis model for ASO delivery. This foundational approach enables us to study more complex animal models in the future and, ultimately, expands the number of feasible nonviral vector options for otherwise undeliverable gene therapies that can treat CMT1A in clinical human trials.
Encoding complex polymer formulations into standardized data schema

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An industrial product formulation typically involves multiple synthesis steps, polymers and additives of various architectures, and a host of characterization tests and processing conditions. Representation of such complex systems into data formats that can be used for advanced data analytics, such as searching for a polymer with specific functionality, or predicting properties using machine learning, would immensely accelerate the development of new products. This presentation will discuss Dow's efforts in developing a standardized data schema for encoding complex polymer formulations comprehensively. Specifically, the schema uses a recently proposed line notation called BigSMILES to represent polymer architecture and a graph-based data format called PolyDAT to store synthesis, processing, and characterization information. The transferability of the schema is improved by representing two widely different formulations using a single schema. Finally, the developed schema is used to compute several molecular fingerprints and descriptors, such as solubility parameters and topological polar surface area, that are universal to many polymeric systems and can be directly supplied as inputs to a machine-learning method for property prediction. Overall, this talk showcases Dow's efforts in making polymer informatics and machine learning more transferrable across various businesses and products, accelerating materials design and discovery to address customers' requirements.
System for anomaly detection and performance analysis in high-dimensional streaming manufacturing data

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ABSTRACT BODY:
Abstract: Manufacturing involves a complex problem space consisting of thousands of parameters that need to be tracked and monitored and arrays of sensors which are providing online readings at fractions of seconds. Effective monitoring of this large dynamic datasets poses a substantial challenge for system analysts and line operators.

Manufacturing analytics is often plagued by the magnitude of streaming data as well as the complexity of having millions of parts, thousands of assembly lines, and recipe customization for particular products. In large manufacturing sites, thousands of tags are coming from various parts of a manufacturing line at sub-second intervals. The complexity and magnitude of the streaming data makes it challenging to diagnose partial equipment failure or degradation prior to catastrophic failures, which result in the complete shutdown of the line and a tedious and slow root cause analysis for repair planning (sometimes on the order of multiple days). Exacerbating this problem is the lack of labeled data which limits the application of any Supervised Learning algorithm.

In this talk, we will be talking about a learning system that we designed using the online sensor reading which can provide near-real-time feedback to technicians or engineers via data-based inferences generated from statistical, machine learning, or advanced AI algorithms. From these inferences, the user can then enact adjustments to the equipment lines to address the anomalous or sub-optimal behavior being identified by the algorithms or even take proactive action (planned maintenance, etc.) based on the learnings provided.
Natural Polymers - A Back to the Future Approach to Deal with Plastics Issues

Cellulose derivatives as natural polymers for eco-friendly applications - Cheng, H.N. (Oral Only)

Natural Polymers: An alternative measure to address plastic pollution - Wang, Jun (Oral Only)

Polysaccharide derivatives: New fields of innovations - Adden, Roland | Lu, Helen (Oral Only)

PHA production using “Next Generation Industrial Biotechnology” based on *Halomonas* - Chen, George (Oral Only)

New PHA composition to amplify the landscape of sustainable packaging - Krishnaswamy, Raj (Oral Only)

How a performance-based natural polymer is challenging traditional packaging formats - Black, Thomas (Oral Only)

Harvesting of naturally-derived building blocks from adult black soldier flies - Tibbetts, Cassidy (Oral Preferred)

Utilization of Nitro-oxidization process (NOP) for agronomic applications - Ilacas, Grenalynn (Oral Preferred)

High value adding with natural polymers: Nanocomposites, coatings, and 3D Printing - Advincula, Rigoberto (Oral Only)

Biofilms from food waste and polyhydroxybutyrate: Improving water vapor barrier properties - Xu, Shu (Oral Preferred)

Industrial development of biodegradable and bioderived polymers for a more sustainable future - Gao, Wei (Oral Only)

Designed enzymatic biomaterials - Lu, Helen (Oral Only)

Stimuli-responsive protein engineered biomaterials - Montclare, Jin (Oral Only)

Renewable and biodegradable polyurethanes from algae: The present and future - Burkart, Michael (Oral Only)

Determination of monomeric ratio compositions in polyhydroxyalkanoates using $^1$H benchtop nuclear magnetic resonance spectroscopy - Riegel, Susanne (Oral Only)

From biological matter to strong, soil-compostable bioplastics - Roumeli, Eleftheria (Oral Only)

Beyond the standard end of life testing of biopolymers - Urgun-Demirtas, Meltem (Oral Only)

Learning from nature and collective wisdom for a brighter future - Yuan, Qiong (Oral Only)

Exploring structure-activity relationships for polymer biodegradability - Chai, Yunzhou (Oral Only)

Synthesis of biodegradable poly(ester-thioether) using click polymerization of tartarates and dianhydrosugar-based thiol - Imamura, Ryota (Poster Only)
Natural Polymers - A Back to the Future Approach to Deal with Plastics Issues

Hydrophobization of cellulose nanofibers using grafted polymers based on plant oils - Shevtsova, Tetiana (Poster Preferred)

Fabrication of Cellulose_Ag/ZnO nanocomposite mat for dye degradation and antimicrobial packaging - Kandel, Krishna Prasad (Poster Only)
Cellulose derivatives as natural polymers for eco-friendly applications

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There is current interest in using natural agro-based polymers and their derivatives for eco-friendly applications. Thus, many polysaccharides, such as starch, cellulose derivatives, and food gums have been studied as edible coatings, films, and food packaging. In particular, cellulose esters are commercially available and have satisfactory physical properties. For example, cellulose acetate is biodegradable, amorphous, non-toxic, odorless, stable in mineral oils, permeable to water vapor, and soluble in acetone depending on the degree of substitution. This polymer can form transparent and flexible films, which may be used in food packaging, photographic films and other applications. Mixed esters of cellulose (e.g., cellulose acetate propionate and cellulose acetate butyrate) can also be used. In earlier studies we have looked at cottonseed hull, cotton burr, wheat straw, barley straw and rice hull as raw materials to produce cellulose esters and ethers. We have also used iodine and Lewis acids as milder and effective promoters for the esterification of polysaccharides. Moreover, we have explored the incorporation of essential oils in cellulosic esters for food packaging applications. The essential oils can serve an antimicrobial function and act like plasticizers that increase the stretchability of the films. An alternative approach is to use dissolvable cellulose ethers as food packaging or coatings. In this talk, a summary of these various approaches will be provided and selected examples presented.
Natural Polymers: An alternative measure to address plastic pollution

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Plastic pollution has become one of the most pressing environmental issues. What are the measures to fix this problem? In addition to recycling plastics and making plastics biobased/biodegradable, a new trend is emerging - to promote the use of natural polymers. Natural polymers, whose backbones are created by nature, have minimal hazard to humans and the environment, can degrade in any natural environment, and whose large-scale production and degradation after end-of-life do not negatively impact the environment. Meanwhile, natural polymers emit a minimum amount of greenhouse gas during their life cycle. In addition, if they are collected, natural polymers can also be recycled, (e.g., paper). Natural polymers have already showcased commercialization for single use packaging and are expected to grow as an effective alternative solution to reduce the plastic pollution to the environment. We'd like to call for more investment and R&D work in this area, which includes, but not limited to: Paper Packaging and its barrier coatings; dissolvable natural polymer packaging forms; carbon negative materials; material bio-engineering technologies to produce natural polymers, e.g. PHAs; synthetic biology; natural/ enzymatic degradation of polymers, etc.
Polysaccharide derivatives: New fields of innovations

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Polysaccharides and their derivatives are widely used in an extensive field of applications including for example pharmaceutical, food, home and personal care, industrial and construction. They are sourced from a variety of natural resources like cotton, wood or seaweed, but also created via fermentation or biotechnological routes. Polysaccharide derivatives in particular cellulose derivatives have been in focus of large scale industrial processing for many decades. Despite the long history those versatile molecules still offer room for innovation and new fields of application continue to be developed. Especially in light of sustainability several fields of research surface where poly-glucans and their derivatives in general can be in focus.

Research on the polymer. Similar to the non-biobased synthetic polymers also polysaccharides should undergo a critical assessment regarding sustainability and on how to optimize sustainable creation and use. Part of this field is the assessment of new raw materials, including sourcing of reactants from ecofriendly pathways, choosing alternative raw materials as well as options to further reduce energy consumption during creation of materials using new processing technologies.

Identification of new compositions with new application value. Cellulose ethers for example offer a design space that includes MW, type of substituent as well as the degree and distribution of substituents. Especially the latter has founded many innovations within the last years. One example to be named is METHOCEL™ Bind, a polymer that provides a new gelation feature by altering the substituent distribution as well as AFFINISOL™ HPMC HME, which improves the solubilization of poorly soluble active pharmaceutical ingredients.

Expanding the design space to apply known routes of creation with enzymatically created backbones. With recent developments the flexibility to create poly-glucans as well as subsequently derivatize them has been made reality. This allows e.g. to exchange incumbent synthetic materials with new highly functional polysaccharide-based ones.
PHA production using “Next Generation Industrial Biotechnology” based on *Halomonas*

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Polyhydroxyalkanotes (PHA) are a family of environmentally friendly biomaterials synthesized by various bacteria. The diversity of PHA reflected by structures and properties has resulted in various applications, making them a promising alternative of petroleum-based plastics, yet their industrialization is challenged owning to the high production cost and instable product quality. Recently the “Next Generation Industrial Biotechnology” (NGIB) has been developed, namely, a long-lasting, open and continuous, energy-saving fermentation process under artificial intelligent control using extremophilic *Halomonas* spp. grown on low-cost mixed substrates NGIB overcomes the disadvantages of the current industrial biotechnology (CIB) to reduce the bioproduction cost and process complexity, leading to successful industrial production of various PHA and several other small molecular products.
New PHA composition to amplify the landscape of sustainable packaging

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PHB (polyhydroxybutanoic acid) copolymers or PHAs are recognized to naturally biodegrade in soil, home compost, industrial compost, fresh water and marine environments. In this presentation, we will highlight the attributes and value proposition of a “new to the world” bio-based **amorphous PHA** rubber. Incorporating amorphous PHA as a component in products based on other compostable polymers such as semi-crystalline PHA, PLA, PBS and PBAT results in considerably faster composting/biodegradation, improved melt processing and handling, higher toughness and flexibility.
How a performance-based natural polymer is challenging traditional packaging formats

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Based on high amylose starch, Kuraray’s Plantic offering is shaking up the world of performance packaging. The ability to provide gas barrier with a plant-based solution is a unique proposal in the area of packaging circularity. A best-in-class LCA shares reduced carbon emissions with a product which offers shelf-life extension and food waste reduction. With end-of-life scenarios of compostability or recyclability, the Plantic offering can be reclaimed in the recovery of rigid plastics or repulped and recycled in the paper stream when used with paper or boardstock. This is truly a compelling offering for the multilayer barrier films market where recyclability is a challenge. The proposed submission plans to highlight the property space, industry demand, commercialization, market adoption and environmental contribution of this unique natural barrier solution.
Harvesting of naturally-derived building blocks from adult black soldier flies

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The urgent threat to our environment created by plastic pollution has continued to grow and develop as we face the well-established problems arising from traditional plastic production using petrochemicals and their accumulation. Polymeric materials constructed from natural building blocks are promising candidates to displace environmentally-persistent petrochemical counterparts, due to their similar thermal and mechanical properties and greater breadth of compositions, structures and properties, sustainability and degradability, thereby redefining the current plastic economy. A key goal in the exploration of building blocks from natural polymers is to avoid competition with resources critical to food, fuel, construction and other societal demands. This requires turning to unique supply chains, such as black soldier flies (BSF).

BSF provides an immense array of potential utility to society, ranging from being a protein source for animal feed to composting waste. However, the larvae are almost exclusively of use for these processes and the adults serve the sole purpose of reproducing. Once the adults die, they are currently considered as waste and disposed of. Intrigued with the opportunity to create a value chain using the adult BSF, studies focusing on optimization and scalability for the digestion of adult black soldier flies to produce high quality chitin and utilize it as a feedstock for the production of super-absorbent hydrogel networks will be discussed.
Utilization of Nitro-oxidization process (NOP) for agronomic applications

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The current agricultural practice is a broken loop leading to global food and clean water crises, and producing a myriad of organic wastes, from agricultural residues to food, animal, and human waste. An innovative concept to combat these problems is to adapt a circular solution that focuses on the upcycling of organic waste into valuable products with a zero-waste processing platform. Nitro-Oxidation Process (NOP) is an economical, low-energy technology that utilizes nitric acid as a major agent, an essential ingredient for making fertilizers, to facilitate the production of liquid fertilizers and nanocellulose from versatile biomass and organic waste feedstocks. NOP has shown to eradicate all human pathogens from food, animal, and human waste, as well as unlock NPK (nitrogen, phosphate, potassium) nutrients from any organic feedstocks rapidly when compared to traditional methods such as composting. The process allows the design of a zero-waste approach by focusing on green chemistry principles and producing two valuable agronomic materials: safe and low cost liquid fertilizer; anionic nanocellulose as a scaffold for tunable ionic-crosslinked gels as water retention and remediation materials for food production and infrasturcral protection.

Nitro-Oxidation Process (NOP) exhibits a zero-waste nanocellulose processing technology using nitric acid and low energy employing agricultural- and bio-waste to produce liquid fertilizer, nanocellulose biogel, and water purification materials.
High value adding with natural polymers: Nanocomposites, coatings, and 3D Printing

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Renewable based polymers, natural polymers, and biobased polymers have many things going especially for plastics replacement. From Miscanthus grass, abaca fibers, chitin, coconut coir, the key is determining their ability to form synergistic blends and composites. This means investigating their miscibility and dispersion properties including a fundamental understanding of their secondary and tertiary structures (alpha-crystallinity and beta-sheets). The nanostructuring involves utilizing their sometimes high-aspect ratio or non-covalent interactions to determine the needs for compatibilizations. Then there is the need to determine their minimum percolation threshold for the desired property at a minimum cost. Very often these "optimization" protocols unlock their true techno-economic value rather than simply using them to "replace plastic". In this talk we will describe strategies and projects where we have focused on preparing nanocomposites for high value adding in applications with coastings and 3D printing.
Biofilms from food waste and polyhydroxybutyrate: Improving water vapor barrier properties

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Plastic waste pollution has become a significant concern worldwide. There is an increasing demand for biodegradable and compostable films as single-use packaging materials for products such as food, beverages, and consumer goods. Natural and biodegradable polymers are excellent starting materials for single-use packaging applications because the waste from these materials will degrade into environmentally benign products. This study aims to improve the water vapor barrier properties of existing film formulations as single-use food packaging based on food waste. We began our synthesis with a mixture of chitosan, an extracted film-forming polysaccharide from crab shells, with food waste extracts from bananas and potatoes. These films demonstrated good thermal stability up to 200 °C and excellent elasticity with elongation up to 121%. However, the water vapor barrier properties of these films still need improvement for packaging usage. We achieved this goal by adding an additional poly(3-hydroxybutyrate) layer of approximately 20 micro meters, which improved the water vapor permeation rate of these films by 85% without severe sacrifice in the elasticity. We also performed the end-of-life testing of these films in natural environments, specifically freshwater and soil environments. These biofilms reached more than 50% biodegradation in both environments within 90 days, with an estimated lifetime of 270 days. Therefore, these bilayer biofilms showed great potential for applications as single-use packaging based on their suitable mechanical and barrier properties and biodegradability in natural environments.
Industrial development of biodegradable and bioderived polymers for a more sustainable future

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Over the past century, polymer science has made tremendous progress on understanding polymer and biopolymers, the principle of polymerizations, and massive production of polymeric materials to improve our life. Nowadays, it is difficult to imagine living without using polymeric products. However, with the massive production and broad usage of polymers by most people all over the planet, we are also facing many inextricably interconnected challenges: social inequity, climate change, waste in our oceans, declining biodiversity, energy shortages, global health, food security, and the need for clean water and air, etc. We must connect the dots between these challenges to build a more sustainable future. Sustainability can have many different definitions from different angles. In 1987, the United Nations Brundtland Commission defined sustainability as “meeting the needs of the present without compromising the ability of future generations to meet their own needs.” In 2016 many world leaders adopted the UN’s 17 global goals/Sustainable Development Goals to improve life all around the world and preserve the earth’s resources and fight climate change. Human-caused emissions of carbon dioxide need to fall 45% from 2010 levels by 2030 and reach net-zero around 2050 to limit climate change catastrophe. The production of plastic is largely reliant on fossil hydrocarbons, which are non-renewable resources which contribute to climate change.

With the new century of polymer science development, the challenges for polymer scientists are on how to better design and produce polymeric materials at large scale from renewable feedstocks at low cost, with good performance for the application, being recyclable and biodegradable after end of life. Dow’s “protect the climate” targets reflect our commitment to accelerate our work with our suppliers, customers and value chain partners to ensure Dow’s ecosystem is carbon neutral by 2050. We want to hold ourselves accountable every step of the way – from our raw materials through the end of life of our products. The development journal of award winning bioderived and biodegradable products will be discussed for us to understand the science and technology gaps for future development of natural polymers.
POLY 3931549

Designed enzymatic biomaterials

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Polysaccharides are important biopolymers with established industrial applications, including coatings, paper, home and personal care. With the ever-increasing market demand for sustainable products, there is a renewed interest in polysaccharides materials. IFF has been developing enzyme polymerized polysaccharide platform technology. The enzyme polymerized technology offers the advantage of the ability to engineer the polysaccharide structure and properties based on the enzyme catalyst, the substrate, and the processing conditions. The polysaccharides are further tailored to the application needs by post polymerization modification.

This presentation will give an overview of IFF’s enzyme polymerized polysaccharide platform. The properties and applications of representative enzyme polymerized polysaccharides will be presented.
Stimuli-responsive protein engineered biomaterials

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Inspired by nature’s biopolymers, we engineer artificial protein materials with entirely new properties and function. We employ synthetic and chemical biology to construct our materials and endow them with stimuli-responsiveness. In particular, we have fabricated protein-derived nanomaterials: helix-elastin block polymers and coiled-coil fibers. We investigate the fundamental self-assembly and molecular recognition capabilities of these systems. More importantly, we are able to harness these structure as well as others to interface with small molecule and protein therapeutics.
Renewable and biodegradable polyurethanes from algae: The present and future

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In order to avoid ecological degradation from plastic waste and ocean-born microplastics, we must transition toward renewably sourced, biodegradable polymers for the majority of single-use applications. This will require the development of drop-in solutions for these products. In the case of polyurethanes (PUs), one challenge to these goals is the development of low viscosity polyester-polyols. Low viscosity polyols not only reduce the requirement for high process temperatures but also decrease manufacturing time. In our efforts to incorporate increasing ratios of bio-based monomers into renewable PUs, we mixed diacids such as even carbon sebacic acid and odd carbon azelaic acid along with a renewable diol. This provided library of polyester-polyols, which offered lower viscosity and enable lower fabrication temperatures to make TPs, and their structure and material metrics were evaluated. TPs prepared from these polyols displayed good physical and mechanical properties, with $T_g$ in the range of $-56.5$ to $-39.7^\circ C$, corresponding to TPU soft block structure, and $T_m$ between 98.3 and 105.1$^\circ C$. These TPs exhibit excellent biodegradation under compost environmental conditions. In addition to TPs, we have developed adhesives out of water-born PU dispersants from the developed polyols, which show excellent adhesive properties and completely biodegrade within 90 days under compost conditions.
Determination of monomeric ratio compositions in polyhydroxyalkanoates using \(^1\mathrm{H}\) benchtop nuclear magnetic resonance spectroscopy

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Polyhydroxyalkanoates (PHAs) are biodegradable polymers produced by various bacteria. By optimizing the conditions under which these bio-based polymers are produced, various homo- and copolymers can be obtained. These PHAs can be transformed into bioplastics and utilized for a myriad of applications traditionally reserved for petrochemically-derived polymers (e.g., polypropylene). While PHAs tend to be more brittle and more expensive to produce, significant improvements in both the costs associated with their production and their mechanical properties have made these much more attractive to various industries in recent years. Unfortunately, the methods used to characterize these polymers can often require significant sample preparation and lengthy analyses.

Benchtop nuclear magnetic resonance (NMR) technology has greatly increased accessibility, affordability, and automatability for this technique. Sample preparation for NMR is minimal, and as a technique, it is inherently quantitative. This means that the area under each signal is directly proportional to the number of equivalent nuclei in a molecule giving rise to that signal. As such, specific reference standards and calibration curves are not required to obtain quantitative information from an NMR analysis. Furthermore, these instruments do not require regular maintenance or the use of cryogens and can easily be used by experts and non-experts alike.

Here, we will be demonstrating the use of \(^1\mathrm{H}\) benchtop NMR (60 MHz and 100 MHz) for the facile analysis of nine PHA copolymers. Specifically, the ratios of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV) in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) will be determined, and the results will be compared to those obtained on a high-field instrument (400 MHz). The utility of this approach from both quality control (QC) and product development perspectives will be demonstrated.

![NMR spectra](image-url)
From biological matter to strong, soil-compostable bioplastics

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In recent years, the field of sustainable polymers has delivered promising solutions to address the environmental issues associated with non-renewable sourcing, polluting manufacturing processes, and end-of-life fate of non-degradable plastics. Bioplastics, which are thermoplastics derived from biological sources, have gained significant traction as potential alternatives to conventional, non-degradable plastics. However, many bioplastics are not both bioderived and biodegradable, and only degrade in controlled aerobic environments, rather than in landfills or the environment where they commonly end up. In this study, we propose novel compositions and fabrication methods to design bioplastics using renewable algal matter, including whole cells and tissues. We present results on bioplastics obtained from either plant cells or algal cells, and highlight the connections between processing conditions and the resulting mechanical and thermal properties of the bioplastics. We use scanning electron microscopy (SEM), flexural tests, and thermogravimetric analysis (TGA) to gain insights into the relationship between micro-morphology, mechanical properties, and thermal properties of the bioplastics. Additionally, we conduct biodegradation assessments through soil burial tests to evaluate the backyard compostability of the prepared bioplastics, and observe similarities to food waste in terms of mass loss profiles. Our findings provide valuable insights into the potential of renewable algal matter for developing biodegradable bioplastics which combine processability with industrial manufacturing methods, desirable physical properties, and degradability in the environment.

Bioplastics from biological matter, their processability and mechanical properties.
Beyond the standard end of life testing of biopolymers

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Fulfilling the promise of novel chemistries enabled by bio-derived building blocks requires knowing and avoiding adverse environmental impacts. The structure/biodegradability relationships for many biodegradable polymers have not been studied in detail, and the degradation routes in both natural (e.g., soil, freshwater) and man-made (e.g., anaerobic digesters, composting facility) environments must be elucidated so that polymer chemists can design their processes and chemistries with these characteristics in mind. Currently, available ASTM and ISO biodegradation testing methods measure the percent conversion of polymeric material to CO₂, hence the new polymer's biodegradation rate in receiving environments.

We have been working to develop new test protocols for biodegradability that explore degradation mechanisms and extend beyond CO₂ generation. These new analyses aim to quantify changes in chemical signature and composition and physical and mechanical properties of polymers as a function of environmental exposure (e.g., detection of degradation products, changes in crystallinity, etc.). 16 s RNA-based metagenomic analysis has been conducted to elucidate the dynamics and core constituents of microbial communities to determine the spatiotemporal dynamics of these communities and their related pathways for transformation. In addition to the new protocols for the detection of changes in polymer properties, bioprospecting studies have been conducted using microbial communities from samples showing biodegradation to explore the full degradative potential of the plastisphere microbiome. The outcomes of these new protocols will provide feedback to polymer design and deconstruction scientists.
Learning from nature and collective wisdom for a brighter future

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For over a century, CAS and its hundreds of scientists have been curating, connecting and analyzing the world’s published science to accelerate discovery. The CAS Content Collection™, the largest human-curated collection of scientific information in the world, includes millions of journal articles and patents related to macromolecular (natural polymers, plastics, carbohydrates, etc.) R&D since the late 1800s. We will provide an overview of natural polymer-related literature and share insights from our analysis of leading natural polymer research, including uses and development worldwide. This work highlights the importance of learning from nature and the value of knowledge sharing and collaboration – leveraging the collective wisdom embedded in scientific publications – to address global sustainability challenges.
Exploring structure-activity relationships for polymer biodegradability

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Research on the environmental biodegradation of polymers has substantially increased recently due to growing demand for biodegradable polymers for certain applications. The biodegradability of a polymer depends to a large extent on the chemical structure of the polymer although environmental factors also play an important role. Quantitative structure-activity relationships (QSARs) have been well-established for the biodegradation of nonpolymeric organic chemicals, but not for the biodegradation of polymers. The authors herein explore structure-activity relationships (SARs) for biodegradability of polymers in various environmental compartments even though existing data are too scarce for the development of QSARs. In general, polyolefins with C-C chain are unfavorable for biodegradation, while polymers containing ester, ether, or amide bonds in their polymer chain may be favorable for biodegradation. Under a univariate scenario, higher MW, higher crosslinking, lower water solubility, higher degree of substitution, and higher crystallinity may result in lower biodegradability of polymers. There is a critical need for better characterization of polymer structures used in biodegradation studies and consistent testing conditions for the ease of cross-comparison and quantitative modeling analysis during future QSAR development.
Synthesis of biodegradable poly(ester-thioether) using click polymerization of tartarates and dianhydrosugar-based thiol

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The urgent need to resolve microplastic-based pollution is prompting polymer chemists to synthesize new types of biodegradable polymer and plastic. In our laboratory, we synthesized tartaric acid-based poly(ester-thioether) by using click polymerization and discovered its high biodegradability. Also, we synthesized dianhydrosugar-based poly(urethane-thioether) using click polymerization and discovered its high glass transition temperature and biodegradability. In this study, we prepared poly(ester-thioether) consisting of tartarates and dianhydrosugar via thiol-ene click polymerization in order to attain high biodegradability as well as thermal properties. Also, we have investigated the effects of stereochemistry on the biodegradability. Tartaric acid was esterified by alkenol with scandium triflate as a catalyst at room temperature for 48 hours to give the corresponding dialkene monomers. Dianhydrosugars were also esterized by mercapto-carboxylic acids to obtain the dithiol monomers. The alkenes and dithiols were polymerized in bulk using AIBN as an initiator (at 70°C, for 24 hours).
Hydrophobization of cellulose nanofibers using grafted polymers based on plant oils

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Cellulose has proven to be a promising natural biopolymer, finding applications in areas such as food, personal care, oilfield chemicals, construction, paper and adhesives. It is of particular value in food packaging applications due to the cellulose high glass transition temperature, high chemical and photochemical stability, hydrogen bonding, water permeability, and low toxicity. Researchers are continuously looking for new ways of cellulose fibers surface modification since most existing methods for hydrophobization are essentially based on non-renewable and expensive hydrophobizing agents, as well as negatively impact the environment. In this study, we develop and investigate the new approach for cellulose nanofibers (microfibrillated cellulose, MFC, Exilva) hydrophobization using covalent grafting of macromolecules made of plant oil-based monomers (POBMs) for modification of MFC. To investigate successful grafting process and modification of the MFC FTIR, TGA, DSC and XPS measurements were used. Obtained results show the grafted poly(POBMs) impact the MFC properties. Furthermore, modified MFC was incorporated into plant protein-based bioplastic films whereas mechanical and barrier properties of resulted films were characterized. The resulted bioplastics films (proteoposites) show good mechanical behavior, but still lacking water permeability. With a goal of improving water permeability both MFC and hydrophobized MFC were incorporated into the proteoposite films.
Fabrication of Cellulose_Ag/ZnO nanocomposite mat for dye degradation and antimicrobial packaging

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Cellulose nanocomposite materials are finding promising applications in building materials, tissue engineering, antimicrobial packaging, and water purification. In this research, a two dimensional cellulose mat was fabricated from cellulosic fiber obtained from Sterculia villosa and Bauhinia vahlii; traditionally important but least studied plant species. A systematic study on physical, mechanical, optical properties of the cellulose mat was made and compared with literature data. Using a single pot hydro-thermal synthetic method, Ag and ZnO nanoparticles were doped in the cellulose mat. Material properties of the nanocomposite mat was investigated using a variety of analytical techniques, including FE-SEM, EDS, X-ray diffraction (XRD), and UV-Vis spectroscopy. FE-SEM images of the mat showed that nanoparticles are evenly distributed in the cellulose mat. Using the paper disc diffusion method, the antibacterial efficacy of the composite mat was evaluated against Escherichia coli, Bacillus subtilis, and Candida albicans. The photodegradation of methylene blue (MB) under UV light illumination was used to evaluate the photocatalytic effectiveness. The synthesized nanocomposite showed promising photo-catalytic and antimicrobial activities. These findings suggested that the nanocomposite mat can be used in antimicrobial packaging and dye removal from water resources.
POLY Poster Session (Sci-Mix)

Catalytic C–H amination creates tough, adhesive materials from polyethylenes - Ciccia, Nicodemo (Poster Preferred)

Aqueous solution properties of linear and star poly(2-hydroxyethyl acrylate)-based polymers: from RAFT-PISA or solution RAFT polymerization - Hermosillo-Ochoa, Eduardo (Poster Preferred)

Tandem ring-opening and ring-closing metathesis polymerization of cyclopentenes containing terminal alkyne - Podiyanachari, Santhosh Kumar (Poster Only)

Fluorescent polymeric viscoelastics for ocular research - Yuan, Lucia (Poster Only)

Grafting well-defined polymers onto poly(vinylidene fluoride) via thiol-ene click reactions - Lin, Ting-Chih (Poster Preferred)

Precision-controlled deconstruction of polyethylene terephthalate (PET) using organocatalysts - Guan, Chao (Poster Only)

Modular synthesis of end-functional polymers for high-throughput supramolecular block copolymer preparation - Wang, Yunfei (Poster Only)

Understanding the influence of different chemical strategies on transfer-dominated branching radical telomerisation (TBRT) and the production of novel hyperbranched polymers - Linthwaite, Beth (Poster Preferred)

Towards chemically recyclable resins for Vat photopolymerization additive manufacturing - Makar-Limanov, Anna (Poster Preferred)

Composites of polyethylene-like polyesters with polar microphases for enhanced degradation in nutrient-poor environments - Bernabeu, Lea (Poster Only)

Evaluation of biobased solvents for the synthesis of poly(2-oxazoline)s and poly(2-oxazine)s by cationic ring-opening polymerization - Lusiani, Niccolograve; (Poster Only)

Fluorescent radical precursors for detecting mechanical degradation of polymers - Yamamoto, Takumi (Poster Preferred)

Design of novel water-soluble purely organic photocatalyst for aqueous PET-RAFT polymerization - Lee, Yungyeong (Poster Only)

Additive manufacturing of novel photopolymeric polybutadiene resin via digital light processing - Saludo, Van Michael (Poster Only)

Fabrication of Cellulose_Ag/ZnO nanocomposite mat for dye degradation and antimicrobial packaging - Kandel, Krishna Prasad (Poster Only)

Synthesis and self-assembly of folate-conjugated block copolymers of poly(ethylene glycol) and poly(L-Leucine) and their targeting efficiency - Akinmola, Adekunle (Poster Only)
POLY Poster Session (Sci-Mix)

Thioaminals as degradable cross-links in polymer networks via exchange with thiols - Sanchez, Cassandra (Poster Only)

Hybrid polymer elastomers composed of strong and weak crosslinkers - Van Zee, Nicholas (Poster Only)

Expanding the applications of metal-free ring-opening metathesis polymerization through functional initiators and chain-transfer agents - Tetzloff, Meg (Poster Preferred)

Elucidation of structural proteins used in construction of mud dauber nests and caddisfly cases for defense applications - Roberts, Jesse (Poster Preferred)

Predicting polymer solubility through machine learning: towards solvent recycling of plastics - Stubbs, Christopher (Poster Preferred)

Vibrational analysis of polyethylene crystallinity for molecular-level recycling - Stavinski, Nicholas (Poster Only)

Stimuli responsive reversible self-folding bilayer thin films - Edirisinghe, Dimuthu (Poster Only)
Catalytic C–H amination creates tough, adhesive materials from polyethylenes

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Polyethylenes are ubiquitous commodity polymers, but the lack of polar groups in the materials generally restricts their use to low-value applications and necessitates additives that complicate recycling. The introduction of nitrogen-based functional groups into polyethylenes is an important goal because the non-covalent interactions of amines, amides, and imides are known to create valuable properties in other classes of polymers and, therefore, could improve the value and reusability of polyethylenes. However, methods for the synthesis of nitrogen-containing polyethylenes are limited; copolymerizations of N-vinyl monomers and ethylene are plagued by catalyst poisoning and direct amination of preexisting polyethylene architectures by catalytic methods are unknown. We report a Cu-catalyzed C–H amination of a series of polyethylenes, including waste plastic, to incorporate a range of nitrogen-based functional groups into more than 4 mol % of the monomer units. Unusual variations to the catalyst structure proved critical to achieve high efficiency without competing scission or crosslinking of the polymer chains. The resulting nitrogen-containing materials offer a valuable combination of bulk and surface properties, including large increases in toughness (up to 8-times tougher) and newfound adhesion to various metal surfaces. This catalytic amination illustrates principles of catalyst design to facilitate reactions in the viscous solution of polyethylenes and should motivate and inform the translation of additional light alkane functionalizations as a means to address the broad challenge of converting plastic waste to higher-value materials.
Aqueous solution properties of linear and star poly(2-hydroxyethyl acrylate)-based polymers: from RAFT-PISA or solution RAFT polymerization

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In this work, linear and star PHEA polymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in dimethylformamide (DMF) at 70 °C, using a RAFT agent trithiocarbonate-type. PHEA polymers were used to prepare block copolymers mediated by two strategies of synthesis (Figure 1). Subsequently, aqueous solution properties were studied.

The first strategy is “RAFT-PISA”, cholic acid-derived monomer (CAE) was used in the chain extension of linear PHEA homopolymer (l-PHEA) by polymerization-induced self-assembly (PISA) in ethanol/water mixture at 70 °C. Following this strategy were obtained nano-objects as spheres (diameters: 114 to 124 nm) and vesicles (diameters: 92 to 163 nm and membrane thickness: 29 to 36 nm) at a solid content of 8% and 11% (for ethanol/water 45:55, v/v), respectively.

The second strategy is “solution RAFT polymerization”. Firstly, aqueous solution properties of star PHEA homopolymers (s-PHEA) with dodecyl and carboxylic acid end-groups were studied. PHEA homopolymers with dodecyl end-group are not water-soluble when degree polymerization (DP) is 7 per arm. PHEA polymers with DP of 33 per arm can be dispersed in distilled water, forming large aggregates with $D_H$ of 1051 nm, but when DP is raised at 85 per arm, PHEA polymers were water dispersible forming stable aggregates with $D_H$ of 525 nm. On the other hand, PHEA homopolymers with carboxylic acid end-group were totally water-soluble. Next, s-PHEA-TTC homopolymers were chain-extended with N-isopropyl acrylamide (NIPAM) in DMF by RAFT. The aqueous solution properties of s-PHEA-b-PNIPAM were similar to its corresponding PHEA polymer. In addition, lower critical solution temperature (LCST) was estimated for PHEA-b-PNIPAM copolymers. Even if the molecular weight of the PHEA or PNIPAM block is modified, LCST was 32 °C and 34 °C for the block copolymers from dodecyl and carboxylic acid end-group, respectively.
Tandem ring-opening and ring-closing metathesis polymerization of cyclopentenes containing terminal alkyne

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Tandem olefin metathesis is a metathesis reaction in which more than one olefin transformations simultaneously occurring in a single step reaction.¹ In this work, we studied one-pot tandem metathesis polymerization of a series of 1-propargyl-1′-carboxylate ester monomers derived from 3-cyclopentene using ruthenium-alkylidene based metathesis initiator (Scheme 1). A detailed DFT calculations and end group analysis using ¹H NMR experiments have been performed to investigate the catalytic mechanism of the metathesis reaction. The energy profile obtained from DFT analysis provides two pathways for the polymerization of monomers having both cycloalkene and alkyne functionalities. The most stable coordination of monomer was found to be via a π-coordination to the triple bond, which is oriented perpendicularly to the ruthenium-alkylidene bond. Both cycloalkene- and alkyne-initiated polymerizations were found to be feasible pathways. However, the alkyne-initiated polymerization mechanism was found to be the preferred pathway and the slightly lower rate-determining step barrier. In addition, the synthesis of the model compound supported our proposed polymerization mechanism as well as the position of the styrene end-group on the polymer chain.² Details of all these results will be presented.

![Scheme 1](image.png)

Scheme 1. Tandem ring-opening and ring-closing metathesis polymerization of cyclopentene containing terminal alkyne
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Fluorescent polymeric viscoelastics for ocular research

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Cataracts turn the human ocular lens cloudy or opaque, and eventually, impaired vision will interfere with daily activities. The NIH National Eye Institute and WHO have identified cataracts as a cause of vision loss in one of six Americans over the age of 40, and notably, the risk of cataract formation increases exponentially with age. Surgery is needed to treat cataracts and usually includes two parts: removal of the clouded lens using phacoemulsification techniques and implantation of an intraocular lens (IOL). During the surgery, ophthalmic viscosurgical devices (OVDs, viscoelastic polymers) are used to protect the corneal endothelium from ultrasonic vibration and to keep the capsular bag inflated to implant the IOL. Therefore, a dispersive OVD (with high coatability) in the first step and a highly cohesive OVD (entangled and removed from the eye as a single mass) in the last step are needed. The dispersive OVD tends to remain in the eye within the corneal concavity, can clog the eye’s drainage system, and cause a spike in intraocular pressure (IOP). These IOP spikes can damage the optic nerve and result in vision loss and blindness after cataract surgery. It has been difficult to track down the remaining OVDs since all commercial OVDs are clear and colorless. Our work is to design and synthesize optically clear and fluorescent OVDs under visible light for cataract surgery. By detecting fluorescent OVDs in the anterior chamber and the capsular bag, the remaining OVDs can be completely aspirated after the surgery to avoid any postoperative complications. We tether a fluorescent dye (Cy3 and fluorescein) to a chain transfer agent and synthesize the polymers through RAFT polymerization using OEGMA-based macromonomers and yield fluorescent polymeric viscoelastics.

Applications of polymeric materials in ocular research
Grafting well-defined polymers onto poly(vinylidene fluoride) via thiol-ene click reactions

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Poly(vinylidene fluoride) (PVDF) is a commercially available fluoropolymer, second in market value only to polytetrafluoroethylene. PVDF displays great thermal and chemical stability, making it a popular material in coatings, membranes, and lithium-ion battery fillers. Pristine PVDF lacks specific functionality, as such, there has been great interest in functionalizing PVDF by synthesizing graft copolymers. These materials have been used in advanced applications such as wearable nanogenerators and solid polymer electrolytes in batteries.

Many authors have reported using PVDF as a backbone for “grafting-from” using atom transfer radical polymerization (ATRP). However, the mechanism of this functionalization is unclear. Homolytic cleavage of the carbon-fluorine bond (BDE ~480 kJ/mol) to generate the initiating radical is difficult, if not impossible. Additionally, PVDF is subject to side reactions with the basic, amine-like ligands commonly used in ATRP in the form of dehydrofluorination. All these factors affect the reactivity of PVDF and result in poorly defined graft copolymers.

Because of the lack of mechanistic insight, we propose an alternative method—grafting onto PVDF. PVDF that has undergone dehydrofluorination will possess unsaturated sites on the backbone that can react with thiol-terminated polymers in a thiol-ene click reaction. Thiol-terminated polymers can be easily synthesized using various controlled radical polymerization techniques like ATRP and reversible addition-fragmentation chain-transfer (RAFT) polymerization. These polymers are uniform and well-defined, and the molecular weight can be determined prior to grafting. This information can then be used to calculate grafting density and efficiency. Herein, we systematically investigate how different starting materials and thiol-ene click reaction mechanisms affect the grafting efficiency of grafting onto PVDF-based materials.
Precision-controlled deconstruction of polyethylene terephthalate (PET) using organocatalysts

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Over 400 million metric tons of plastics are generated globally every year, but only ~9% are recycled. This not only causes environmental pollution but also leads to the waste of valuable resources. The performance of recycled products inevitably diminishes because of the undesired oxidation and degradation in the traditional mechanical recycling processes. Therefore, it is urgent to develop efficient methods to upcycle waste plastics rather than downcycle them. Condensation polymers, such as PET, are considered one of the ideal candidates for precise degradation due to their relatively high reactivity. Given that, we have developed a new route for the controlled deconstruction of PET to a series of well-defined oligomers using organocatalysts. These well-defined building blocks can be used to separate specific small molecules selectively and further upcycled to higher-performance polymeric materials. Therefore, this closed-loop technology via the precision-controlled deconstruction of polymer waste would provide a solid basis for a circular economy and benefit the environment.
Modular synthesis of end-functional polymers for high-throughput supramolecular block copolymer preparation

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Block copolymers (BCPs), with two or more homopolymer blocks, represent extraordinary materials applied in various fields, including ultrafiltration membranes, sensors, solar cells, etc. However, traditional block copolymer development requires a laborious process of synthesis, processing, and quantifying new material, which limits the throughput of the materials discovery rate. Supramolecular block copolymers (SBPs) are BCPs assembled with non-covalent end-functional group pairs (i.e., DAT/Thy for H-bonding). Synthesis of SBPs with different architectures, chain lengths, and chain length ratios can be simply achieved by physically blending two polymers, which shows great potential for rapid and high-throughput synthesis. To accomplish the high-throughput synthesis of SBPs, a large number of end-functional polymer blocks are required, which is still complicated. Inspired by the concept of ‘LEGO’, in this work, we developed a modular synthesis method that successfully achieved mass production of end-group functional polymers. We separated the synthesis into two parts, including functional polymers (Polymer-A) and functional H-bonding groups (HGroup-B). The Polymer-A were first polymerized via various controlled polymerization methods. Then click reaction was utilized to connect the HGroup-B to all kinds of Polymer-As via the 'grafting to' method. The HGroup-B was also clicked to initiator to initiate the polymerization to achieve the 'grafting from' process. Such synthetic method is flexible, universal, and adaptable to various kinds of polymers. Therefore, it shows numerous potentials to prepare functional polymers for the high-throughput synthesis of SBPs.
Transfer-dominated Branching Radical Telomerisation (TBRT) is a new synthetic strategy for the preparation of high molecular weight branched polymers exhibiting step-growth characteristics but using conventional chain-growth free-radical chemistries. TBRT utilises the radical telomerisation of multivinyl monomers, or taxogens (MVTs) in the presence of an excess of telogen, commonly an aliphatic thiol, to facilitate the formation of fully-soluble hyper-branched polymers to >99% vinyl conversion. Additionally, copolymerisation offers access to physical properties often unattainable by homopolymerisation, and is achievable through the mixing of co-MVTs, co-telogens, or by introducing monofunctional co-monomers to the telomerisation.

A series of branched polymers incorporating variable telogen functionalities have been prepared via TBRT. Mayo experiments were performed to determine the chain transfer coefficients, $C_T$, of each telogen and the results correlated to observed differences in the formation of infinite cross-linked networks (gelation). Ultimately, by mixing telogens with significantly different $C_T$, at varied concentrations, the resulting branched polyesters showed composition dependent effects on branching behaviour during TBRT (Figure 1). This demonstrated the ability to control and prevent gelation by mixed telogen co-polymerisation.

The scope of the macrostructures generated by this approach is vast and understanding the factors that influence polymer properties is fundamental to the understanding of TBRT. A library of materials has been prepared in order to study the relationship between polymer composition and solubility. The resultant copolymers, demonstrating varying hydrophilicities, were assessed in a range of solvents and the solubilities subsequently quantified. The hyperbranched polymer structures produced by TBRT demonstrate readily tuneable physical properties that can be exploited to generate novel materials in an industrially applicable process.

**Figure 1** Schematic representation of the functional variation in branched copolymers derived from mixed-telogen co-polymerisation.
Towards chemically recyclable resins for Vat photopolymerization additive manufacturing

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Vat photopolymerization additive manufacturing, including Continuous Liquid Interface Production (CLIP), produces cross-linked thermosets that cannot be recycled by traditional methods, such as melt reprocessing. With the advancement of these technologies, it is critical to design new materials with end-of-life in mind. In particular, chemical recycling to monomer is a promising strategy for addressing polymer waste. This work presents the design of oligomeric star-shaped, CLIP-compatible methacrylate-functionalized resins synthesized by ring-opening polymerization. The effect of monomer composition and molecular weight on thermomechanical properties will be discussed.

Graphical abstract showing the proposed chemical recycling scheme from resin synthesis, to additive manufacturing, to chemical depolymerization of the printed part back to monomer.
Composites of polyethylene-like polyesters with polar microphases for enhanced degradation in nutrient-poor environments

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Plastics are a cornerstone of today’s modern materials. Their ubiquitous use also results in environmental pollution. Even with the implementation of more responsible waste management in the future, this problem needs to be addressed. Compared to conventional plastics like polyolefins, biodegradable polyesters can be less persistent and less amenable to undesired accumulation if lost to the environment. However, degradation rates vary hugely depending on the specific environment and moreover a specific trigger would be desirable. We report on composites with semicrystalline, aliphatic polyesters with favorable polyethylene-like materials properties as a continuous phase, with polar microphases. Release of specific otherwise deficient nutrients from the latter is envisioned to promote the breakdown by microorganisms even in challenging environments like sea or freshwater.
Evaluation of biobased solvents for the synthesis of poly(2-oxazoline)s and poly(2-oxazine)s by cationic ring-opening polymerization

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The rising interest in poly(2-oxazoline)s and poly(2-oxazine)s, fueled by their multifaceted properties like biocompatibility, stealth behavior and thermoresponsivity, is bringing these polymers closer to industrial scale production, where process sustainability is becoming an increasing concern. Today, acetonitrile is a well-established solvent at the laboratory scale for the synthesis of these polymers due to the excellent control it provides over the polymerization process.

In the perspective of granting these polymers a further competitive advantage, we studied the polymerization of 2-ethyl-2-oxazoline, 2-ethyl-2-oxazine, and 2-phenyl-2-oxazoline in bio-derived, high boiling solvents like dimethyl isosorbide (DMI), representing the greener alternative to acetonitrile, maintaining the polymerization temperature (140 °C), initial monomer concentration (3 M or 4 M) and targeted degree of polymerization (DP = 60) constant. We confirmed the livingness of the polymerization of these monomers in DMI by kinetic measurements and a comparable level of chain transfer with acetonitrile by size exclusion chromatography measurements. In summary, DMI proved to be a promising bio-based solvent for the cationic polymerization of 2-oxazolines and 2-oxazines.
Fluorescent radical precursors for detecting mechanical degradation of polymers

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Polymeric mechanoradicals generated by polymer chain scission are important to elucidate the mechanical degradation of polymers. However, the detection of mechanoradicals in the bulk state is challenging due to their high reactivity. To overcome this problem, we reported a new method for efficiently detecting mechanoradicals using diarylacetonitrile (DAAN) derivatives. DAAN reacts with highly reactive mechanoradicals to produce DAAN radicals (Fig. 1). Since DAAN radicals are relatively stable radicals that emit fluorescence under UV irradiation, it is possible to evaluate polymer main-chain scission in a complementary manner using fluorescence intensity and electron paramagnetic resonance (EPR) measurements. On the luminescence properties of open-shell radicals, however, since many radicals act as quenching groups, the number of reports of the luminescent radical is still limited and therefore their relationship between structure and fluorescence properties has not been fully investigated.

With these backgrounds, we designed and synthesized a series of DAAN derivatives with different substituents and investigated their properties. As a result, the fluorescence wavelength could be systematically tuned by changing the substituents of DAAN derivatives (Fig. 2a). In addition, mechanoradical detectability changed by changing the substituents of DAAN derivatives (Fig. 2b). These properties can be predicted using density functional theory (DFT) and time-dependent DFT calculations.
Design of novel water-soluble purely organic photocatalyst for aqueous PET-RAFT polymerization

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We report a design of novel water-soluble purely organic photocatalyst (PC) and its application to aqueous photoinduced electron/energy transfer-reversible addition fragmentation chain transfer (PET-RAFT) polymerization. Ultra-low concentrations of the designed PC (5 ppm to monomers) enabled an oxygen-tolerant (or oxygen-accelerated) PET-RAFT polymerization of a variety of acrylate and acrylamide monomers in water and buffer. In addition, using chain transfer agent-modified bovine serum albumin (BSA), protein-polymer conjugates (PPCs) were successfully synthesized via grafting-from polymerization method under mild reaction conditions (e.g., at room temperature and under green light irradiation (515 nm, around 10 mW/cm²) - notably in the absence of deoxygenation process or any additives such as sacrificial reducing agents including tertiary amines and ascorbic acid. Neutral, anionic, cationic, and zwitterionic polymers affected the enzymatic activity of the corresponding PPCs, indicating that enzymatic activity of protein could be tailored by the characteristics of conjugated polymers. As oxygen-tolerant aqueous PET-RAFT polymerization eliminates high-cost and time-consuming deoxygenation process, accordingly facile preparation of PPCs would expand their utility to a wide range of applications. We also anticipate this novel PC to be employed for a variety of photocatalysis processes in aqueous and/or biologically relevant media.

Novel water-soluble purely organic photocatalyst 3DP-MSDP-IPN was discovered and enabled the efficient synthesis of protein-polymer conjugates through a “grafting-from” PET-RAFT polymerization from protein initiator at ambient aqueous conditions without any additives.
Additive manufacturing of novel photopolymeric polybutadiene resin via digital light processing

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The field of research in additive manufacturing (AM) of elastomeric materials, similarly with the advancements of AM technology, is a rapidly maturing environment. With great advancements in AM technology comes the greater need to scout, develop, and modify novel elastomeric materials that can be applied to these technologies. Previous work utilized an unmodified polybutadiene (PB) with a dithiol curative and UV-sensitive initiator as the resin in vat photopolymerization via an LCD printer. Successful 3D-printed test articles were produced, however, there were significant amounts of overcure which can be attributed to the inherent light bleed that LCD printing systems possess. Given the LCD printer disadvantages, digital light processing (DLP) 3D-printer was employed. The increased light intensity and direct projection of the image onto the vat instead of an LCD mitigates issues faced with the LCD printer. PB test resin was optimized by addition of a UV absorber, Oil Red O (OR-O), into the resin to improve feature fidelity for printed structures while decreasing pervasive light scattering, which causes overcuring. 3D-printed articles were printed using the novel photopolymeric resin and were qualitatively compared to 3D-printed articles without OR-O.

Graphical display of vat polymerization via Digital Light Processing (DLP). Novel photopolymeric polybutadiene resin was successfully 3D printed. Printed article is a lattice structure, shown above.
Fabrication of Cellulose_Ag/ZnO nanocomposite mat for dye degradation and antimicrobial packaging

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Cellulose nanocomposite materials are finding promising applications in building materials, tissue engineering, antimicrobial packaging, and water purification. In this research, a two dimensional cellulose mat was fabricated from cellulosic fiber obtained from Sterculia villosa and Bauhinia vahlii; traditionally important but least studied plant species. A systematic study on physical, mechanical, optical properties of the cellulose mat was made and compared with literature data. Using a single pot hydro-thermal synthetic method, Ag and ZnO nanoparticles were doped in the cellulose mat. Material properties of the nanocomposite mat was investigated using a variety of analytical techniques, including FE-SEM, EDS, X-ray diffraction (XRD), and UV-Vis spectroscopy. FE-SEM images of the mat showed that nanoparticles are evenly distributed in the cellulose mat. Using the paper disc diffusion method, the antibacterial efficacy of the composite mat was evaluated against Escherichia coli, Bacillus subtilis, and Candida albicans. The photodegradation of methylene blue (MB) under UV light illumination was used to evaluate the photocatalytic effectiveness. The synthesized nanocomposite showed promising photo-catalytic and antimicrobial activities. These findings suggested that the nanocomposite mat can could be used in antimicrobial packaging and dye removal from water resources.

Figure 2: (A) SEM image and (B) EDX spectrum of the Nanocomposite
Synthesis and self-assembly of folate-conjugated block copolymers of poly(ethylene glycol) and poly(L-Leucine) and their targeting efficiency

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It's essential that materials designed to be administered into the human system are biocompatible and biodegradable, and the reception of such materials by the human tissue is important to achieve its purpose. Ring-opening polymerization of amino acid N-carboxy anhydrides was investigated with α-hydroxy-ω-amino polyethylene glycol (PEG) as macro initiator to synthesize amphiphilic block copolymers with varied chain lengths. The block copolymers are explored as delivery vehicles for drugs and imaging agents by processing them into micelles. The amphiphilic properties of the copolymer were investigated for physical entrapment of hydrophobic drugs and imaging agents. Further conjugation of folic acid to the block copolymer enhances the binding efficacy of the micelles to targeted cells, increasing drug concentration on the targeted site. Folate-conjugated PEGylated poly(L-Leucine) with varying leucine monomer ratios were synthesized and processed into micelles to deliver iron oxide nanoparticles. The imaging characteristics of the micelles were investigated. Iron oxide encapsulated micelles exhibit higher relaxivities at low iron oxide concentration. The monomer ratio of the amino acid block was observed to determine the micelles' properties, and relaxivities as a result of particle spacing.

Polymeric micelle
Thioaminals as degradable cross-links in polymer networks via exchange with thiols

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Thioaminals are a functional group where a carbon atom is bonded to one nitrogen and one sulfur atom. These groups can undergo exchange with thiols, resulting in a new thioaminal. When thioaminals are incorporated into polymer networks, the thiol-thioaminal exchange reaction allows the thioaminal to serve as a degradable link, resulting in a degradable crosslinked network. We’ve shown that polymer networks containing various thioaminal crosslinks can be degraded by reaction with a number of different thiols, and that timescale for these reactions varies with different functional groups on both thiol and thioaminal. Moving forward from that, we’re investigating the effect of varying functional groups on the equilibrium and kinetics of the thiol-thioaminal reaction through small molecule studies. Understanding the effect of different functional groups on thiol and thioaminal will allow us to apply the knowledge to thioaminal polymer networks; create networks that can be tuned to desired properties through the thioaminal functional group; and synthesize networks that can be degraded at desired rates, temperatures, and extents based on the thiol used to exchange.

a. thiol-thioaminal exchange reaction scheme

b. thioaminal crosslinked polymer network degradation via thiol-thioaminal exchange
Hybrid polymer elastomers composed of strong and weak crosslinkers

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The drive for tough materials has given rise to several distinct branches of the polymer elastomer platform including the inclusion of fillers, double networks, and composites. In general, these strategies take advantage of dissipation mechanisms to reduce the stress that would otherwise lead to polymer chain rupture and catastrophic failure of the network. Our group has recently discovered a new tool to enhance toughness, utilizing mechanically weak crosslinkers (WCs) that preferentially break upon the application of force. For example, cyclobutane based crosslinkers, which undergo a facile force-coupled cycloreversion reaction under tension, exhibited up to 9 times greater fracture energy compared to analogous strong crosslinker (SC) systems. This is despite the two networks being identical in terms of dynamics and topology. In this investigation, the mechanism of WC toughening is elucidated by measuring the effect of parameters including strong/weak crosslinker composition, primary chain length, and crosslinking density. We found that the inclusion of WCs allows for selective bond cleavage of the network while under stress, providing a path for energy to dissipate without catastrophic network failure. Additionally, the path-dependent mechanism leads to a non-monotonic increase in toughness with higher WC compositions due to the interplay between the accessible length and mobility of the primary chain while under tension.
Expanding the applications of metal-free ring-opening metathesis polymerization through functional initiators and chain-transfer agents

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Metal-free ring-opening metathesis polymerization (MF-ROMP) is an efficient route to achieving high-value linear polymers equivalent to those made using metal-mediated ROMP. Because MF-ROMP eliminates the need for transition metal-based initiators by instead using an organic enol ether initiator activated by a pyrylium photocatalyst, the applications of polymers made using this technique can be expanded into areas previously inaccessible to ROMP-based polymers, including biomedical and electronic applications where residual transition metals can be detrimental to the environment in which they are used. However, the low functional-group tolerance of MF-ROMP has made synthesis of structurally useful polymers challenging. In this research we will explore how the orthogonality of MF-ROMP towards various functional groups can allow for the synthesis of completely metal-free heterotelechelic polymers that can be used to make interesting and useful materials.
Elucidation of structural proteins used in construction of mud dauber nests and caddisfly cases for defense applications

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Mud daubers are capable of constructing water resistant, thermally regulating, and durable nests using structural proteins from their saliva. Although the construction methods, foraging behavior, and the physical and mechanical properties of the mud dauber nests have been widely studied, there is little information regarding the biopolymers found within the mud dauber salivary secretions. It is believed that mud daubers secrete salivary mucoproteins to provide adhesive and hydrophobic properties within the nest, allowing them to structurally withstand extreme environmental conditions.

This study investigated the presence of mud dauber proteins within the constructed nests, along with analysis of the corresponding soils used during nest construction. Here, we present the development of novel protein extraction and analysis techniques using caddisfly silk samples that contain widely studied structural proteins. The developed workflow was carried over to mud dauber specimens and nests that were collected across the United States to extract and analyze the biopolymers from dissected salivary glands and nest materials. The metaproteomic extraction method developed involved SDS-phenol extractions and SDS-PAGE gel electrophoresis for size exclusion separation. We used state-of-the-art instrumentation, including MALDI-TOF-MS, XRD, and elemental analysis to elucidate the protein sequence and soil characteristics.

Our work delivers the foundational method development that can translate to extractions for many other insects and nest biomaterials. The proteamic findings for the mud dauber saliva and nest materials provides insight into how these biomolecules enhance structural adhesiveness and whether the mud daubers themselves can bio regulate the amount of protein based on different environmental and soil conditions. We anticipate that the protein structure knowledge can inform future research in areas of structural engineering and synthetic biology. Ultimately, it provides a foundation for future material development and proteomic research for DoD applications, including use as dust control agents for verticle lift aircraft.
Predicting polymer solubility through machine learning: towards solvent recycling of plastics

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Polymer solubility is one of the most important physical properties for synthesis and processing, with microprocessor fabrication, paint formulation, and drug delivery applications. Despite this importance, it has remained relatively understudied. This can largely be attributed to many theoretical and experimental challenges specific to macromolecule solubility, which makes theoretical formulations challenging and invalidates common solubility measures used in small molecules. By utilizing a data-driven machine learning approach, one can avoid many challenges while quickly and accurately predicting polymer solubility over a diverse chemical space. Motivated by the effectiveness of machine learning and by the current plastics crisis, in this presentation we discuss our work to predict selective solvents for the solvent recycling of waste thermoplastics. Specifically, we will highlight our recent research on predicting binary solubility labels for polymers via message-passing neural networks alongside non-deep models such as random forests. We consider both homopolymers and copolymers in our model input, which were represented as both graphs and text strings. Our physics-informed approach to model construction results in an accurate and extensible model and demonstrates practical applications of the resultant machine learning models.
Vibrational analysis of polyethylene crystallinity for molecular-level recycling

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Globally, only about 10% of postconsumer polymers are recycled, with the other 90% winding up in landfills, surrounding ecosystems, or incinerators. To mitigate the irreversible impact of the plastic waste crisis via new technologies, there has been a major shift in both academia and industry towards understanding the chemistry of mixed plastic waste. From a physical chemical viewpoint, the vibrational characteristics of polyethylene film plastics and bulk postconsumer plastics will be presented. Polymer crystallinity is the property-of-interest in these studies, as it may be leveraged for enhanced separation, purification, and recovery of recycled polymers. Thanks to a joint experimental and modeling approach, new insights from a phenomenological model reflecting the dissolution process of polyethylene were found to be supported by temperature-controlled Fourier Transform-Infrared (FT-IR) spectroscopy. Two-dimensional correlation spectroscopy was used to elucidate dynamic events occurring within the FT-IR cell at different temperatures, such as solvent diffusion, polymer swelling, chain disentanglement, and transformation from crystalline to amorphous domains. These insights may assist with the design of more efficient chemical recycling systems and processing conditions for dissolution-based packaging film separations. Moreover, understanding the fundamental mechanical properties of mixed plastic waste may also contribute to innovation in spectroscopic mechanical sorting systems.
Stimuli responsive reversible self-folding bilayer thin films

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The development of stimuli-responsive, self-folding materials is important in designing various smart, functional materials and actuators. Polymer-based self-folding materials are interesting due to their unique mechanical properties and chemical properties that can be modified to obtain sensitivity toward a broad range of stimuli. Well-adhered polymer bilayers are an interesting approach to designing self-folding structures. One polymer layer should be inactive or comparatively less active toward the particular stimulus to obtain the reversible folding and unfolding caused by swelling/dwelling or expansion/shrinking of the one polymer layer compared to the other one. The development of reversible self-folding polymer bilayers that are sensitive to chemical changes in the environment is presented in this project. Different polymer combinations of Polystyrene (PS), Poly(butyl methacrylate) (PBMA) dissolved in toluene, Poly(4-vinyl pyridine) (P4VP) dissolved in ethanol (EtOH), and Polyvinylpyrrolidone (PVPyr) dissolved in water have been used to develop polymer bilayers. Polymer bi-layer behavior after exposure to different chemical environments has been studied via UV-Vis spectroscopy and Raman spectroscopy.
Polymers for Defense Applications

Polymer additive manufacturing for defense applications - McAninch, Ian (Oral Preferred)

Precision vs. random: A decade long pursue - Xu, Ting (Oral Only)

Light-based advanced manufacturing to all-polymer multimaterial composites - Page, Zachariah (Oral Only)

Processing routes for tunable structural color - Griep, Mark (Oral Only)

Unmodified polybutadiene as a substrate for thiol-ene click chemistry in vat photopolymerization 3D printing - Moore, Levi (Oral Only)

Towards dynamically self-amplifying omniphoric multiscale metamaterials - Boechler, Nicholas (Oral Only)

Tying surface chemical processes to bulk viscoelastic transitions in polyurethane systems - McCollum, Jena (Oral Only)

Exploring dynamic bonds to tailor the behavior of dense colloidal suspensions - Rowan, Stuart (Oral Only)

Impact of cross-linker structure on the thermal and mechanical properties of selectively degradable, high-performance silyl-containing polyurethane networks - Daniels, Grant (Oral Only)

Direct-to-metal conductive polymer primer coatings meeting military specifications for primer coatings - Zarras, Peter (Oral Only)

Interface tailoring for applications in advanced polymer composites - Henderson, Luke (Oral Only)

Reactive high-performance Resins (REAPER) for additive manufacturing - Dingemans, Theo (Oral Only)

Predicting heats of formation of polymer systems via theoretical computations - Buszek, Robert (Oral Preferred)

Depolymerizable build materials for powder melt extrusion additive manufacturing - Boydston, AJ (Oral Preferred)

Improving compatibility of polysiloxanes with boron nitride nanomaterials - Cash, Jessica (Oral Only)

High-temperature thermosetting resins derived from bio-based phenols - Harvey, Benjamin (Oral Only)

Controlling the thermoelectric properties of vapor-deposited poly(3,4-ethylenedioxythiphene) (PEDOT) thin films - DeSario, Paul (Oral Preferred)
Polymers for Defense Applications

Role of antioxidant in stability of nitroplasticizer - Yang, Dali (Oral Only)

Rational design of double-network hydrogels from fundamentals to applications - Zheng, Jie (Oral Preferred)

Reconfigurable materials based on Diels-Alder polymer networks - Sukhishvili, Svetlana (Oral Only)

One-pot, solvent-free synthesis of UV-curable resins via sequential thiol-epoxy and thiol-ene reactions for additive manufacturing of elastomers - Lonnecker, Alexander (Oral Only)

Fluorine-containing polymers for propellant binder applications - Redeker, Neil (Oral Preferred)

Adaptive Structural Resins: How do you design rapid response in a polymer glass or composite? - Dennis, Joseph (Oral Only)

Vanillin-derived monomers for additive manufacturing - Hevus, Ivan (Oral Preferred)

Investigating structure-property relationships in polyesters and polyurethanes - Schulz, Michael (Oral Only)

Polycarbosilanes as enabling precursors for new concepts in the processing and high-temperature ceramic - Dickerson, Matthew (Oral Only)

Light harvesting star polymer photocatalysts using fluorescence resonance energy transfer - Seo, Jin Young (Oral Preferred)

Functionalization of titania particles for improved mechanical performance of HTPB composites - Enfiajyan, Hakob (Oral Only)

Heat shielding nanobrick wall for carbon fiber reinforced polymer composites - Rodriguez-Melendez, Danixa (Oral Preferred)

Autonomous alignment and healing in multilayer soft electronics using immiscible dynamic polymers - Cooper, Christopher (Oral Only)

Design low-fouling zwitterionic polymers for resuscitation of hypovolemic shock - Peng, Yifeng (Oral Only)

Surface treatment of pitch-based discontinuous carbon fibers - Tran, Ngon (Oral Preferred)

Multifunctional fabric with flame retardant and antimicrobial properties for soldier protection - Kulkarni, Sourabh (Oral Only)

Polymer property impacts on processing propellant composites - Dobbs, Alexandra (Oral Preferred)
Polymer additive manufacturing for defense applications

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Polymers are a critical component in propellants for defense applications. Unlike in many other applications, the performance expectations can be extreme: operating temperatures can range from -55 to 75 °C, both high and low strains must be withstood without permanent deformation, and long-term durability is expected. Traditionally these materials are either cast-cured or extruded into their final form, which has limited the potential shapes that can be made. The difficulty arises in that many traditional propellant binders are not well suited for additive manufacturing. For example, hydroxy-terminated polybutadiene (HTPB) cured with isophorone diisocyanate is the dominant polymeric binder used in solid rocket motors; however, it requires days at elevated temperature to fully cure. This talk will discuss efforts to develop polymers that are amenable to additive manufacturing as well as meet the stringent requirements for propellant applications. This will include both inert and energetic polymers for reactive extrusion and photocured AM.
Precision vs. random: A decade long pursue

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To engineer synthetic polymers capable of recapitulating proteins' phase behaviors and functions requires chemical diversity. As we increase the monomer variety, the natural question arised regarding on the sequence control. I will revisit our path over the last decades traveling from monomeric specific peptide-based materials to heteropolymers with statistically random sequence control. Studies of these model systems based on peptide-polymer conjugates and their functional materials provided critical foundational knowledge and lent us the confidence to pursue random heteropolymers. I will share our latest thoughts and efforts to tame RHPs full of complexities and unknowns.
Light-based advanced manufacturing to all-polymer multimaterial composites

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Light as an energy source has enabled transformative technologies in imaging, lithography, adhesives, and 3D printing. Its broad utility arises from the unparalleled spatiotemporal control over chemical transformations that it offers. However, contemporary methods rely on high energy UV light (< 400 nm) to produce monolithic (single material) polymer networks. Excitingly, the recent commercialization of inexpensive light emitting diodes (LEDs) has opened up an avenue to examine mild and selective synthetic transformations in photochemistry towards the advanced manufacturing of all-polymer multimaterial composites for defense applications. This presentation will focus on how the ZAP Group has developed and leveraged low energy light driven polymerizations to generate a versatile array of multimaterial, 3D objects with unprecedented speed and precision. Furthermore, an emphasis on the resultant diversity in mechanical properties and relevance to the department of defense via damping and pre-programmed deformation will be discussed. Fundamental research funded by the Army Research Office that has unveiled design principles to enable rapid solidification of photopolymer resins using LEDs will also be discussed, along with their utility and optimization in high resolution light-based 3D printing.
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Processing routes for tunable structural color

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Advanced processes towards the design and fabrication of nanophotonic structures have yielded numerous material concepts for customizable light-matter interactions. Tailored sub-wavelength structures of select materials, such as plasmonic metasurfaces and polymeric bragg reflectors, enable strong electromagnetic (EM) interactions that can be tuned to select frequencies across the spectrum. While such systems can be independently tailored towards precise colorimetric outputs in both static and dynamic configurations, new opportunities emerge in hybridized forms that enable more precise spectral control. In this work the processing routes and spectral tunability of metasurface-bragg reflectors will be discussed. Of emphasis is the scalable nature of the fabrication approaches and opportunities to control the hybridized interactions.
Unmodified polybutadiene as a substrate for thiol-ene click chemistry in vat photopolymerization 3D printing

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Low molecular weight liquid polybutadiene was used as a substrate for thiol-ene click chemistry, and photosensitive resins for vat photopolymerization were formulated and utilized to print complex structures in a digital light processing (DLP) 3D printer. This use of polybutadiene expands the variety of liquid resins available for the production of 3D printed elastomeric articles such as gaskets, bushings, and seals. Advancement in 3D printing materials could increase the serviceable lifetime of high-value equipment by enabling limited production runs of crucial obsolete soft materials, without the need for expensive bespoke production. Liquid polybutadienes of differing molecular weights were formulated against differing amounts of polythiol curative, and their mechanical properties interrogated. A candidate resin was down-selected and formulated with a light-blocking agent to increase print resolution and fidelity. Working curves were constructed, and atypical behavior for a 3D-printing resin was observed, attributed to “dark polymerization” as a result of thiol-ene chemistry’s oxygen insensitivity. Finally, complex geometries were printed with differing prepolymer molecular weights and exhibited mechanical response consistent with a change in the materials’ crosslink density.
Towards dynamically self-amplifying omniphoric multiscale metamaterials

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Recent decades have seen the advent of two material systems with extraordinary properties, namely, designed microstructured materials (e.g. mechanical metamaterials) and stimuli-responsive materials. With a few exceptions, these systems have not intersected. Where they have, their active response has been slow compared to mechanical waves, as well as one-way with no internal feedback, and zero frequency topological mechanics has not been leveraged. This talk will overview our team’s efforts to enable material systems, which we term as “Dynamically Self-Amplifying Omniphoric Multiscale Metamaterials”, that address these gaps. Key advances include: new understanding of the nonlinear mechanics of zero frequency topological and bistable materials, and incorporation of activity therein via liquid crystal elastomers; realizing piezochemical feedback loops; new approaches for the 3D printing of piezoresponsive polymers; and the creation of new mechanoresponsive polymers using acid-and strain-induced-crystallization chemistries. We anticipate the knowledge gained via these activities will have application to protective systems, morphing and dynamically adaptive vehicle structures, and autonomously responsive materials.

Example of Dynamically Self-Amplifying Omniphoric Multiscale Metamaterial concept.
Tying surface chemical processes to bulk viscoelastic transitions in polyurethane systems

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Spatially prescribing local properties through additive manufacturing (AM) techniques is an attractive option that has intrigued a variety of application spaces. The most ubiquitous AM techniques that utilize thermosetting polymers include stereolithography (SLA) and direct ink writing (DIW). DIW is a highly versatile form of 3D printing since it can utilize many feedstocks including cement and food. However, growth in the using this method of AM is still limited compared to more common procedures, such as fused filament fabrication, due to the chemical reaction complexity during processing. Tying formulation-specific cure kinetics to processing conditions to final, bulk response will drastically enhance DIW utility in many application spaces. Furthermore, if layering techniques (e.g., DIW) are utilized, extrudate surface chemistry will dominate bulk response layer-to-layer, which necessitate experimental methods that can elucidate kinetics at the interface and viscoelastic transitions in the bulk. Since the transition of the material from a liquid to a solid will greatly dictate the properties of bulk material, rheology and FTIR provide the most pertinent details. Even though HTPB has been thoroughly characterized by FTIR or rheology, much of the kinetic information is lost and the two techniques oftentimes cannot examine the same sample.

In this presentation, I will introduce the coupled rheology and FTIR (attenuated total reflection (ATR)) device. HTPB cure characterization will be described. Simultaneous data collection improves the comparison between these two techniques since the sample is common and FTIR is taken to a higher resolution (every 10 minutes). The benefits of each technique can be combined to comprehensively understand the curing process since the formulation changes can change the results from the two tests differently. The combination of FTIR and rheology permits the direct observation and correlation of gel point of the cross-linking system, as measured by the crossover in loss and storage modulus, to a specific conversion value without the added uncertainty that running separate rheology and IR conversion entails. Herein, we describe a first-of-its-kind investigation of isocyanate-cured HTPB that couples analysis from FTIR and rheology.
Exploring dynamic bonds to tailor the behavior of dense colloidal suspensions

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Shear-induced jamming and the impact-induced solidification behavior of dense suspensions is a crucial feature for stress mitigating functional materials. Frictional network formation has become a paradigm for understanding the non-Newtonian shear-thickening behavior of such dense suspensions. Most studies have exclusively focused on interparticle friction that instantaneously vanishes when the applied shear is ceased. We have been exploring how dynamic covalent bonds can be used to alter/adapt the rheological properties of colloidal systems. In one case we have investigated how dynamic covalent chemistry can be used to access sticky friction between the particles. The data shows that dynamic-bond-induced sticky friction can be used to systematically control the time dependence of the non-Newtonian suspension rheology. We have also been investigating redox active particles that consist of dynamic covalent networks that allow access to stimuli-induced jamming of their dense suspensions and explored how the mechanical properties of these jammed systems can be tailored.
Impact of cross-linker structure on the thermal and mechanical properties of selectively degradable, high-performance silyl-containing polyurethane networks

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Cross-linked polymeric materials are utilized in numerous consumer and industrial coating applications due to their unique chemical and physical properties. However, degradation of these materials require environmentally harsh and potentially unsafe chemical treatments to break the covalent bonds within their cross-linked networks. Furthermore, removal of these cross-linked materials from substrates, such as epoxy-based primers or composites, often result in physical damage to the substrate. This work describes the synthesis, characterization, and properties of several novel stimuli-responsive silyl-polyurethane (SPU) thermosets. The synthesized SPUs display a range of properties similar to commercial polyurethanes, with $T_g$'s ranging from 29 to 45 °C along with elongation of 102% to 290%. Additionally, the rate of degradation with a fluoride salt stimulus varied from 15 min to 120 min for samples coated on aluminum panels. The mechanical/thermal properties and rates of removal are shown to depend on the structure of the silyl alcohol, thereby imparting tunability for various applications. A select SPU formula with filler and pigments was applied over an epoxy network to fabricate a coating system that could be compared to current DoD systems (polyurethane and epoxy). It was found that the SPU can be removed from the epoxy without damaging it and withstood 500 h in a weatherometer with better retention of Young's modulus and elongation than the commercial polyurethane. We envision that selective and complete removal of the SPUs from an underlying network can reduce or eliminate environmental and safety issues with current chemical strippers, in addition to enabling a life-extension of polymeric substrates.
Direct-to-metal conductive polymer primer coatings meeting military specifications for primer coatings

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Currently, there is increased scrutiny of all chromated material usage. The recently proposed TLV-TWA limits from the ACGIH has called for a reduction in chromium exposure. The limits are for 0.0002 mg/m³ Cr(VI) inhalable fraction and vapor/inhalable particulate matter and the limit for Cr(III) is 0.003 mg/m³ inhalable particulate matter. If these restrictions go into effect, it would have a significant impact on DoN/DoD operations meeting these targets during application and removal of Cr(VI) pretreatment/primer.

Conductive polymers (CPs) are an attractive alternative to current Cr(VI)/Cr(III) pretreatments and primers. CP coatings such as polyaniline, polypyrrole, and polythiophene have been proposed and studied for corrosion inhibition. These CP coatings have demonstrated corrosion protection even when the coating is scratched and exposed to aqueous salts and hydrochloric acid.

CP coatings developed by the NAWCWD have shown similar performance to chromate conversion coatings (CCCs) from both laboratory and field tests. However implementation and subsequent buy-in from the DoD did not occur due to the higher costs associated with applying the BAM-PPV (poly(2,5-bis(N-methyl-N-hexylamino)phenylene vinylene) vs. current CCC/TCP coatings. Recently, the NAWCWD has improved the solubility and processability of BAM-PPV in VOC-exempt solvents and the NAWCWD is incorporating the improved BAM-PPV powder with and without reactive organic inhibitors ((1E, 3E)-1,4-bis (1-methyl-1H-pyrrol-2-yl)buta-1,3-diene monomer) into primer formulations (VOC-exempt solvent-based) for adhesion and corrosion-inhibiting studies. This process will eliminate the pretreatment step. The BAM-PPV will be applied as a "direct-to-metal" conductive primer coating onto aluminum alloys. These studies will examine both passivation and self-healing mechanism(s) for CPs doped with the (1E, 3E)-1,4-bis (1-methyl-1H-pyrrol-2-yl)buta-1,3-diene monomer.

Figure: Synthesis of reactive organic corrosion inhibiting monomer and rapid polymerization under oxidative conditions
Interface tailoring for applications in advanced polymer composites

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The fibre-matrix interface plays a critical role in determining the mechanical performance of fibre-reinforced composites. The interface is responsible for transferring load between the reinforcing fibres and the matrix, and any defects or weaknesses can significantly degrade the composite's strength and durability.

This talk will discuss my group's efforts to tailor the fibre-matrix interface at a molecular level, which offers a powerful new way to enhance composite performance. The goal of our work is to imbue the composite with specific chemical and physical properties, such as adhesion strength, toughness, and thermal stability. Tailoring the interface in this way can lead to significant improvements in composite properties, including strength, stiffness, toughness, fatigue resistance, and damage tolerance. It can also enable the development of new composite materials with unique combinations of properties that were previously unattainable.
Reactive high-performance Resins (REAPER) for additive manufacturing

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High-performance polymers are generally considered ‘impossible to print.’ We have demonstrated that our thermoplastic reactive oligomer approach lends itself to standard 3D printing methodologies. The REAPER platform exploits the low melt viscosity of high glass transition resins (Tg’s > 200 °C) thereby enabling one to 3D print all-aromatic high-performance polymers. The properties of the REAPER resins equal or exceed those of the targeted, commercially available resins such as Ultem® and Torlon®. The lecture will cover the subtleties of printing reactive thermoplastic oligomers and illustrate example printed parts with attendant physical properties.
Conventional formulations of solid rocket propellants include three primary components: fuels, oxidizers, and a polymer binder/plasticizer to integrate them together while providing the desired bulk mechanical and physical properties. A widely used binder ingredient is hydroxyl-terminated polybutadiene (HTPB). However, despite its long-standing and frequent use in propellant binder formulations, determination of the enthalpy of formation of HTPB has been elusive due to a variety of factors, with a wide spread of values reported in the literature. HTPB polymers are computationally large systems, with a single polymer having a molecular weight in the range of 2000-5000 g/mol, representing anywhere from 30-60 monomers. Using quantum chemical methods to predict the energetic properties of these systems of this size is not trivial, due to both size and microstructure variations of such large systems. This presentation will discuss the use of computational methods in the determination of enthalpies of formation of both conventional polymers such as HTPB and other potential binder ingredients.
Depolymerizable build materials for powder melt extrusion additive manufacturing

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Multimaterial additive manufacturing (AM) can enable creation of three-dimensional (3D) parts that have spatially resolved properties, reactivities, and functions. Inspired by several demonstrations of self-immolative polymers and related materials that undergo some mechanism of autonomous deconstruction, we took aim at incorporating depolymerizable polymers into multimaterial AM. Working with build materials that are inherently designed to depolymerize upon application of specific stimuli, such as heat, light, or mechanical load, creates immediate challenges for adoption into AM processes. Additionally, reactivities of depolymerizable materials can vary widely. Our research team focused on an inexpensive and readily customizable powder melt extrusion platform to help mitigate the challenges of reactive build materials. Our presentation will describe the equipment build out, customizable features, and 3D printing capabilities of our PME system, as well as our findings from working with combinations of depolymerizable materials and commodity polymers.
Improving compatibility of polysiloxanes with boron nitride nanomaterials

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Dynamic elastomers have a number of possible applications, including coatings, where improved adhesion through molecularly conforming bonds is desirable not only in the neat polymer, but also relating to nanomaterial incorporation. Polymer networks that include exchangeable bonds, compared to other elastomer designs, can have increased strength at interfaces. The purpose of this project is to examine a model dually cross-linked system with permanent crosslinks between polymer chains and potentially dynamic dative bonds between functionalized polymer and dispersed nanoparticles. To do this, we chose to investigate a system designed for corrosion protection. For anti-corrosion coatings, of which nanocomposites are often investigated, the polymer/nanomaterial interface can determine the performance. We selected a polysiloxane modified with a boron-based functionality and incorporated various quantities of boron nitride nanomaterials. Thermal and mechanical characterization, initial examinations of corrosion protection, and characterization of nanoparticle-polymer interactions will be used to expand understanding and probe behavior of this type of unique dually cross-linking system.
High-temperature thermosetting resins derived from bio-based phenols

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Naturally occurring phenolic compounds are a diverse class of molecules that offer structural motifs not commonly found in petroleum-derived monomers. Sustainable phenols can be generated from lignocellulosic biomass through direct valorization and chemical modification or fermentation of biomass sugars with metabolically engineered microorganisms. The ability to produce these building blocks on relevant scales, from cheap and abundant starting materials, allows the unique structural characteristics of bio-based phenols to be utilized for thermosetting resins with enhanced properties. Key improvements obtained through this approach may include higher Tg, higher char yield, enhanced thermal stability, fire-resistance, lower water uptake, and the ability to cross-link through unique mechanisms. This presentation will discuss recent work focused on the synthesis and characterization of high-temperature bio-based propargyl ethers and phthalonitriles prepared from a variety of substrates including lignin-derived bisphenols and resveratrol. The thermomechanical properties of the bio-based networks will be described and approaches to improve the processability of the resin systems through chemical modification and blending will be discussed.
Controlling the thermoelectric properties of vapor-deposited poly(3,4-ethylenedioxythiphene) (PEDOT) thin films

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Thermoelectric (TE) devices offer attractive operational characteristics because they are noiseless, contain no moving parts, and can operate without maintenance or recharging. With recent advances in polymer-based TEs, new applications for thermal management or generating power from diffuse, low-grade waste heat sources are closer to becoming a reality. Polymer-based TEs have several advantages over inorganics for these applications because they are flexible and lightweight and achieve peak thermoelectric figure of merit (ZT) near room temperature. Poly(3,4-ethylenedioxythiphene) (PEDOT) is one of the most promising TE polymers whose thermal and electronic transport properties vary drastically depending upon oxidation level, dopant concentration, and degree of ordering and alignment, and therefore, its TE performance is highly dependent upon synthesis and processing conditions.

We utilize oxidative chemical vapor deposition (oCVD) to deposit conformal PEDOT thin films on planar and 3D substrates. We characterize the electronic and thermal transport properties of the PEDOT films using Van-der Pauw method (σ), 3ω method (κ), and thermopower measurements and determine how the films’ thermoelectric behavior is dictated by oCVD growth conditions (ex. substrate temperature and partial pressure of oxidant and monomer). By changing oCVD growth conditions, we can increase conjugation length and dopant concentration in PEDOT films resulting in orders-of-magnitude improvements in electrical conductivity (σ, ~1 to ~7,000 S m⁻¹) while thermal conductivity only varies within a relatively small range (κ, ~2–5 W m⁻¹ K⁻¹). The disproportionate changes in σ and κ result in an overall improvement in thermopower (S, 5 to 245 μV K⁻¹). These findings highlight the utility of oCVD as an alternative to solution-based synthetic methods for controlling polymer properties that yield overall improvements in the thermoelectric figure of merit (ZT).
Role of antioxidant in stability of nitroplasticizer

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To investigate the initiation and progression degradation mechanisms of the eutectic mixture of BDNPA and BDNPF (1:1 mass ratio) (called NP), experimental and theoretical studies have been carried out systematically under two environments (dry vs. wet) and four temperatures (38, 45, 55, and 64°C) for 44 months. The properties of aged samples were analyzed using a suite of analytic techniques. Experimental results demonstrate that NP degradation shows two stages: primary and secondary. As shown in the following figure, NP degradation initially starts from HONO elimination at moderate temperatures. While the cage effect minimizes HONO decomposition and results in NP isomerization, PBNA, an antioxidant, scavenges NO₂ radicals generated from HONO decomposition; accordingly, water accumulates. As PBNA and mono-/dinitro-PBNA deplete, increased acidity leads to rapid NP hydrolysis in the later stage of NP degradation. The propagation of PBNA nitration is found to depend on the temperature and acidity of the NP system, and can be utilized as an indirect, yet reliable, means of determining the extent of NP degradation. On the theoretical front, density functional electronic structure calculations confirm that the HONO elimination is an energetically favorable reaction over the NO₂ homolysis as an initial step in NP degradation at moderate temperatures. The effect of acidity on the free energy of NP pronation/hydrolysis is estimated theoretically. Finally, a critical review of the past ten-year research on NP stability studies is given.
Rational design of double-network hydrogels from fundamentals to applications

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Synthetic polymer hydrogels as soft-wet materials, consisting of three-dimensional cross-linked networks and a large amount of water (50–90%), possess many unique properties such as swelling/deswelling, stimuli-responsiveness, shock absorption, and low sliding friction, making them as potential excellent biomimetics for substitution of soft living materials. However, conventional hydrogels often suffer from weak mechanical properties, which greatly limit their extensive uses for many other applications. In this talk, we will present different design strategies to prepare tough and multifunctional hydrogels with unconventional double-network structures and extraordinary properties. Guided by our design principle, we will demonstrate different hydrogels with high mechanical properties, self-healing, actuation, antifouling, fluorescent, antifreezing, and/or wound healing to mimic cartilages, artificial muscles, and mussel-inspired glues. In parallel, molecular simulations will be presented to given atomic-details of structure-properties relationship. Finally, several unique aspects for future development of tough hydrogels will be suggested.
Reconfigurable materials based on Diels-Alder polymer networks

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We demonstrate that Diel-Alder polymer (DAP) networks formed through the reaction between furan and maleimide present a versatile platform for simultaneously achieving the desired thermomechanical properties and reconfigurability of materials. The network mechanical properties, response to mechanical load and temperature can be precisely controlled by the crosslinking density and crosslinker identity. In particular, materials with a wide range of the Young’s modulus (from several MPa to several GPa), glass transition temperature and reconfigurability of permanent shape using just several building components. Regardless of the thermomechanical properties, the networks can be easily transformed to the liquid state when heated above 120 °C, enabling fast self-healing. Cooling of the molten networks “locked” the network structure through the DA click reaction that produces two types of stereochemistry-dicted crosslink - weaker endo and stronger exo junctions - that regulate the ease of the material’s shape reconfigurability and stress relaxation properties. We show that the modular approach to materials’ constructions, intrinsic self-healing of the DAP networks, and their controlled network plasticity make them promising for building multimaterial constructs with spatiotemporal control of shape morphing. We also demonstrate how the above features of the DA networks can be leveraged for constructing reconfigurable nanocomposites with an extremely low percolation threshold. Understanding of reconfigurability properties of DAP networks can inform the development of future soft robots and morphing platforms with specific response, adaptation and reconfigurability characteristics.
One-pot, solvent-free synthesis of UV-curable resins via sequential thiol-epoxy and thiol-ene reactions for additive manufacturing of elastomers

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Digital light processing (DLP) is an additive manufacturing technique that allows for the fabrication of solid objects via photopolymerization of a liquid resin with high precision and low material consumption. Although rapid advances have been made in this industry, 3D printed materials often utilize acrylate- or epoxy-functionalized photopolymers, resulting in stiff networks whereas studies on developing high-performance elastomeric materials are limited. In this work, two thiol click reactions (thiol-epoxy and thiol-ene) are leveraged to prepare a high-yielding, one-pot method for synthesizing photocurable resins. This process involves the reaction of allyl glycidyl ether (AGE) with polyfunctional thiols to form AB-type resins that possess thiol and alkene functionalities, which can subsequently be UV-cured into crosslinked networks. The modular design allows for a wide range of thermomechanical properties, including elastomers with low glass transition temperatures, by simple adjustments to the thiol-to-AGE ratio and thiol composition. Due to the good fluidity, low volatility, and high cure rate, the resins are amenable to DLP 3D printing and various 3D structures have been printed.
Fluorine-containing polymers for propellant binder applications

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Fluorinated binder materials have the potential to enhance performance for aluminized propellants by improving combustion energy and efficiency. Although recent work has shown promising results in this area, the effects of fluorine content on binder and propellant properties are still not fully understood, and molecular modeling simulations in this area are limited. This work aims to investigate these relationships through the examination a series of semi-fluorinated glycidyl ethers with varying fluorine content, which have been synthesized and polymerized. Fluorinated binder candidates have been cured into crosslinked gumstock samples, which were characterized. Molecular dynamics simulations were also performed both for the prepolymer and gumstock samples, and the material properties of the simulated system were also examined. The effects of increasing fluorine content on the experimental and simulated material properties are compared and discussed.

Figure 1: Depiction of simulated poly(1H,1H,5H-octafluoropentyl glycidyl ether).
Adaptive Structural Resins: How do you design rapid response in a polymer glass or composite?

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Structural resins are used ubiquitously across various industries as lightweight adhesives. As the automotive, aerospace and electronics industries look to increase performance, novel resin design becomes paramount. A cross-cutting need is improved ductility in glassy materials. Epoxy-amine based adhesives are an encouraging model platform because of high strength, and environmental stability, but they are intractable and suffer from brittle-like behavior well below the $T_g$. Adaptive glasses provide a relatively unexplored avenue to manage an "on-demand" mechanical response. Three response mechanisms will be outlined to provide a range of mechanical behaviors: (i) shape-changing functionalities which locally yield or soften the material to stimulate chain mobility; (ii) bond forming (or breaking) chemistries which increase (or decrease) the stiffness of the material; and (iii) energy absorbing groups which convert the incoming stimuli into a spatially controlled heating and result in a designed softening of the material. However, many challenges still remain in achieving controlled responses deep in the glassy state.
Vanillin-derived monomers for additive manufacturing

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Styrene is a popular monomer widely used in thermally curable thermosets as a comonomer or reactive diluent due to its excellent polymerizability and mechanical properties. However, the use of styrene in UV-curable compositions, including 3D printable resin systems, is limited by its high volatility and toxicity. Replacing styrene with structural analogs without these drawbacks opens the way for styrene-like vinyl monomers into UV-curable resins. To this end, using bio-based platforms offers a new source of aromatic intermediates for synthesizing sustainable styrene equivalents.

We have synthesized a range of aromatic monomers from vanillin, a commercial bio-based platform molecule for use in UV-curable additive manufacturing applications. Several of these monomers can be utilized in resin synthesis for additive manufacturing, while the others are low-viscosity liquids suitable for use as reactive diluents. In particular, the bio-based functional styrene analogs demonstrated a performance advantage over commercial controls in stereolithography resin compositions. Properties of 3D printed samples fabricated using bio-based styrene-like monomers depend on their structural features, with polyfunctional molecules providing higher glass transition temperature and strength characteristics and monofunctional monomers showing superior toughness. The high toughness shown by samples printed using styrene-like monomers enables their use as reactive resin components in high-performance composite 3D printing applications.
Polyesters and polyurethanes are ubiquitous in the modern world. Their structural versatility gives rise to an array of properties that has led to their use in numerous technologies. As technology continues to evolve, new materials properties are often needed, necessitating new polymer structures and increasingly detailed information on structure-property relationships. To meet these challenges, we have synthesized polyesters and polyurethanes with systematically varied structures—focusing particularly on aliphatic polyesters, both as materials in themselves and as soft segments in polyurethanes, as well as on polybutadiene-based polyurethanes. Thermomechanical and rheological characterization reveals how the material properties of these polymers may be tuned by adjusting the molecular structure, ultimately informing their potential use in various applications including composite binders, elastomers, and additive manufacturing.
Polycarbosilanes as enabling precursors for new concepts in the processing and high-temperature ceramic

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Amongst macromolecules, preceramic polymers are unique in their ability to be converted from a workable polymeric material to ceramics via heat treatment. One of the most widely utilized preceramic polymers are polycarbosilanes, which yield SiC on conversion. Critically, polycarbosilanes may be processed utilizing traditional polymeric techniques (e.g., fiber spinning) and the form factor of the material preserved on conversion to inorganic. For example, polycarbosilanes can be spun into fibers and heat treated to create high-performance SiC fibers. In addition to fiber spinning, the unique properties of polycarbosilanes lend these polymers to new avenues of research in structure-property relationships with respect to polymer chemistry, hybrid material fabrication, additive manufacturing, and resulting polymer-derived ceramics. In this presentation, we will discuss our recent progress in the synthesis of polycarbosilane-nanoparticle hybrid materials (preceramic polymer grafted nanoparticles(PGNPs)). Specifically, we will discuss the impact of polycarbosilane chemistry on the rheology and curing of these PGNPs as well as the composition of the resulting ceramic materials. Beyond hybrid particles, the production of hierarchically structured ceramics via the additive manufacturing of polycarbosilanes with structure directing additives will be presented. The effects of processing parameters and ink formulation as well as processing parameters will be discussed with respect to the final structure of the nanoporous printed ceramics and their mechanical properties. Here, hierarchically structured ceramic materials exhibit excellent mechanical energy absorption, comparable to metal alloy foams as well as low thermal conductivity.
Light harvesting star polymer photocatalysts using fluorescence resonance energy transfer

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Photochemistry has emerged as a hot topic in terms of sustainability. In particular, the photocatalyst is a promising method to deal with environmental pollution, but only a few light resources with limited wavelengths were utilized to activate photosensitizers. Herein, we broaden the range of activation wavelength of porphyrin-core amphiphilic star polymer photocatalysts by light-harvesting functionality. The coumarin moiety was polymerized from the porphyrin core while maintaining the amphiphilic microenvironment of the star polymer. The fluorescence resonance energy transfer (FRET) between the porphyrin and the coumarin leads to activating photocatalysts under both UV-A and UV-B light. Moreover, the effect of copolymer sequence and polymer swelling on FRET efficiency was severely discussed. The amphiphilic star block copolymer exhibits superior energy transfer efficiency under polar solvent and its photocatalytic activity was evaluated by 2,5-DMF photooxidation.
Functionalization of titania particles for improved mechanical performance of HTPB composites

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Solid rocket propellants are crucial for military objectives, space exploration, and national security. These propellants require solid fuels (e.g., hydroxyl-terminated polybutadiene or HTPB) that act as fuel and binder for the particulate oxidizer (e.g., ammonium perchlorate or AP). Metal powders (e.g., titanium dioxide or TiO$_2$) are used as burning rate modifiers to increase the burning rate. Previous work has not investigated the potential to use these metal oxide surfaces to improve propellant mechanical properties. This study aimed to investigate the effects of surface functionalized titania nanoparticles on the mechanical properties of HTPB composites. Anatase TiO$_2$ particles were functionalized with 11-phophonoundecanoic acid with four different concentrations to prepare carboxylate (COOH-) terminated TiO$_2$, thus, to improve crosslinking between the particle surfaces and HTPB. The mechanical properties of HTPB/60 wt% TiO$_2$ particle composites cured with isophorone diisocyanate were studied. The mechanical properties of the HTPB/60% wt were tested using nanoindentation and tensile testing. The nanoindentation showed improvement in surface hardness and modulus while the tensile testing showed improvement in tensile strength and Young's modulus.

An image of the indentation made by the Hysitron TS-77 nanoindenter on the top left. Tensile test done on ASTM D638 Type V mold being pulled by the tensile tester on the right. Data obtained from nanoindenter on the bottom left.
Heat shielding nanobrick wall for carbon fiber reinforced polymer composites

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Owing to their excellent mechanical properties, carbon fiber reinforced polymer (CFRP) composites have a broad spectrum of applications in aerospace, civil engineering, automotive, and numerous industrial fields. Despite their many advantages, the inherent lack of thermal stability of the polymer matrix results in the loss of the composite’s mechanical properties when exposed to elevated temperatures. In an effort to provide thermal protection, a multilayer film composed of tris(hydroxymethyl)-aminomethane (THAM)-buffered polyethylenimine (PEI) and vermiculite (VMT) clay were deposited on CFRP composites via layer-by-layer assembly. When subjected to the flame from a butane torch and mechanical loading, the polymer-clay nanobrick wall provides substantial thermal insulation, decreasing the temperature on the backside of the CFRP composites by as much as 100 °C. The PEI-THAM/VMT coating also helps to maintain the storage modulus of the composite and offers significant protection from oxidative degradation, as confirmed by dynamic mechanical analysis and X-ray photoelectron spectroscopy. The performance of this polymer-clay multilayer film provides excellent thermal barrier that can be used to protect advanced composite materials from extreme heat.
Can we design multilayer electronics that spontaneously heal themselves after damage? Having this functionality would protect electronic devices from traditional “wear and tear” damages, improving product lifetime, as well as from intense mechanical damage that would otherwise cause product failure. Compared to the self-healing of a single polymer composite, the self-healing of complex, multilayered devices requires simultaneous healing between multiple layers with distinct functions. Currently, this is achieved by manual alignment of the layers after damage. In this work, we demonstrate a multilayer electronic device that can autonomously realign and heal after damage using immiscible dynamic polymers. We show that dynamic polymers with controlled orthogonality exhibit significant and predictable variations in interfacial healing dynamics, allowing for autonomous self-recognition. When misaligned after damage, these multilayer structures possess surface tension gradients that drive directional chain diffusion to enable realignment. We experimentally characterize the interface between different immiscible dynamic polymers and compare our results to coarse-grained molecular dynamics simulations and self-consistent field theory. Using these polymers, we prepare conductive and high dielectric composites to create thin film capacitors that can autonomously heal with thicknesses below 100 microns. We also demonstrate macroscopic self-assembly of these polymers after damage using magnetic composites. This work provides the first proof-of-concept demonstration of autonomously self-healing multilayered devices and opens a pathway for future autonomous self-assembly in multi-component dynamic materials via pattern recognition.
Hemorrhage-induced hypovolemic shock (HS) is a major cause of preventable deaths on the battlefield. The priority in the treatment of HS is the rapid restoration of intravascular volume by transfusion of whole blood or blood components. Unfortunately, most instances of severe HS occur in prehospital settings where access to blood products is limited. Synthetic polymers, known as volume expanders, have been long used as resuscitation fluids for hypovolemic shock for many decades, as they increase plasma oncotic pressure and expand intravascular volume. The development of these materials marked the beginning of biomaterials research. However, in recent years, numerous studies showed that commonly used synthetic colloids cause many adverse events in patients including organ toxicities and coagulopathy, as a result, their clinical use has largely halted. Are there still possibilities to design synthetic polymers for this age-old application. In this work, a low-fouling amine(N)-oxide-based zwitterionic polymer as an alternative volume expander with improved biocompatibility and efficacy is designed. It is demonstrated that the polymer possesses antifouling ability, resisting cell interaction and deposition in major organs, and is rapidly cleared via renal filtration and hepatic circulation, reducing the risk of long-term side effects. Furthermore, in vitro and in vivo studies show an absence of adverse effects on hemostasis or any acute safety risks. Finally, it is shown that, in a head-to-head comparison with existing colloids and plasma, the zwitterionic polymer serves as a more potent oncotic agent for restoring intravascular volume in a hemorrhagic shock model. The design of N-oxide-based zwitterionic polymers may lead to the development of alternative fluid therapies to treat hypovolemic shock and to improve fluid management in general.
Surface treatment of pitch-based discontinuous carbon fibers

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Given the exponential growth in the manufacture of carbon fiber-containing products, it is both environmentally and economically practical to recycle carbon fibers. Recycled carbon fibers can fill the anticipated gap between supply and demand instead of being disposed in landfills. A major barrier to reintroducing recovered and recycled carbon fibers is the lack of an efficient method for surface treating reclaimed chopped fibers that have undergone recycling processes (e.g., pyrolysis), which leave the fiber surface without functional groups that are required to ensure good fiber-matrix adhesion. Previously, we developed a novel and efficient electrochemical surface treatment method for discontinuous carbon fibers, and we demonstrated that similar surface functionalization can be achieved as those via conventional continuous surface treatments. In this presentation, we expanded the electrolytes used in this process to increase and to tune surface functionalization of these discontinuous fibers. Specifically, we demonstrate control over surface oxygen:nitrogen ratio and performed mechanistic studies to understand why some electrolytes deposit greater heteroatom loadings on fiber surfaces. We further showed that we can change the surface chemistry from aromatic-based functionalization to aliphatic-based functionalization by simply changing the electrolyte. Changes in surface chemistry were quantified/monitored using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS).
Multifunctional fabric with flame retardant and antimicrobial properties for soldier protection

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Nyco fabric (50-50 wt.% Nylon 66 and cotton) has a promising good balance of properties of comfort and strength. The nylon provides mechanical strength and abrasion resistance while the cotton provides good breathability and comfort. Nyco is the fabric of choice for various uniform materials including the Army Combat Uniform (ACU) used by the US Army and Marine Corps Combat Utility Uniform (MCCUU) used by the US Navy and US Marine Corps. Despite the above mentioned balance of properties, Nyco fabric does not offer any flame protection and has no antimicrobial properties. These two functionalities are of utmost importance for uniforms. In this work, Flame retardancy (FR) and anti-microbial (AM) characteristics were imparted onto Nyco fabric using a two-step method. The first step involves the covalent attachment of an antimicrobial agent -chlorohexidine. This was performed by synthesizing a colorless reactive dye followed by attaching the AM agent. The AM treated fabric was then covalently attached with phosphoric acid as the FR moiety. The attachment of FR was performed using an industrially scalable technique employing the dip-dry-cure process. The covalent attachment was confirmed using Fourier transform infrared spectroscopy (FTIR) in ATR mode. The multifunctional nyco (FR+AM) was characterized for its thermal stability using thermogravimetric analysis (TGA). The heat release properties were evaluated using microscale combustion calorimetry (MCC) and cone calorimetry. Flame spread properties of the fabrics were evaluated using vertical flame testing (VFT) and the treated fabrics showed self-extinguishing behavior with less than 6” char length. The AM efficacy of the treated fabrics was > 90%. The procedure for fabricating the multifunctional nyco and results from various characterizations will be discussed during the conference.

(Left) Post Vertical Flame Test images of Nyco control, and FR Treated Nyco with and without AM and (Right) Antimicrobial Test results for Nyco control, and AM treated Nyco with and without FR
Improving the way we process propellant composites is pivotal for the production of novel material formulations that meet performance demands, integrate with new technologies, and are more environmentally conscious. There is a need in the field to define fundamental formulation-processing relationships that can be leveraged to address the challenging nature of developing and processing highly loaded particulate composites. The key challenge of interest to this work is the formation of inhomogeneities in the particle spatial distribution upon shaping of the dense paste propellant precursor. Dense pastes undergo particle network deformation under applied stresses above the yield stress that often cause irreversible particle migration and the formation inhomogeneities. These inhomogeneities are then cured into the propellant grain and can hamper mechanical properties and performance. Herein, inhomogeneity formation after significant deformation is examined via rheological thixotropy testing and is investigated as a function of binder formulation. Model suspensions of inert glass microparticles were employed and the total solids content was kept consistent at 61.4 vol% of an efficient bimodal distribution of small and large glass spheres. Polymer concentration and molecular weight in the binder were systematically varied using polyvinylpyrrolidone (PVP) polymers dissolved in water. Thixotropy tests show that increasing polymer content effectively reduces inhomogeneity formation; and that viscosity is not the only predictor for thixotropic behavior in dense pastes. This observation may be due to polymer entanglements acting to stabilize the particle network. Elucidating the formulation-processing relationship between polymer formulation and thixotropic behavior will fill fundamental knowledge gaps and help enable informed polymer selection during formulation development.
Influence of NHC structure on the mechanophore reactivity of NHC-carbodiimide in polymeric network - Bae, Hyeonjeong (Oral Preferred)

Mechanochemistry in polymer networks - Craig, Stephen (Oral Only)

Living copolymerizations as a tool to tailor the architecture and fracture properties of polymer networks - Sanoja, Gabriel (Oral Only)

Probing mechanochemical kinetics in a double-network elastomer - Wang, Junpeng (Oral Only)

Physics-based modeling of mechanochemically-responsive polymer networks - Silberstein, Meredith (Oral Only)

Sonication labile PEG based polymer hydrogels - Arguien, Meagan (Poster Only)

Strain-softening of metal-ligand crosslinked polymer networks - Locke, Cameron (Poster Only)

Thermally stable photomechanical molecular hinge: Sterically hindered stiff-stilbene photoswitch mechanically isomerizes - Imato, Keiichi (Oral Only)

Mechano-responsive polymers for stress self-reporting and self-strengthening - Chen, Yulan (Oral Only)

Polymer mechanochemistry based on radical-type mechanophores - Otsuka, Hideyuki (Oral Only)

Mechanochromic polymers made with interacting dye pairs - Weder, Christoph (Oral Only)

Hybrid polymer elastomers composed of strong and weak crosslinkers - Van Zee, Nicholas (Poster Only)

Sacrificial bonds deter oxidative stress from mechanoradicals in collagen - Monego, Debora (Oral Preferred)

Mechanochemical activation in nanostructured triblock copolymers: A computational study - Statt, Antonia (Oral Only)

Adaptive and active polymer materials with advanced mechano-chemistry tools - Walther, Andreas (Oral Only)

Fluorescent radical precursors for detecting mechanical degradation of polymers - Yamamoto, Takumi (Poster Preferred)

Post-functionalization strategies for every-day mechanophore sensors - Grolman, Joshua (Oral Only)

Mechano-mapping in polymers with pigments and mechanophores - Clough, Jess (Oral Only)

Supramolecular approaches toward mechanochromic polymers - Schrettl, Stephen (Oral Only)
Polymer Mechanochemistry

Mechanoresponsive self-reporting polymer systems - Muff, Livius (Oral Only)

Precision force sensing through dynamic polymer mechanochemistry - Lu, Xiaocun (Oral Only)

Leveraging mechanochromic naphthopyrans for stress sensing applications - McFadden, Molly (Oral Preferred)

Solid-state mechanochemical upcycling of post-consumer polystyrene - Skala, Morgan (Oral Only)

Surface-activated grinding spheres enable the direct mechano-catalytic depolymerization of polypropylene waste in the solid state - Vollmer, Ina (Oral Only)

Stages and Kinetics of Mechanochemical Depolymerization of Poly(Ethylene Terephthalate) - Tricker, Andrew (Oral Only)

Molecular design strategies for mechanically triggered release - Robb, Maxwell (Oral Only)

Mechanochemical synthesis of stimuli responsive microgels - Pich, Andrij (Oral Only)

Towards C-C bond activation by polymer mechanochemistry - Diesendruck, Charles (Oral Only)

Mechanochemical dynamic cancer therapy using HIFU-triggered mechanophores - Wang, Jian (Oral Preferred)

Mechanically mediated mineralization for adapting materials and self assembly of nano-fibers using Piezo-electric particles - Esser-Kahn, Aaron (Oral Only)

Deep dive into fused cyclobutane polymechanophores - Horst, Matias (Oral Preferred)

Steering reaction pathways using mechanochemical input - Liu, Yun (Oral Only)

Influence of polymer architecture in polymer mechanochemistry - Peterson, Gregory (Oral Only)

Carbamoylketoximes as thermally stable mechanophores for polymer mechanochemistry - Aydonat, Simay (Poster Only)

Fundamental and applied studies on mechanophores and mechano-responsive materials - Boydston, AJ (Oral Preferred)

Sonochemically induced retro Diels-Alder activation of alicyclic diimide mechanophores - Schilling, Cody (Oral Preferred)

Transducing mechanochemical activation to force-free chemistry in polymers - Zheng, Ke (Oral Preferred)

Static and dynamic aspects in mechanochemistry - Martinez, Todd (Oral Only)

Development of molecular switch-based mechanophores - Qian, Hai (Oral Only)

505
Polymer Mechanochemistry

Investigation into the mechanical stability of Diels-Alder mechanophores by AFM-based single-molecule force spectroscopy - Carabin, Thomas (Oral Preferred)

Force spectroscopy as a tool to study microgel monolayers at the solid-liquid interface: Progress in understanding emulsion stabilization - Kratzenberg, Timon (Oral Preferred)

Mechanophore postulate: A linear model for Mechanophore reactivities - Sun, Yunyan (Oral Preferred)

Controlling reactivity under tension - De Bo, Guillaume (Oral Only)

Microgels in monolayers: A force spectroscopic study - Schog, Simon (Oral Preferred)

Force strain model for mechanistic insights and predictive model development in mechanochemistry - Kevlishvili, Ilia (Oral Only)

Single-molecule mechanics with AFM: Force, motion, dynamics, and function - Duwez, Anne-Sophie (Oral Only)

Ambient reactive extrusion additive manufacturing of polyurethanes and polythiouurethanes - Savage, Alice (Poster Preferred)

Improved impact resistant composites through randomly oriented discontinuous fibers - Hanna, Hayden (Poster Only)

Formulation of MOF-808 core-shell fibers for organophosphate hydrolysis under non-buffered conditions - Garibay, Sergio (Poster Only)

Plasticizer evaluation for polyamide compositions - Orlicki, Joshua (Poster Only)

Nontraditional composites for improved mechanical properties through basalt fiber and graphene - Hanna, Hayden (Poster Only)

Additive manufacturing of novel photopolymeric polybutadiene resin via digital light processing - Saludo, Van Michael (Poster Only)

Elucidation of structural proteins used in construction of mud dauber nests and caddisfly cases for defense applications - Roberts, Jesse (Poster Preferred)

Super-recovery of ultimate strength in double network hydrogels through scission-induced topological remodeling of polymer networks - Zheng, Xujun (Poster Preferred)
Influence of NHC structure on the mechanophore reactivity of NHC-carbodiimide in polymeric network

Hyeonjeong Bae, hbae34@wisc.edu, AJ Boydston. Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States

Nucleophilicity and Lewis basicity of N-heterocyclic carbene (NHC) are determined by its structure and they affect the mechanophore reactivity of NHCs. In this study, different types of NHCs are paired with styrene carbodiimide (CDI) and integrated into a polymer network as a mechanophore moiety in the polymer backbone. This mechanophore is activated by elongational force and bonds between CDIs and NHCs are broken to release NHCs. Under the hypothesis that nucleophilicity and Lewis basicity of NHCs affect the equilibrium between bound and unbound states of NHCs, a series of experiments were conducted to confirm this hypothesis. First, NHC-CDI pairs that can stand radical polymerization condition were screened through thermal and radical stability test. The selected NHCs then were subjected to kinetic analysis where NHCs react with different kinds of electrophiles and reaction rates were recorded to determine nucleophilicity parameter N. Lastly, since Lewis basicity of NHC is so high that it is hard to be determined experimentally, the basicity was calculated through DFT quantum calculation. Data from these experiments will be used to predict the activation of the NHC-CDI mechanophores in the polymer network, and this prediction will be compared with the actual activation rate (%) of the mechanophore. From this study, we anticipate that a structure-property relationship can be established for NHC-based mechanophores, and this relationship can be used for mechanophore design.
Mechanochemistry in polymer networks

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One of the major, broad accomplishments within the field polymer mechanochemistry in recent years is the use of mechanochemical responses to probe and understand the behavior of polymeric materials. Less developed at the moment is the use of polymer mechanochemistry to fundamentally alter the mechanical behavior and performance limits of polymer networks. This talk will describe opportunities that arise from the reactive, mechanochemical remodeling of individual strands and scission of strands and junctions within polymer networks that have been stretched to their nominal physical limits. Mechanistic insights based on structure-activity relationships provide guidance that informs future pursuits.
Living copolymerizations as a tool to tailor the architecture and fracture properties of polymer networks

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Soft materials are irreplaceable in applications that require large reversible deformations such as elastomers in rubber tires, and seals; and hydrogels in contact lenses, and artificial prosthetics. Despite finding widespread use in our daily lives, soft materials still suffer from excessive brittleness at high temperatures or solvent concentrations. The reason is rather simple. Soft materials are constituted of polymer networks and typically rely on chain friction to dissipate energy in the vicinity of cracks. At high temperatures or solvent concentrations, chain friction is negligible and the energy is dissipated by chain scission or fracture.

Early in the 21st century, Gong and co-workers introduced a network architecture that could help solve this problem, interpenetrating a stiff and brittle filler network into a soft and extensible matrix network. The resulting materials, referred to as multiple-networks, dissipate considerable energy by scission of filler network bonds and, as a result, are remarkably tough at high temperatures or solvent concentrations. Yet, how the architecture of the constituent networks ultimately affects the scission of filler network bonds and the resistance to fracture remains unknown.

We address this question by considering multiple-networks constituted of filler networks synthesized either by RAFT or free radical copolymerizations and labeled with fluorogenic mechanophores. By fracturing these material over a range of temperatures and rates and quantifying their damage by confocal microscopy, we demonstrate that more homogeneous filler networks afford tougher multiple-networks not only due to an increase in the size of the dissipation zone, but also because of considerable chain friction as chains untangle and stretch near their limiting extensibility. Thus, we provide molecular rationale for leveraging living copolymerizations to tune the mechanisms responsible for dissipating energy and design soft materials that resist fracture.
Probing mechanochemical kinetics in a double-network elastomer

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Covalent polymer mechanochemistry has in recent years provided access to new chemical reactions, mechanistic insights, and polymer transformations. In bulk materials, mechanochemical activation has been used as the basis for new classes of responsive polymers that demonstrate stress/strain sensing, molecular level remodeling and stress-strengthening, and the release of small molecules that are potentially capable of triggering further chemical or material response. It is therefore desirable to understand the kinetics of mechanochemistry in bulk materials. However, largely due to limited levels of mechanophore activation, direct measurement of mechanochemical kinetics is rare. The lack of efficient mechanochemical activity is a result of the inhomogeneous stress distribution in a polymer network—stress is localized in a small portion of chains. In a double network where the first network serves as the sacrificial network, and the stress is homogeneously distributed in the first network. We found that the mechanophore activation of an anthracene-maleimide adduct mechanophore can be substantially enhanced when the mechanophore is placed in the first network of a double network elastomer—from <5% in a single network to >40% in a double network. The improved mechanophore activation allows us to quantify the kinetics of the mechanochemical activation and its dependence on the strain rate. The quantified kinetics shed fundamental insights into the reaction mechanism and material design.
Physics-based modeling of mechanochemically-responsive polymer networks

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Elastomers are used in a wide range of applications because of their large strain to failure, low density, and tailorable stiffness and toughness. The mechanical behavior of elastomers derives mainly from the entropic elasticity of the underlying network of polymer chains. However, as the elastomer network is deformed more extensively, mechanochemistry relevant forces are transmitted through the polymer chains. These forces can drive either non-specific bond fracture or, in the case of mechanophore incorporation, tailored desirable responses. In this talk we will discuss physics-based continuum and mesoscale models for understanding how force is transmitted throughout an elastomer network when the material is deformed, how that force drives specific and non-specific mechanochemical reactions, and what happens to the network as these reactions propagate. We will compare the model predictions to experimental data for a variety of elastomers and gels.
Sonication labile PEG based polymer hydrogels

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In the growing field of polymers, the development of materials that are responsive to external stimuli has gained momentum, especially with the interest in enabling transitions of mechanical or chemical properties to allow a single polymer to be used where previously multiple may have been required. This work uses phthalaldehyde functionalized polyethylene glycol (PEG) macromers, crosslinked through an alkene to synthesize hydrogels that respond to mechanical triggers. The phthalaldehyde mechanophore linkage has been shown to be sonication labile when incorporated into a polymer backbone. This work characterizes the mechanical properties of crosslinked PEG-phthalaldehyde hydrogels as sonication is applied, illustrating the degradation profile of these hydrogels and degradation into water soluble components. The use of mechanical triggers, such as sonication or ultrasound, was leveraged to degrade polymers in optically dense or thermally sensitive environments while maintaining the spatial – temporal control characteristic of photo triggered degradation.

Sonication of hydrogel network leads to polymer chains breaking at the location of a mechanophore (phthalaldehyde moiety) built into the polymer chain backbone.
Bio-inspired polymers with new functionalities and enhanced mechanical properties are highly desirable for new material applications. Traditional synthetic polymers have not yet achieved the same dynamic behavior as materials found in nature. Mimicking biological materials by implementing dynamic bonds into polymer materials to create supramolecular networks has previously shown significant improvements in polymer durability and utility while also introducing unique stimuli-responsive properties. Moreover, crosslinking polymers with noncovalent interactions produce materials that exhibit strain-softening during shear deformation but to our knowledge, significant softening has been rarely achieved for polymers submitted to tensile deformation. In this work, we report a new metallo-supramolecular network that is mechanically robust and exhibits ultrahigh stretchability, processability at elevated temperatures, and unprecedented strain-softening under tensile deformation. Furthermore, by understanding the mechanisms of force transduction in the polymer material, we can make modifications to the chemical structures to tune network dynamics and the resulting material characteristics.

(A) Stress-strain plot for polymer with a 1:3 metal to ligand ratio at varying strain rates. (B) Stress-strain plot for polymer with a 1:2 metal to ligand ratio at varying strain rates. (C) Pictures of polymer with a 1:3 metal to ligand ratio during uniaxial extension tensile test at a strain rate of 5 mm per minute. Deformation of polymer sample is shown at varying strain % of 0, 50, and 825.
Thermally stable photomechanical molecular hinge: Sterically hindered stiff-stilbene photoswitch mechanically isomerizes

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Molecular photoswitches are extensively used as molecular machines due to the small structures, simple motions, and advantages of light including high spatiotemporal resolution. Applications of photoswitches have been considered and selected based on the mechanical responses, i.e., whether they can generate motions against mechanical forces as actuators or can be activated and controlled by mechanical forces as mechanophores. Sterically hindered stiff stilbene (HSS) is a promising photoswitch offering large hinge-like motions in the E/Z isomerization, high thermal stability of the relatively unstable Z isomer with a half-life of ca. 1000 years at room temperature, and near-quantitative two-way photoisomerization. However, its mechanical response is entirely unexplored. In this study, we elucidated the mechanochemical reactivity of HSS by incorporating one Z or E isomer into the center of polymer chains and ultrasonating the polymer solutions to apply elongational forces to the embedded HSS. The present study demonstrated that HSS mechanically isomerizes only in the Z to E direction and reversibly isomerizes in combination with UV light, i.e., works as a photomechanical hinge. The photomechanically inducible (with high conversions) but thermally irreversible (at mild temperature) hinge-like motions render HSS unique and sophisticated and promise unconventional applications differently from existing photoswitches, mechanophores, and hinges.

Sterically hindered stiff stilbene mechanically isomerizes only in the Z to E direction and reversibly isomerizes in combination with UV light, i.e., it works as a photomechanical hinge.
Mechano-responsive polymers for stress self-reporting and self-strengthening

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Stress induced covalent bond scission underlies the macroscopic failure of polymeric materials. The possibility to monitor mechanical stress and/or deformation is of fundamental research interest. On the other hand, unlike biological materials that can sense mechanical force and actively remodel locally, synthetic polymers typically break down under stress. Chemomechanical coupling into polymers that can capture otherwise destructive mechanical energy and funnel it into productive and constructive processes is of great significance to the practical applications of synthetic materials. We are interested in creating more sophisticated mechano-responsive polymers for self-reporting excessive stress with clearly perceptible optical signals, meanwhile with the mechano-remodeling feature. Recently, several strategies towards sensitive mechanochromicfluorescent polymers have been developed by our group. These strategies empower polymeric materials with abilities to report whether, where and when mechanical events take place. Moreover, we also reported a kind of elastomers in which destructive forces are channelled into productive and bond-forming reactions by using dynamic covalent mechanophores. Polyurethane has been functionalized with labile Se-Se bonds, whose mechanical activation generates seleno radicals that trigger radical transfer and cross-linking reactions in situ. The resulting covalent networks possess turn-on mechano-fluorescence and increased moduli, which provide the functions of stress reporting, mechano-healing, and mechano-remodeling for the deformed film.

Schematic illustration of mechano-responsive polymers with stress self-reporting and self-strengthening
Mechanochromic elastomers that exhibit force-induced cross-linking reactions in the bulk state are presented. The segmented polyurethanes (SPUs) that contain difluorenylsuccinonitrile (DFSN) moieties in the main chain and methacryloyl groups in the side chains were synthesized. DFSN was selected as the mechanophore because it dissociates under mechanical stimuli to form pink cyano fluorene (CF) radicals, which can also initiate the radical polymerization of methacrylate monomers. The obtained elastomers generated CF radicals and changed their color by compression or extension; they also became insoluble due to the mechanically induced cross-linking reactions. Additionally, an SPU containing diphenylmethane units also exhibited highly sensitive mechano fluorescence.

Furthermore, multi-network polymers containing DFSN cross-linkers in the pre-stretched first network can generate stable pink radical species from the cleavage of their central carbon–carbon bonds in response to mechanical stress, demonstrating their higher mechanochemical reactivity than conventional single networks. The highly sensitive network polymers also show mechano chromism provoked by the change in the volume with solvent swelling. We examined the mechanism underlying the swelling-induced mechanochemical reaction in the multi-network polymers.

a) Chemical equilibrium and properties of DFSN. b) Schematic illustrations of multinetwork process to enhance the mechanosensitivity.
Mechanochromic polymers made with interacting dye pairs

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Mechanically responsive sensor molecules that contain pairs of electronically interacting dyes can be used to impart polymers with mechanochromic (luminescent) behaviour. The overarching principle that is exploited in such materials is a mechano-transduction process, through which the proximity of the chromophores is altered. The resulting response is usually instant and a priori reversible. Several types of mechanically responsive motifs that rely on this general design approach will be discussed, including rotaxanes and cyclophanes that contain two interacting chromophores. The operating principles exploited include processes such as fluorescence quenching, excimer formation, energy transfer, as well as charge-transfer formation. The solid-state mecanoresponsive characteristics of polymers in which such sensor motifs were covalently incorporated will be presented. We also discuss a mechanochromic additive based on a telechelic poly(ethylene-co-butylene) with excimer-forming cyano-oligo(p-phenylene-vinylene) end groups. This compound can be simply mixed with the host polymer and functions as a highly sensitive and reversible strain sensor in a broad variety of matrices. Confocal laser scanning microscopy was used to probe the mechanisms that govern the mechanochromism in these blends. Intriguingly, the additive forms emissive, spherical microdomains that are elongated upon uniaxial deformation, and this process causes the reversible separation of aggregated luminophores, which changes the ratio of excimer and monomer emission intensities.
Hybrid polymer elastomers composed of strong and weak crosslinkers

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The drive for tough materials has given rise to several distinct branches of the polymer elastomer platform including the inclusion of fillers, double networks, and composites. In general, these strategies take advantage of dissipation mechanisms to reduce the stress that would otherwise lead to polymer chain rupture and catastrophic failure of the network. Our group has recently discovered a new tool to enhance toughness, utilizing mechanically weak crosslinkers (WCs) that preferentially break upon the application of force. For example, cyclobutane based crosslinkers, which undergo a facile force-coupled cycloreversion reaction under tension, exhibited up to 9 times greater fracture energy compared to analogous strong crosslinker (SC) systems. This is despite the two networks being identical in terms of dynamics and topology. In this investigation, the mechanism of WC toughening is elucidated by measuring the effect of parameters including strong/weak crosslinker composition, primary chain length, and crosslinking density. We found that the inclusion of WCs allows for selective bond cleavage of the network while under stress, providing a path for energy to dissipate without catastrophic network failure. Additionally, the path-dependent mechanism leads to a non-monotonic increase in toughness with higher WC compositions due to the interplay between the accessible length and mobility of the primary chain while under tension.
Sacrificial bonds deter oxidative stress from mechanoradicals in collagen

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Collagen proteins are composed of successive collagenous (triple helix structure) and non-collagenous domains (N- and/or C-terminal end of alpha chains) crosslinked by short peptides. The resulting fibrils exhibit considerable biomechanical properties and provide tensile strength and load bearing to the tissue. Similarly to what is observed in chemical polymers, high loads produce mechanoradicals in collagen by homolytic bond scission. The location and type of initial rupture sites critically determine both the mechanical and chemical impact of these micro-ruptures on the tissue. We use scale-bridging reactive Kinetic Monte Carlo/Molecular Dynamics (KIMMDY) simulations to determine sites of micro-ruptures in collagen. We find that collagen crosslinks, not the backbone, harbor the weakest bonds. Specifically, we identify a particular bond in trivalent crosslinks as the most dominant rupture site; this bond is sacrificial in nature, rupturing prior to other bonds and allowing the material to maintain its integrity as a consequence. Further, the rupture of such weak bonds produces exceptionally stable radical species, reducing potential uncontrolled chemical damage to the fibril. Our results suggest that the unique failure mode of collagen may be tailored towards resisting the early onset of macroscopic failure and material ageing.

Propensity of bond breakages in our collagen model. Most ruptures concentrate in the crosslinked area, while there are some scattered backbone ruptures. Inset: Pie chart of summed up ruptures in the crosslinks vs. the backbones in the crosslinked area (up to 5 residues before/behind) vs. elsewhere in the backbone.
Mechanochemical activation in nanostructured triblock copolymers: A computational study

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Force-driven chemical reactions have emerged as an attractive platform for diverse applications in polymeric materials. However, the microscopic chain conformations and topologies necessary for efficiently transducing macroscopic forces to the molecular scale are not well-understood. Using molecular dynamics of a simple coarse-grained model, we demonstrate the importance of polymer conformations and nano-scale morphology for force-responsive copolymers. Our particle-based simulations allow us to investigate the impact of network-like topology on mechanochemical activation in self-assembled triblock copolymer systems, where one block is rubbery, and the other block is glassy. We find that activation during uniaxial tensile deformation depends strongly on both the polymer composition and chain conformation in these materials, with activation requiring higher stress in materials with a higher glassy block content, and most activation occurring in the tie chains connecting different glassy domains. Additionally, we observe a spatial pattern of activation which appears to be tied to distortion of the self-assembled morphology. Higher activation is observed in the tips of the chevrons formed during deformation of lamellar samples, as well as in the centers between the cylinders in the cylindrical morphology. We also investigate the effect of chain dispersity in these triblock morphologies and find preferential mechanochemical activation of short chains in bidisperse systems. We demonstrate that selective placement of mechanophores in the highest-force or highest-extension chains can be used to improve overall activation yields. Overall, our work shows that changes in the network-like topology and dispersity of chains in different morphologies significantly impact mechanochemical activation efficiencies in these materials, suggesting that this area will be a fruitful avenue for further research.
Adaptive and active polymer materials with advanced mechano-chemistry tools

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Adaptation and energy-driven behavior are fundamental features of living systems. In synthetic systems, we have been very successful in engineering responsiveness, whereby a system switches passively between two states. In this talk, I will discuss two approaches for using advanced mechano-chemistry tools to enable adaptation and active matter type behavior. In the first part, I will show how to use DNA mechanoprobes in different settings (e.g. in polymer materials or artificial cells) to create strain-adaptive behavior, whereby the mechanical information is captured as memory. In the second part, I will discuss how to implement light-driven molecular motors (not switches) into large scale polymer materials to convert light energy into local rotary motion and finally into macroscale soft robotic devices.
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Fluorescent radical precursors for detecting mechanical degradation of polymers

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Polymeric mechanoradicals generated by polymer chain scission are important to elucidate the mechanical degradation of polymers. However, the detection of mechanoradicals in the bulk state is challenging due to their high reactivity. To overcome this problem, we reported a new method for efficiently detecting mechanoradicals using diarylacetonitrile (DAAN) derivatives. DAAN reacts with highly reactive mechanoradicals to produce DAAN radicals (Fig. 1). Since DAAN radicals are relatively stable radicals that emit fluorescence under UV irradiation, it is possible to evaluate polymer main-chain scission in a complementary manner using fluorescence intensity and electron paramagnetic resonance (EPR) measurements. On the luminescence properties of open-shell radicals, however, since many radicals act as quenching groups, the number of reports of the luminescent radical is still limited and therefore their relationship between structure and fluorescence properties has not been fully investigated.

With these backgrounds, we designed and synthesized a series of DAAN derivatives with different substituents and investigated their properties. As a result, the fluorescence wavelength could be systematically tuned by changing the substituents of DAAN derivatives (Fig. 2a). In addition, mechanoradical detectability changed by changing the substituents of DAAN derivatives (Fig. 2b). These properties can be predicted using density functional theory (DFT) and time-dependent DFT calculations.
Post-functionalization strategies for every-day mechanophore sensors

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Mechanophores are molecules that undergo a reaction when exposed to mechanical force. Though they have been utilized in the past as force sensors in bulk synthetic polymers, it typically involved growing polymer off them. This prevents the mechanophores from being used in many commercial products, as polymer synthesis is often separated commercially from conventional polymer product molding. It also precludes mechanophores from being used in naturally-derived products, which are already polymerized. This gap in material application stems from the previous inability to employ them in a post-functionalizing method, and as a result, has since prevented small molecule mechanophores from use as integrated sensors in biological systems, despite their quantitative and reusable nature. Measuring small forces on the cellular level has seen a renaissance in the biomaterial community, as we are finding more evidence how mechanics play a major role in many diseases ranging from Parkinson’s, tumor metastasis, and even preterm births. Yet with current methods, we can only characterize the mechanics in these situations either quantitatively, dynamically, or in biologically-relevant conditions. We demonstrate the novel strategy of incorporating mechanophores into polymers using Click chemistry, which integrates the mechanophores by bioconjugating them to natural polymers such as sugars and proteins, as well as commonly used plastics such as polystyrene. This technique opens up mechanophores in exciting new applications, aiming to provide the next-generation tools for scientific, industrial, and clinical understanding.

Post-polymerization functionalization of both synthetic and naturally-derived polymers
Mechano-mapping in polymers with pigments and mechanophores

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Mechanochromic probes have great potential as tools to visualize and investigate mechanical phenomena in polymers that lead to damage and material failure. In this contribution, we present two generalizable strain-mapping approaches for polymeric materials that can be used to spatially resolve heterogeneous mechanical deformation over a wide strain range. The first platform is a hierarchically structured microparticle additive, or “mechano-pigment”, that contains non-close-packed silica nanoparticles in an elastic matrix cross-linked with a spiropyran mechanophore. The pigments are readily incorporated in polymeric matrices, where they report on local mechanical deformation by changes to their photonic structure and the mechanochemical activation of spiropyran. By marrying these two different mechanochromic transduction principles, localized deformation phenomena, such as necking and indentation, can be studied over a wide strain range in various polymeric matrices. For the second approach, we used supramolecular mechanophores to map strain distributions around deliberately introduced defects, such as holes and inclusions, employing a protocol based on optical microscopy, tensile testing, and image processing. Strain-sensing was demonstrated over a wide range, with high strain sensitivity and spatial resolution limited only by the detection set-up. Moreover, the data reveal that local strains in the vicinity of defects can greatly deviate from the externally applied strain, emphasizing the importance of defects in understanding and predicting the mechanical failure of polymers.

Two approaches to strain-mapping in polymers. A: Mechano-pigments containing a photonic array and spiropyran mechanophores respond to deformation by periodicity changes of the photonic assembly and mechano-activation of spiropyran to purple-colored merocyanine. B: Photonic color changes in mechano-pigments incorporated in PDMS upon indentation, converted by calibration to a local strain map. C: Operating principle of supramolecular mechanophores, which change their fluorescence emission on mechano-activation. D: Strain map of a polyurethane film equipped with a supramolecular mechanophore, containing a hole and subjected to tensile strain.
Supramolecular approaches toward mechanochromic polymers

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Mechanochemical transduction is a common process in Nature, allowing biological systems to convert mechanical stress into specific output signals. This principle has been utilized in artificial polymers to create mechanoresponsive materials that can translate mechanical stimuli into optical or chemical signals, amongst others. To achieve this, chemical motifs called mechanophores with weak covalent bonds have been integrated into different types of polymers. However, non-covalent interactions can also be used as a design element in the development of these materials. Upon mechanical stimulation supramolecular interactions can act as weak linkages that break while also reversibly re-forming after sample relaxation.

This presentation will discuss our recent research, which focused on investigating the use of supramolecular interactions as responsive motifs for achieving defined mechanotransduction processes in polymers. We incorporated supramolecular binding motifs such as linked dye pairs and hydrogen-bonding interactions into polymers and subjected the materials to mechanical deformation. This caused a reversible dissociation of the non-covalent linkages, resulting in a highly specific and measurable mechanochromic response in the solid-state that was directly proportional to the degree of mechanical deformation. Moreover, through detailed spectroscopic investigations, we were to establish a correlation between the optical output signals and the extent of dye association or hydrogen bonding in polymer samples. This provides further insight into the influence of supramolecular binding on bulk materials properties, which is essential for developing functional materials with tailored mechanical and optical responses.

Dye-interactions only... or hydrogen-bonded dye pairs...

as supramolecular approaches toward mechanochromic polymers.
Mechanoresponsive self-reporting polymer systems

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Materials that change their color, shape, and mechanical properties in response to external stimuli, such as light, heat, electricity, or magnetic fields, have piqued the curiosity of scientists from different research areas for decades. Research on stimuli-responsive motifs, including photoswitches, mechanophores, and shape memory materials have enabled recent advances in soft robotics, drug delivery systems, and sensors. Despite these advances, widespread commercial applications of stimuli-responsive materials have been modest with photochromic sunglasses remaining the sole notable example. These challenges are based on the complexity, sensitivity, and inefficiency of the chemistry involved in the synthesis and integration of stimuli-responsive motifs. To address these issues, we propose stimuli-responsive motifs that can be incorporated as co-polymerizable additives to existing, industrially relevant polyurethane syntheses. Following this strategy, a new class of high-thermal-expansion polyurethane was developed and employed as electro-thermally operated soft actuator in a “worm” robot. In addition, the incorporation of mechanophores as both universal crosslinking agents and self-reporting sensors into commercially relevant polymers that change colors when subjected to strain or to fabricate mechanically morphing materials that can be triggered using visible light will be discussed.

Schematic rearrangement of mechano-opto-responsive motif in a polymer backbone that undergoes reversible dimensional and color changes in response to external stimuli.
Precision force sensing through dynamic polymer mechanochemistry

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Multiscale stress mapping and precision force sensing play a critical role in the development of next-generation mechanically sensitive materials, such as soft robotics, flexible electronics, tactile sensors, and biomimicry materials. Current mechanically-sensitive materials rely primarily on force-induced electronic outputs, including capacitivity, piezoelectricity, piezoresistivity, and inductivity. However, the major challenge is that electronic power supplies are mandatory and high-resolution force sensing is limited by the size of sensor arrays. Polymer mechanochemistry provides a unique way to achieve mechanochromism via mechanophores, which are sensitive molecular units that undergo molecular-level chemical transformations triggered by mechanical force. Mechanochromism utilizes photonic outputs to visualize force without using external power supplies. Compared to functional polymer composites, polymer mechanochemistry enhances materials compatibility and reduces the complexity of manufacturing processes. Currently, only limited visual colors and luminescence have been reported in polymer mechanochromism, significantly hindering various potential applications. Another significant missing feature is a force-dependent multicolor mechanochromic system. My presentation will focus on utilizing dynamic polymer mechanochemistry to achieve precision force sensing with tunable visible-NIR colors and luminescence. Compared to visible light, near-infrared (NIR) luminescence exhibits a deep penetration depth and low energy loss in light-material interactions. Two dynamic mechanophores will be discussed to highlight force-induced near-infrared (NIR) chromism in polymeric materials and dynamic force sensing with a multicolor mechanochromic sensor. These research advances will have considerable potential in mechanical force sensing (force mapping and viscosity sensing), smart materials (self-healing and self-reporting materials), bioimaging (ultrasound and photoacoustic imaging), and biomechanics (cell mechanics and tribology).
Leveraging mechanochromic naphthopyrans for stress sensing applications

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A wide range of force-coupled reactions have been developed since the emergence of the contemporary field of polymer mechanochemistry. The development of new mechanophores expands the range of applications for force-responsive materials and, importantly, can expand fundamental understanding of force-mediated reactivity. Naphthopyrans are mechanophores that undergo a ring-opening reaction under force to generate intensely colored merocyanines, while recyclization often occurs with light or heat under ambient conditions, resulting in loss of color. The synthetically modular naphthopyran mechanophore has been diversified to access mechanochromic polymers with variable colors, fading rates, and even force-dependent multicolor responses. We recently discovered a new class of mechanochromically active naphthopyrans that generates an unusually stable merocyanine dye under mechanical force. The modularity of the platform has also facilitated structure-property relationships and investigations of the nature of force-mediated reactivities, and their frequent divergence from pathways accessed under other stimuli.
Solid-state mechanochemical upcycling of post-consumer polystyrene

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Solid-state mechanochemistry that utilizes ball milling presents an opportunity to address a part of the world's plastic problem and circumvent issues in current solution-state upcycling processes. We propose upcycling polystyrene (PS) waste via a mechanochemical trifluoromethylation to give an extended life to discarded plastic as a hydrophobic polymer coating through a sustainable process. This work also serves as a proof of concept for future mechanochemical polymer upcycling. Initial model compound studies show promise for translation to functionalization of dyed and high molecular weight polymeric materials. Methodology work toward the mechanochemical post-polymerization modification of PS via addition of a trifluoromethyl radical will be discussed.

Aim 1: Model compound methodology

![Bibenzyl reacts with CF₃ radical to form TFM-Bibenzyl](image)

Aim 2: Adapt to polymer upcycling

![Waste polystyrene (PS) reacts with CF₃ radical to form TFM-PS](image)

Small molecule reaction methodology translated to the mechanochemical upcycling of post-consumer plastic, focusing on dyed and high molecular weight polystyrene.
Surface-activated grinding spheres enable the direct mechano-catalytic depolymerization of polypropylene waste in the solid state

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Only 12% of plastic waste is recycled, mainly because the commonly employed melting and re-extrusion produces a lower quality material. Alternatively, depolymerization yields monomers to make high-quality plastics again. However, thermal and even catalytic pyrolysis of polypropylene (PP) offers only low selectivities and low-value product mixtures, due to the high temperatures applied, which are required for thermal C–C bond cleavage. In contrast, organic radicals form even at −196 °C when PP is exposed to mechanical force. In this study, we combine mechano-chemical bond scission with heterogeneous catalysis to explore the direct mechanocatalytic depolymerization of PP.

Mechano-chemical depolymerization of both model and waste polypropylene was achieved in the solid state, at room temperature. Significantly higher propene formation rates were achieved by direct mechano-catalysis enabled by catalytic functionalization of ZrO₂ grinding spheres using a sulfuric acid treatment at 650 °C. Catalytic ball milling at 80 °C further boosted initial propene formation rates. Radicals produced by homolytic cleavage of backbone C–C bonds induced by the strong forces arising in the shaker mill were detected by spin trapping with nitrosobenzene using electron spin resonance and likely caused the mechano-chemical depolymerization. Catalytic functionalization of grinding spheres offers a means of introducing a catalyst directly at the cleavage site and in close contact with the polymer, allowing for full utilization of active surface. Furthermore, the catalytic grinding spheres are recoverable and easy to separate from the products.

Figure 1. Results from ball-milling polypropylene at RT. Panel A: Ball mill reactor, Panel B: Crushing of a polymer particle leading to homolytic cleavage detected by ESR, Panel C: propene formation for waste and model PP, and Panel D: Propene formation during milling with unmodified and sulfuric acid treated ZrO₂ spheres.
Stages and Kinetics of Mechanochemical Depolymerization of Poly(Ethylene Terephthalate)

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Developing efficient processes to chemically recycle consumer plastics is a crucial step needed to achieve a circular material economy.\(^1\) Mechanochemistry offers a promising approach for the green chemical recycling of plastics by avoiding the use of solvents and high reaction temperatures.\(^2\) To this end, the progression and kinetics of the mechanochemical hydrolysis of PET under dry conditions at room temperature is investigated.\(^3\) The rapid and complete depolymerization of PET is demonstrated within 20 min via ball milling with stoichiometric amounts of sodium hydroxide. Over the duration of the reaction, the yield of monomers increases steadily, while the molecular weight of the unreacted PET remains unchanged, indicating a reaction where PET completely depolymerizes within a local reaction environment, while chains outside this region are unaffected. A rapid increase in the depolymerization rate is observed when \(~50\%\) conversion of the PET is reached, which corresponds to a transition of the PET powder into a homogenous wax. The transition to a wax increases accessibility of the PET chains, facilitating the more rapid hydrolysis. Finally, the rate of depolymerization is studied while adjusting milling parameter, specifically milling frequency, ball-to-powder ratio, and vessel temperature. From this, a unified kinetic expression to describe the conversion of PET is developed based on the milling energy dose.
Molecular design strategies for mechanically triggered release

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The incorporation of mechanophores into polymers enables programmable chemical function in response to externally applied mechanical forces. Mechanophores that release small molecules upon mechanical activation are promising motifs for a wide range of applications including delivery and sensing. Complementing other exciting developments in the field, our research group has developed a mechanophore design based on masked 2-furylcarbinol derivatives that permits the mechanically triggered release of functionally diverse cargo molecules with excellent control. Recent advances in molecular design overcome limitations of cargo scope as well as payload capacity.
Mechanochemical synthesis of stimuli responsive microgels

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Mechanochemical approaches are widely used for the efficient, solvent-free synthesis of organic molecules, however their applicability to the synthesis of functional polymers has remained underexplored. Herein, we demonstrate that mechanochemically triggered free-radical polymerization allows solvent- and initiator-free syntheses of structurally and morphologically well-defined complex functional macromolecular architectures, namely stimuli-responsive microgels.

We discovered that stimuli responsive microgels can be obtained by a mechanochemical solvent- and initiator-free synthesis route. The developed protocol obviates the need for an additional initiator of the classic microgel synthesis in solution. The polymerization kinetic data suggest a typical free-radical pathway for the microgel synthesis. The synthesized microgels exhibit excellent colloidal stability in aqueous media, and the size of the microgels can be modulated by controlling the crosslinker concentration in a ball mill. A temperature responsiveness of the microgels was deduced from the turbidity change and swelling-deswelling behavior induced by temperature variations. Moreover, we also demonstrated the applicability of various N-vinyl lactams and other relevant monomers to synthesize microgels by mechanochemistry. A combination of experimental and computational studies suggests a free-radical polymerization process, which is initiated by single electron transfer from milling equipment to crosslinker BIS. The developed mechanochemical polymerization approach is applicable to a variety of monomers and allows synthesizing microgels with tunable chemical structure, variable size, controlled number of crosslinks and reactive functional end-groups.
Towards C-C bond activation by polymer mechanochemistry

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Selective activation of simple C-C bonds is a highly desirable transformation in organic chemistry. This process can sometimes be achieved under specific conditions using transition metal catalysis, using strained rings or making use of directing substituents. Meanwhile, C-C bond scission is the most common outcome in polymer mechanochemistry, in which mechanical energy is converted to chemical energy typically through the scission of chemical bonds. In this talk, I'll describe our initial results towards increased C-C bond scission selectivity by tuning the polymer backbone. In addition, I'll show how polymer mechanochemistry can be utilized to introduce both C-C bond scission and functional groups introduction onto the newly formed macroradicals, leading to the formation of semi-telechelic polymer chains. Using ball-milling, more than 70% of PEG chains can be functionalized with (bromoacetyl)arenes, which can be used to install chromophores or halides which can be used for further functionalization.
Mechanochemical dynamic cancer therapy using HIFU-triggered mechanophores

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Photodynamic therapy (PDT) is a localized radical therapy that uses light and photosensitizers to generate reactive oxygen species (ROS), proximate to cancer cells. PDT is non-invasive, precisely targeted, and without long-term side effects but is limited by the relatively shallow depth of light penetration in tissues. Sonodynamic therapy (SDT) refers more specifically to sensitizer-dependent sonochemical or sonophotochemical events in an acoustic field that leads to cytotoxicity. It uses an ultrasound-sensitive drug (sensitizers) to treat deep-seated tumors with high-energy ultrasound pulses but suffers from potential tissue thermal damage due to inertial cavitation, low precision, and relatively high energy input.

Here we develop a new class of nanoparticle sensitizers, termed mechanochemical sensitizers (MeCS), that can be activated and kill tumors with low-energy high intensity focused ultrasound (HIFU) pulses. We report MeCS nanoparticles that are poly(Poly(Ethylene Glycol) Methyl Ether Methacrylate) (PPEGMEMA) grafted silica particles with azo groups incorporated at silica particle-polymer interface. The azo group is a well-studied mechanophore. Upon incorporation in the middle of the polymer chain or at the interface of a polymer and a particle, it can be activated to generate reactive oxygen species (ROS) under force field in the presence of water and oxygen. Utilizing this effect, we find that these azo based MeCS show cytotoxicity under low power HIFU treatment. Control particles with no azo groups do not show cell cytotoxicity under the same condition. Moreover, MeCS alone shows excellent biocompatibility in the absence of HIFU treatment. We have also proved that the activated MeCS produces sufficient ROS to cause the death of three cancer cell lines. More importantly, the energy density we have used was more than five times lower than the typical energy density reported in SDT, which further decrease the side effect of traditional HIFU treatment. Finally, the MeCS shows therapeutic effects in an in vivo mouse tumor model using intratumor injection.
Mechanically mediated mineralization for adapting materials and self assembly of nanofibers using Piezo-electric particles

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Biological systems employ mineralization as a long-lasting method to selectively strengthen materials in response to site specific mechanical stress. Achieving, a similar form of toughening in synthetic polymer composites remains challenging. In previous work, we developed methods to promote chemical reactions with mechanical responses of inorganic, ZnO nanoparticles. Herein, we report an example of a mechanically-mediated reaction in which the ZnO is an active participant leading to the formation of new microrods composed of a Zn/S mineral inside an organogel. The resulting mineralized microrods can be used to selectively create mineralized deposits within the material resulting in a toughening of the overall resulting composite material.
Deep dive into fused cyclobutane polymechanophores

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Polymerizable, fused cyclobutanes are versatile nonscissile mechanochemical designs that can dramatically transform polymer structures and properties or unleash latent reactivity. We have used a combination of synthesis, single molecule force spectroscopy (SMFS), and force-modified potential energy surface calculations to understand and characterize the mechanochemical behavior of a family of ladder-type fused cyclobutane mechanophores. The ring strain of fused rings distal to the polymer main chain is poorly correlated with ring opening forces, suggesting that mechanoactivation occurs with an early transition state and that the stereoelectronic features of the first bond are the primary determinant of threshold forces in these systems. We explored the quantitative relationships between the energies and kinetics of mechanoactivation and structural features in these fused cyclobutane mechanophores. Finally, we present mechanoactivation of such polymechanophores through diverse modes of force application beyond using ultrasonication.
Steering reaction pathways using mechanochemical input

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Force drives chemical change in selective and productive way. The productivity is prompted by the work done by the external force to lower reaction barrier. The resulting selectivity is different from thermal and photochemistry as the coupling of energy depends on the directionality of the applied force. Using polymer as the antenna, force effectively concentrates and triggers reactions on the reactive centers, the mechanophores. Thus, polymer mechanochemistry offers a unique and versatile approach to understand and manipulate organic reactions and their pathways. In this talk, we will discuss our recent effort on force-enabled reaction pathway control. We show that mechanical force selectively accelerates the ring-opening reactions of stereochemically defined cyclobutanes. Despite of the stepwise mechanism, the mechanical force excites the molecular extension exclusively such that stereochemistry-conserving ring-opening pathway outcompetes single-bond rotation pathway to furnish product with a non-statistically high stereoselectivity. Thinking beyond the paradigm of steering resembling reaction pathways, we envision that a multicyclic mechanophore will open door to orthogonal mechanochemistry. By harnessing the vector characteristics of force, it is possible to enact orthogonal transformations on one single mechanophore.
Influence of polymer architecture in polymer mechanochemistry

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Over the last several years, we have extensively studied how the graft polymer architecture can influence the location and rates of chain scission events that lead to polymer fragmentation and/or mechanophore activation. Backbone length, grafting density, arm composition, arm architecture (e.g., linear vs dendronized), and arm size, for instance, can all influence the rates of backbone scission. Some of these structural parameters can also affect the rates of arm scission and mechanophore activation in graft multimechanophore polymers. By studying graft polymer mechanochemistry with ultrasonication and ball-mill grinding (BMG), however, we have determined that the impact of these structural parameters cannot be generalized to all methods used to conduct mechanochemistry. This was further illustrated in our recent work studying the mechanochemical reactivity of cyclic polymers, where the reactivities with ultrasonication and BMG were quite dissimilar. Overall, our work demonstrates the benefits of using polymer architecture as a design parameter to modulate mechanochemical reactivity, but should bring caution to over-generalizing the influence of design parameters identified using only a single mechanochemical method, such as ultrasonication.

Various polymer architectures studied by ultrasonication and ball-mill grinding.
Carbamoylketoximes as thermally stable mechanophores for polymer mechanochemistry

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The reasonably selective activation of mechanophores in polymer materials necessitates that the force to break them must be smaller than the force required for non-selective mechanochemical transformations in the material under investigation. Adaption of the force response is generally achieved by adjusting the bond dissociation energy (BDE) of the mechanophore. However, since the mechanochemical BDE usually correlates to the thermal BDE, the incorporation of mechanophores into polymers processed at high temperatures is a challenge. Industrial manufacturing conditions of many technical polymers entail processing temperatures of more than 140 °C, which is beyond the thermal stability of most mechanophores.

Recently we have presented carbamoylaldoximes as latent amine generators (Scheme 1). We have shown that carbamoylaldoximes can undergo force-induced homolytic bond scission at the N–O oxime bond in polymers thus uncaging an amine. In the process, we have discovered that the polymer mechanochemical reaction proceeds in analogy to its photochemical counterpart. Having validated the aldoxime-based mechanophore, we moved our attention towards possible optimizations of the mechanoresponsive scaffold, in terms of the mechanochemical sensitivity and thermal stability. By changing our focus to carbamoylketoximes, we have found that they exhibit considerably higher thermal stabilities and simultaneously exhibit higher mechanochemical reaction rates challenging the previously mentioned paradigm of the interconnected thermal and mechanochemical BDEs. Herein, we explain the underlying principles through both experimental and computational mechanistic investigations.
Fundamental and applied studies on mechanophores and mechano-responsive materials

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Polymer mechanochemistry has grown into an excitingly multidisciplinary field of study. In our research group, we aim to understand general structure-reactivity relationships of mechanophores to create links between mechanically-guided reaction outcomes and fundamentals of physical organic chemistry. From this perspective, we view mechanophores as an exciting focal point for fundamental investigations. Additionally, we draw from the deep well of known mechanophores and look to incorporate functional variants into the design of responsive materials. From this perspective, we view established mechanophores as useful tools for creating responsive macroscale systems. In this talk, we will present details of our work on mechanophore designs as well as examples of mechanophores in applications-oriented research. Key examples will include structural modifications on mechanophores to elucidate reactivity profiles and incorporation of mechanophores into build materials for additive manufacturing and 3D printing.
Sonochemically induced retro Diels-Alder activation of alicyclic diimide mechanophores

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Polymer mechanochemistry, or the use of mechanical force to direct chemical reactions within force-responsive units in polymer backbones, has provided a rich platform for the fundamental understanding of force transduction within polymer systems. The design of both new force sensitive units, or mechanophores, as well as their incorporation in both linear and network polymer systems have yielded demonstrations spanning the range of force sensing, small molecule delivery, and material reprocessing or toughening. A subset of mechanophores have leveraged the retro Diels-Alder reaction, but few have relied solely on non-aromatic components in their design. Herein we synthesized a series of poly(methyl acrylate) polymers via controlled radical polymerization from alicyclic bis-diimide initiators derived from bicyclo[2.2.2]oct-7-ene dianhydrides. By changing the substitution pattern at the bridgehead positions, we demonstrate the ability to tune the rate of mechanochemical activation under ultrasonication through the determination of initial rates of chain scission as well as trapping experiments of the reactive chain ends generated upon activation with fluorescent tags.
Mechanochemistry and thermochemistry take on different reaction pathways, but may also be intertwined in complex multi-step reaction schemes. Our group has developed several types of mechanophore monomers that can be directly polymerized and undergo force-triggered chemical transformation to change an array of properties of their polymers. In the polymechanophores, the repeat units of mechanophores are closely coupled. We wondered if there would be cooperative activation across neighboring units or if a mechanochemical activation event can lead to multiple chemical events that can occur in the absence of applied force. We will present systems where mechanically triggered generation of radicals leads to cooperative chemical reactions to transform the polymer structures.
Static and dynamic aspects in mechanochemistry

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We discuss the use of force-modified potential energy surfaces to explain mechanochemistry, and the associated use of transition state theory to determine competing rates. We also consider cases where the assumption of quasi-equilibrium fails and dynamic effects (such as chemical activation and flyby trajectories) can be important. We comment on the possibility that dynamic effects might be even more common in mechanochemistry compared to thermally activated reactions.
Development of molecular switch-based mechanophores

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Mechanical force has been long-existing as a ubiquitous stimulus in nature, but the use of mechanical force to accurately modulate molecular structures and subsequently functions only begins in the past two decades. Since then, a variety of force sensitive molecules are reported, and we call them ‘mechanophores’. This family of molecules normally undergoes stress-induced structural changes, including covalent bond scission, non-covalent interaction disruption, and intramolecular conformational/configurational isomerization. To the best of our knowledge, almost all mechanophores undergo one way of mechanochemical activation, while the mechanophore deactivation process is always triggered by another stimulus other than mechanical force. Molecular switches are a family of molecules that can be reversibly switched between two or more states in response to external stimuli (e.g. light, heat, chemicals, and electricity). By employing the unique stimulus-responsiveness and reversibility of a molecular switch, here we introduce a new mechanochromic mechanophore based on the structural motif of hydrazone, which is previously known as a configuration-based photochromic and chemical-activated molecular switch. CoGEF (Constrained Geometries for simulating External Force) simulation reveals that both $E \rightarrow Z$ and $Z \rightarrow E$ isomerization in hydrazone can be mechanically activated by precisely applying mechanical force at different pulling positions. These predictions are further validated by ultrasonicating different $M_w$ polymethyl methacrylate (PMA) polymers with a hydrazone covalently incorporated at the central position of a polymer chain. Mechanical isomerization and random scission kinetics, and mechanical stationary states of each isomerization step are evaluated and the mechanochemical origins behind all phenomena are discussed. Hydrazone is the first mechanophore scaffold that demonstrates a dual mechanically-induced isomerization and could potentially become the first generation of reversible ‘Mechanoswitch’.

The schematic illustration of a dual mechanically activated hydrazone scaffold
Investigation into the mechanical stability of Diels-Alder mechanophores by AFM-based single-molecule force spectroscopy

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Dynamic covalent bonds, like the archetypal furan–maleimide Diels–Alder (DA) adduct, are vastly used in synthetic chemistry and polymer science for their ability to undergo reversible breakage, and are now expanding into biology. Furan-maleimide adducts are characterized by dynamical covalent bonds. The DA reactions on these adducts proceed via a low reaction barrier that leads to reversible reactions. In solution, the adducts need to be heated at high temperatures to break open. Four adducts with a different regio- and stereochemistry can be synthesized, namely the *endo* or *exo* configurations and *proximal* or *distal* geometries (Figure 1). These features make the furan–maleimide adducts attractive to design intelligent materials and logic devices driven by mechanical forces. However, a complete and quantitative picture of the effects of regio- and stereochemistry on the mechanics of DA adducts is clearly missing.

Here, we describe the results obtained when using atomic force microscopy (AFM)-based single-molecule force spectroscopy to pull on the four Diels-Alder adducts incorporated into a polymer chain (Figure 2). Our single-molecule pulling experiments allowed us to measure the characteristic rupture forces required to break-open the four adducts. By comparing the mechanical response of these adducts that differ in their regio- and stereochemistry, we intend to establish the general relationships between the rupture force under mechanical load and molecular properties that govern the mechanical stability of these compounds.
Microgels are nanometer-sized soluble polymer networks which combine features of surfactants, polymers, and colloids. Their soft nature paired with their surface activity makes them ideal candidates as emulsion stabilizers. The combination with a responsive polymer network allows to stabilize or destabilize the emulsions on demand triggered by an external stimulus such as temperature or pH. Despite numerous publications related to the interfacial behavior of microgels, the stabilization and destabilization mechanisms are still not fully understood as a result of the microgel's complex 2- and 3-dimensional phase behavior. Our work is based on the study of thermoresponsive PNIPAM microgel monolayers at the solid-liquid interface using the colloidal probe technique which allows us to study the interactions between different probe types and the microgel monolayer as a function of microgel concentration and temperature. This allows us to probe changes in elasticity as well as short- and long-range interactions on a local scale. Different probe types such as modified silica particles or microgel beads were used to evaluate the nature of the underlying interactions, thus, enabling us to get insights into the interactions occurring in-situ.

Stiffness histograms obtained from measurements with a silica probe (top) and heat maps of long-range attraction measured with a microgel bead (bottom) on PNIPAM microgel monolayers.
Mechanophore postulate: A linear model for Mechanophore reactivities

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Our intuition of molecular structure-reactivity relationships rests on foundational concepts framed as Rules, Postulates, Principles, and Equations in physical organic chemistry. The application of these concepts to reactions under external force is not straightforward for two reasons: force reshapes the reaction trajectories and its coupling to potential energy surface. Here, we systematically investigated the activation of norborn-2-en-7-one (NEO) moiety as a model system that exhibits structure-dependent mechanochemical reactivities. We identified that activation barriers under extrinsic force can be correlated with two thermodynamic parameters. A linear model based on these two thermodynamic parameters was then established to generally predict the kinetic behavior of over 20 force sensitive motifs (i.e. mechanophores). The model provides both quantitative predictability of force and qualitative mechanistic insights with a simple computational workflow.
Controlling reactivity under tension

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Mechanical force is a formidable, and relatively unexplored, source of energy that, with its ability to distort, bend and stretch chemical bonds, is unique in the way it activates chemical reactions. The precise control of this force could revolutionise how we build and rearrange molecules and change the way we think about chemical transformations. Pulling both ends of a macromolecule apart creates highly directional strain with its highest intensity in the middle of the chain and, in polymer mechanochemistry, the force is transduced to force-sensitive moieties (mechanophores) embedded within the polymeric backbone. Here we investigate how geometry, topology, and substitution can be used to control the mechanical reactivity of a mechanophore.
Microgels in monolayers: A force spectroscopic study

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Microgels are three-dimensionally crosslinked polymer networks that swell in a good solvent. They can change their size and internal structure in response to external stimuli such as temperature, pH, or ionic strength. In addition, they are highly interfacially active and possess a rich phase behavior due to their soft and inhomogeneous structure. Based on their interfacial properties, they can be used in various applications, e.g., as emulsion stabilizers or surface coatings. However, there is very little data on the internal structure of microgels in dense monolayers.

In this study, we used Langmuir-Blodgett type depositions to transfer microgel monolayers at different surface pressures onto solid substrates [1]. These monolayers were then investigated ex-situ by atomic force microscopy to investigate (a) their two-dimensional structure and (b) the topography and internal structure of the microgels within the monolayers via force spectroscopy [2].

The results of our measurements show that the confinement of microgels within dense monolayers has a profound impact on their internal structure. Single microgels exhibit an inhomogeneous internal structure at the solid-water interface with a stiff core in the center and a decreasing stiffness towards the periphery of the microgels. With increasing compression of the microgels within the monolayer, the microgels become noticeably stiffer without changes in their lateral and vertical dimensions (Figure 1).

Figure 1: Average contact stiffness profiles of (A) single microgels and (B) microgels in a dense monolayer.
Force strain model for mechanistic insights and predictive model development in mechanochemistry

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Computational models that can decompose activation energy into chemically meaningful terms have seen a wide array of applications in organic chemistry and catalysis for gaining key mechanistic insights and guiding discovery of new reactions. However, similar approaches have not been utilized to study force-modified reactivities to the same extent. In this work, we present the force strain model, an energy decomposition scheme that decouples force-modified activation energy (ΔE‡) into electronic energy (ΔE_{scf}‡) and force stabilization energy (ΔE_{force}‡). Furthermore, using approaches such as ALMO-EDA, electronic energies can be further decomposed into chemically meaningful components, leading to insights on how external force can affect key secondary interactions in both ground and transition states. The force strain model was used to gain mechanistic insights into reactivity and selectivity of force-modified reactions. This approach was applied to study a wide variety of mechanophores, including but not limited to ferrocenes, norbornenones, gemdihalo-cyclopropanes, cyclobutanes and retro-Diels-Alder mechanophores. We used these mechanistic insights to develop predictive multivariate linear models of experimentally measured threshold forces and to discover new design rules for highly reactive ferrocene-based mechanophores. We believe that the force strain model can provide unique insights into force-coupled reactivity and can be used as a guiding principle for mechanistically informed discovery of novel mechanophores.

\[
\Delta E^\ddagger = \Delta E_{scf}^\ddagger + \Delta E_{force}^\ddagger \\
\Delta E_{force}^\ddagger = -F_{ext}(X_{TS} - X_{GS})
\]
In 1952, Erwin Schrödinger wrote that we would never experiment with just one electron, one atom, or one molecule. Forty years later, methods derived from scanning probe microscopies allowed us to manipulate single atoms and molecules, and even single bonds. Single-molecule force spectroscopy, which consists in trapping and stretching a molecule between an AFM tip and a surface, enables to probe (and/or to induce) molecular processes in situ and in real time through the application of mechanical forces. Such elegant experiments have provided unprecedented insights into the structure and function of many (biological) systems.

Here, we will discuss some of our recent results in the field of AFM-based single-molecule force spectroscopy on synthetic polymers, supramolecular systems, and molecular machines to illustrate what the technique can bring to mechanochemistry.
Ambient reactive extrusion additive manufacturing of polyurethanes and polythiourethanes

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Polyurethanes are produced consistently in multiple different industrial markets accounting for over 7 billion pounds of polymers in 2021. They comprise a wide range of monomeric and oligomeric building blocks that produce an even wider range of physical and mechanical properties. Additive manufacturing provides the potential to incorporate a structural component into a materials design space to further extend the polyurethane industry. The ambient reactive extrusion additive manufacturing (ARE-AM) of a polyurethane will be discussed including its printability, kinetic, and mechanical properties. This technique involves the combination of two reactive sides (polymeric building blocks) in a static mixer directly before deposition. Comparison between polyurethane and polythiourethane polymerizations will be discussed along with other printing considerations like viscosity, chemical kinetics, miscibility, and processibility of the polymeric systems.
Poly 3917156

Improved impact resistant composites through randomly oriented discontinuous fibers

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High performance composites are ideal for many applications requiring high strength to weight ratios. However, while continuous fiber structural composite materials are exceptionally ideal for static load bearings they fail to meet the necessary requirements for high energy dynamic loads. Traditionally, high performance, multi-axial composites are commonly manufactured from fiberglass and vinyl ester resin systems to lower cost and improve processability. This research evaluates the addition of randomly oriented discontinuous fibers to elucidate the effects of fiber form on impact performance. Fiber areal weight and ply orientation of non-traditional interply (combinations of fiber chemistries in continuous or discontinuous forms) hybrid epoxy-matrix composites were altered to investigate their effects on impact resistance. Composites constructed from combinations of E-glass, basalt, and carbon fibers were fabricated via Vacuum Assisted Resin Transfer Molding (VARTM) before measuring un-notched uniaxial tension, flexural, and impact properties. Composite parts containing Chopped Strand Matting (CSM) form fiber demonstrated up to a 30% increase in impact resistance over their continuous fiber counterparts, while simultaneously maintaining other key mechanical properties with little to no increase in cost and up to 25% weight reduction. Randomly oriented fibers are superior with respect to dynamic impact properties and additional investigations should be executed to vet the influence of fiber form with respect to various fiber chemistries, matrices, and interdependencies therein.
Formulation of MOF-808 core-shell fibers for organophosphate hydrolysis under non-buffered conditions

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Metal-organic frameworks (MOFs) that contain Z₆O₄(OH)₄ secondary building units (SBUs) have been shown to facilitate organophosphate hydrolysis, however, they often necessitate amine buffers to facilitate high activity and turnover. The buffer facilitates removal of carboxylic modulators which generate “missing-linker” sites that provide active site binding for organophosphate hydrolysis. While non-volatile buffers can be integrated into MOF composites with amine polymers, all solid-state MOFs formulations suffer reduced organophosphate hydrolysis due to the reduction of MOF accessibility and hydrophilicity within composites. Herein, we utilized a hydrophilic biopolymer in conjunction with MOF-808 to fabricate highly active composites for the hydrolysis of dimethyl-p-nitrophenylphosphate (DMNP) under non-buffered conditions. In addition, we used an acrylic 3D printed dual nozzle in the fabrication of highly reactive core-shell wet spun fibers. This fabrication process is amenable to different core polymers and facilitates modular fiber strength and elastic properties. We demonstrate that polyelectrolyte complexation facilitates enhanced MOF sheath coverage of the core fibers and consequently increased DMNP hydrolysis. To enhance MOF sheath retention upon physical manipulation of elastic fibers, we chemically adhered the MOF/biopolymer sheath to a functionalized elastic polymer through a simple dip-coating procedure. We believe that our newly fabricated active fibers offer advancements for the practical and recyclable utilization of MOF composites for organophosphate protection.

Approved for public release: distribution unlimited.
Plasticizer evaluation for polyamide compositions

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One strategy to improve the insect repellency of textile fibers is to incorporate functional components into the fiber at the time of filament production or during the weaving step. An NRL-led SERDP effort is using electrospinning to incorporate insect repellents to screen a number of fiber and repellent compositions and morphologies. To support this effort, DEVCOM ARL has been evaluating the use of plasticizers to inhibit the crystallization of nylon matrix materials (e.g. nylon-11, -12). Using a small batch conical twin screw extruder, varying compositions of matrix and plasticizer were prepared and evaluated using thermal analysis techniques. Impacts on the peak crystalline melting temperature were determined, and a down-selected composition was prepared as a master-batch to enable subsequent low-temperature melt processing of the plasticized blend and a variety of insect repellents and insecticides. Details of each composition and recommendations for further development will be presented.
Nontraditional composites for improved mechanical properties through basalt fiber and graphene

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Structures and personnel exposed to high energy impact loads require nontraditional protective measures in order to ensure occupant survivability. The need for these extraordinary structures arises due to the unpredictable nature of the impact and also for practicality in the field such as protective retrofitting that is durable, lightweight, and rapidly-deployable. Due to their high strength to weight ratio, polymer composites offer an effective means of rapidly-deployable protection. Traditionally-used materials, such as E-glass and vinyl ester resin systems, have low-cost, can be manufactured easily, and have good performance in structural applications, but are environmentally-harmful, abrasive in handling, and fall short in high energy impact load protection. Basalt fiber presents an emerging alternative to E-glass due to its comparable price and more environmentally-friendly manufacturing process. This research investigates the mechanical performance of basalt fiber and E-glass composites in an epoxy resin system that is enhanced with graphene-related nanoparticles. The composites were manufactured via Vacuum Assisted Resin Transfer Molding and their mechanical performance was evaluated via un-notched tension, flexural, and impact testing. The results show that basalt fiber composites with graphene-related additives have superior mechanical properties compared to their E-glass counterparts. Furthermore, the nanoparticles result in noticeable improvements in mechanical properties with virtually no additional weight, cost, or processing requirements. As a result, these nontraditional composites will have important implications for the design of impact protection systems where strength, weight, and cost are critical parameters.

Polymer composite panels for impact protection
Additive manufacturing of novel photopolymeric polybutadiene resin via digital light processing

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The field of research in additive manufacturing (AM) of elastomeric materials, similarly with the advancements of AM technology, is a rapidly maturing environment. With great advancements in AM technology comes the greater need to scout, develop, and modify novel elastomeric materials that can be applied to these technologies. Previous work utilized an unmodified polybutadiene (PB) with a dithiol curative and UV-sensitive initiator as the resin in vat photopolymerization via an LCD printer. Successful 3D-printed test articles were produced, however, there were significant amounts of overcure which can be attributed to the inherent light bleed that LCD printing systems possess. Given the LCD printer disadvantages, digital light processing (DLP) 3D-printer was employed. The increased light intensity and direct projection of the image onto the vat instead of an LCD mitigates issues faced with the LCD printer. PB test resin was optimized by addition of a UV absorber, Oil Red O (OR-O), into the resin to improve feature fidelity for printed structures while decreasing pervasive light scattering, which causes overcuring. 3D-printed articles were printed using the novel photopolymeric resin and were qualitatively compared to 3D-printed articles without OR-O.

Graphical display of vat polymeriztion via Digitital Light Processing (DLP). Novel photopolymeric polybutadiene resin was successfully 3D printed. Printed article is a lattice structure, shown above.
Elucidation of structural proteins used in construction of mud dauber nests and caddisfly cases for defense applications

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Mud daubers are capable of constructing water resistant, thermally regulating, and durable nests using structural proteins from their saliva. Although the construction methods, foraging behavior, and the physical and mechanical properties of the mud dauber nests have been widely studied, there is little information regarding the biopolymers found within the mud dauber salivary secretions. It is believed that mud daubers secrete salivary mucoproteins to provide adhesive and hydrophobic properties within the nest, allowing them to structurally withstand extreme environmental conditions.

This study investigated the presence of mud dauber proteins within the constructed nests, along with analysis of the corresponding soils used during nest construction. Here, we present the development of novel protein extraction and analysis techniques using caddisfly silk samples that contain widely studied structural proteins. The developed workflow was carried over to mud dauber specimens and nests that were collected across the United States to extract and analyze the biopolymers from dissected salivary glands and nest materials. The metaproteomic extraction method developed involved SDS-phenol extractions and SDS-PAGE gel electrophoresis for size exclusion separation. We used state-of-the-art instrumentation, including MALDI-TOF-MS, XRD, and elemental analysis to elucidate the protein sequence and soil characteristics.

Our work delivers the foundational method development that can translate to extractions for many other insects and nest biomaterials. The proteomic findings for the mud dauber saliva and nest materials provides insight into how these biomolecules enhance structural adhesiveness and whether the mud daubers themselves can bio regulate the amount of protein based on different environmental and soil conditions. We anticipate that the protein structure knowledge can inform future research in areas of structural engineering and synthetic biology. Ultimately, it provides a foundation for future material development and proteomic research for DoD applications, including use as dust control agents for verticle lift aircraft.
Super-recovery of ultimate strength in double network hydrogels through scission-induced topological remodeling of polymer networks

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The ultimate strength of polymer networks is often enhanced by molecular mechanisms of energy dissipation, specifically the scission of sacrificial covalent bonds or the dissociation/exchange of reversible bonds based on hydrogen bonding or metal coordination. The former results in a permanent loss of modulus, whereas the latter often allows a material to recover almost its full original properties. Here, we report an interesting DN hydrogel in which a combination of permanent and reversible bond scission results in materials that not only recover their initial mechanical properties, but also become stronger after recovering from the initial strain. We introduce metal-ligand (ML) coordination in between the first and second networks of DN hydrogel, making these dynamic interactions efficiently heal hydrogels over time in response to large strains, ultimately achieving a higher yield stress and recovery energy. This toughening is only observed in covalent DNs and not in a single network with the same chemical composition nor DN without inter-network ML coordination. We attribute the strengthening behavior to the topological remodeling of the first network that occurs due to sacrificial scission of covalent bonds within it, which subsequently alters the distribution of metal-mediated and entanglement-mediated load transfer between the two networks. As stretching an intact DN break results in both covalent bond scission and ML dissociation which showed a large hysteresis energy; while the reconstructed network preferentially breaks dynamic bonds and then acquired fully recoverable properties over subsequent cycles, leading to a tremendous difference in energy dissipation inside DNs. The enhancements in DN hydrogels lead to differences in internal topology of polymer networks affecting their mechanical properties, and further complement other existing strengthening strategies.
Simulation and Data Science Approaches to Design Biologically Relevant Polymers and their Applications

Polymer informatics for the design of homopolymers, copolymers, blends and bioplastics - Ramprasad, Rampi (Oral Only)

Constructing a large-scale biomedical knowledge graph and its applications - Zhang, Jinfeng (Oral Only)

Harnessing the power of language models to accelerate material design - Manica, Matteo (Oral Only)

Application trend of biomedical 3D printing: Insights of recent development - Hsu, Chia-Wei (Oral Only)

Can self supervised models make a difference in real world drug discovery? - Ramsundar, Bharath (Oral Only)

Rapid polymer screening using AI - Kroenlein, Kenneth (Oral Only)

Solvent responsive amphiphilic polymer gels with inherent antimicrobial activity - Kumar, Amit (Oral Only)

Machine-assisted discovery of novel protein-polymer hybrid materials - Webb, Michael (Oral Only)

Design of nanostructured materials from sequence-controlled biopolymers - Olsen, Bradley (Oral Only)

Development of scalable and generalizable machine learned force field for polymers - Leswing, Karl (Oral Only)

Understanding polyhydroxyalkanoate biopolymer properties and performance using data-enabled machine learning approaches - Marrone, Babetta (Oral Only)

Effect of Tau protein phosphorylation on the process of its adsorption on the neuronal membrane - Rakowski, Kamil (Oral Preferred)
Polymer informatics for the design of homopolymers, copolymers, blends and bioplastics

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The Materials Genome Initiative (MGI) has heralded a sea change in the philosophy of materials design. In an increasing number of applications, the successful deployment of novel materials has benefited from the use of computational, experimental and informatics methodologies. Here, we describe the role played by computational and experimental data generation and capture, polymer fingerprinting, machine-learning based property prediction models, and how such methods will have to evolve to handle situations including the design of homopolymers, copolymers, blend polymers and bioplastics. These efforts have culminated in the creation of an online Polymer Informatics platform (https://www.polymergenome.org) to guide ongoing and future polymer discovery and design. Challenges that remain will be examined, and systematic steps that may be taken to extend the applicability of such informatics efforts to meet a wide range of societal and technological domains will be discussed. Recent work on using such methods to search the polyhydroxyalkanoate space to identify suitable bioplastics will be highlighted.
Constructing a large-scale biomedical knowledge graph and its applications

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In the past few decades, the biomedical research community has acquired a wealth of knowledge, much of which is stored in scientific literature as unstructured text. Converting this text into structured form is crucial for developing new methodologies and applications that can fully utilize this knowledge. To achieve this goal, two basic problems must be addressed: named entity recognition (NER) and relation extraction (RE). NER involves identifying the concepts or entities in texts, such as diseases, genes/proteins, and chemical compounds. RE, on the other hand, aims to extract the relationships between these entities. The information extracted from NER and RE can be used to create a knowledge graph, where nodes represent entities in the text and edges represent their relationships. This presentation will discuss our team’s work on the LitCoin NLP Challenge organized by NIH, for which we were awarded first place. Using pipelines developed for the challenge, we processed all PubMed articles and created a large-scale biomedical knowledge graph. The accuracy of this large-scale relation extraction is estimated to be 84% based on manual verification of a sample of the extracted data. We also incorporated relation information from 40 public databases and relations inferred from publicly available genomics datasets. Our knowledge graph consists of over 10 million entities and more than 30 million relations, and we have developed versatile query functions for accessing this graph. Finally, we will discuss some important applications enabled by this large-scale knowledge graph.
Harnessing the power of language models to accelerate material design

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In recent years, language models have disrupted multiple application domains, from natural language to chemistry and material science. Since their inception, they have enabled a revolutionary way to hypothesize the design of novel materials, shown remarkable capabilities in modeling reactivity and successfully adopted in automating chemical synthesis planning.

This talk will cover our recent research on applying language models to accelerate scientific discovery in chemistry, from small molecules to polymers and proteins.

Our methodologies cover textual representation of molecules, natural language, and hybrid representations, which allow leveraging different data modalities to build holistic foundation models.

Besides introducing the methodologies, we will also cover various applications of language models for material design and synthesis.

By harnessing the power of language models and the growing availability of datasets, we can transform the discovery process at different stages, paving the way for a revolutionary computer-aided approach to designing, optimizing, and validating novel materials.
Application trend of biomedical 3D printing: Insights of recent development

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Concepts of 3D printing originated in the 1980s, followed by inventions of techniques such as photopolymerization, powder bed fusion, jetting, and extrusion. Nowadays, 3D printing techniques and their applications have gotten involved in multidisciplinary fields such as education, construction, biomedicine, etc. Herein we will present a CAS approach to reveal the recent advancements of biomedical 3D printing. With the CAS Content Collection, we manifest (1) the annual publication of biomedical 3D printing; (2) a landscape view of primary 3D printing techniques utilized in biomedical; (3) top concepts related to 3D printing in biomedical applications; (4) major substances used in different biomedical fields. We further show the contribution of journals and patents from the origin of countries in our data analysis.
Can self-supervised models make a difference in real world drug discovery?

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When starting a drug discovery project, there often isn't much data available. How can we bootstrap machine learning approaches to drug discovery in the presence of limited data? Self-supervised approaches provide a systematic methodology to solve the low data problem in real world drug discovery. I will explore a variety of different self-supervised strategies to learn in the absence of experimental data, including some very recent work leveraging large language models such as GPT3 for chemistry. I will share some results from past and on-going work at Deep Forest Sciences working to extend self-supervision to real-world drug discovery.
Consumer demand for green products is increasing, and suppliers are offering new, greener raw ingredients for polymer synthesis. Key players in the chemical industry subsequently face an increasing need to determine which of these new ingredients can be used to synthesize greener polymers that still meet the demanding material performance targets of modern applications, and ideally they need to do this as quickly as possible. However, designing new polymers and optimizing their properties requires costly and time-consuming synthesis and testing, and can often additionally require rigorous computational resources for molecular simulations to guide decision-making on what to synthesize.

We will discuss our AI-based approach using the Citrine Platform to rapidly screen novel polymers based on their predicted thermal properties, using promising monomer building blocks. Should the downstream customer requirements change for these novel polymer products, the machine learning model and multi-objective optimization can be quickly adapted to new target properties. This solution simultaneously reduces a chemical company’s experimental costs, is faster and less computationally-intensive than molecular simulations, and also enables more agile and flexible responses to ever-changing market conditions and customer requests.
Solvent responsive ampiphilic polymer gels with inherent antimicrobial activity

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Solvent responsive polymer gels are a class of materials that can undergo reversible changes in their physical properties in response to changes in the solvent environment. Recently, solvent responsive polymer gels with inherent antimicrobial properties have been developed, which can be used to create materials with enhanced antimicrobial activity. These materials can be used to create surfaces with improved antimicrobial properties, which can be used in a variety of applications, such as medical devices, food packaging, and water treatment.

Polymeric gels functionalised with active quaternary ammonium cation attached to hydrocarbon chain have been fabricated. The prepared gels were characterized using field emission scanning electron microscopy (FE-SEM) and water uptake studies to determine the swelling behaviour in water as well as in ethanol. In addition, antimicrobial activity of the gels has been determined for *E. Coli*, *P. Aeruginosa*, *B. Subtilis*, *S. Aureus*, which are gram negative and gram-positive bacteria respectively.

![Polymer gel film in water and ethanol](image)
Machine-assisted discovery of novel protein-polymer hybrid materials

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Enzymes offer elevated activity and selectivity for target reactions with high cyclability, making them desirable for myriad applications in pharmaceutical, food and drug, and chemical industries. Unfortunately, few enzymes are capable of sustaining their functionality outside of their native environments, which limits their deployment. In this talk, I will discuss an iterative design framework predicated on robotic synthesis, machine learning, and Bayesian optimization that facilitates the design of random heteropolymers that are tailored to enhance the activity of target enzymes in non-native environments or exposed to particular stressors. I will discuss the particular advances related to polymer featurization and optimization facilitate efficient discovery of high-performing materials. I will further discuss how post hoc analysis and interpretation of machine learning models helps us to reveal the mechanisms by which enzyme stabilization is achieved as well as how data seeding strategies can be deployed to improve design outcomes.
Design of nanostructured materials from sequence-controlled biopolymers

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Biological polymers offer an as-yet unparalleled level of sequence control in polymer design, enabling them to achieve a wide variety of properties in natural systems. This sequence control inspires chemists to harness the potential of these polymers for a wide variety of applications in new polymer design, particularly in biomaterials and nanomaterials. However, the design space for sequence-controlled polymers is massive, even with the comparatively limited chemical diversity of monomers in natural polymers such as proteins. Therefore, new paradigms for exploring and designing in this extremely high-dimensional space are required to effectively navigate through it and accelerate the pace of material discovery.

To provide a formalism for sequence-controlled polymer modelling, we have developed a variation of the classical self-consistent field theory formalism that allows field theoretic simulation of sequence-defined polymer self-assembly for arbitrary polymer sequences. By representing the polymer sequence as continuously differentiable interaction function, we can model a wide variety of different monomer interactions in a simplified form, and the efficacy of the model is validated on relatively simple sequence-defined polymers such as tapered block copolymers. The model provides an intellectual formalism for analysing the relevant length scales for self-assembly using Fourier transforms of the sequence functions providing key insight into how different Fourier components affect nanostructure formation.

Using elastin-like proteins as model biopolymers, we have also explored different methods for the parameterization of these sequence functions and experimental routes for generating the necessary thermodynamic data. When properly parameterized, the simulation approach has potential for use in inverse design algorithms that can help to discover novel nanomaterial structures based on these biopolymers.
Development of scalable and generalizable machine learned force field for polymers

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Understanding and predicting the properties of polymers is vital to developing tailored polymer molecules for desired applications. Classical force fields may fail to capture key properties, for example, the transport properties of certain polymer systems such as polyethylene glycol. As a solution, we present an alternative potential energy surface, a charge recursive neural network (QRNN) model trained on DFT calculations made on smaller atomic clusters that generalizes well to oligomers comprising larger atomic clusters or longer chains. We demonstrate the validity of the polymer QRNN workflow by modeling the oligomers of ethylene glycol. We apply two rounds of active learning (addition of new training clusters based on current model performance) and implement a novel model training approach that uses partial charges from a semi-empirical method. Our developed QRNN model for polymers produces stable molecular dynamics (MD) simulation trajectory and captures the dynamics of polymer chains as indicated by the striking agreement with experimental values. Our model allows working on much larger systems than allowed by DFT simulations, at the same time providing a more accurate force field than classical force fields which provides a promising avenue for large-scale molecular simulations of polymeric systems.

Figure 10: Graphical abstract.
Understanding polyhydroxyalkanoate biopolymer properties and performance using data-enabled machine learning approaches

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Plastics made from fossil feedstocks are ubiquitous in our daily lives, but the environmental problems they create are driving an urgent search for bio-based alternatives. Ideally, we look to bio-based plastics to be sufficiently durable for specific applications, but more easily degradable in the environment. Bio-derived molecules have diverse chemical functionalities and offer a rich resource for discovering novel biopolymers for conversion into plastics materials with enhanced performance. We are using polyhydroxyalkanoate (PHA) polymers synthesized naturally in cyanobacteria as a model system; and developing machine learning (ML) tools to optimize polymer design. To develop new biopolymers with desired properties, we need to gain a better understanding of what is possible to produce biosynthetically; and what biopolymer chemistries would be needed to achieve the desired properties. Thus, we are developing ML approaches to enable understanding of both the chemical structure:property relationships of the PHA class of biopolymers (Chemistry Loop) and the biosynthetic routes that can be used or improved to synthesize such polymers (Biology Loop). The Chemistry Loop uses a database of physical and mechanical characterization data, and degradation data, for known PHAs to inform chemical structure-property-performance relationships. The Biology Loop uses DNA sequence and protein family databases for comparison of genes among cyanobacterial strains to identify novel genes involved in PHA synthesis. The Biology and Chemistry Loops are supplemented with in-house experimental data on PHA biosynthesis, material property testing, and degradation studies. Our ML approach and workflow consists of domain-knowledge-based feature selection, feature engineering, machine learning model training, and validation and optimization routines for efficient polymer property predictions and design. Our work will provide a foundational knowledge base to advance the development of novel biopolymers for the manufacture of bioplastics for a wide range of applications and optimal end-of-life degradation.
Effect of Tau protein phosphorylation on the process of its adsorption on the neuronal membrane

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The Tau protein, which stabilizes the cytoskeleton of neural cells, represents a major challenge for modern medicine. Tau is a key initiator of neurodegeneration under pathological conditions. Cryo-electron microscopy methods have shed new light on the conformational complexity of Tau deposits, yielding deposited crystallographic structures of protofilaments. Disruption of the protein's natural states of chemical modifications such as phosphorylation leads to uncontrolled desorption of Tau from the cytoskeleton and starts the process of misfolding. Several experimental methods have investigated the post-translational modifications that can lead to the most toxic non-fibrillar sites. Currently, non-fibrillar objects capable of escaping from the cell interior and diffusing into the intercellular space are of great interest. However, their mechanism of interaction with the membrane surface is still unknown. The structural disorder of Tau, including incompletely resolved crystallographic structures, makes it difficult to gain insight into the chain's behavior at atomic resolution. MD simulations conducted on Tau domains (R1-R4) have demonstrated the affinity of the Tau monomer for negatively charged membranes. The simulations indicate that potentially toxic non-fibrillar (3P) systems adsorb to complex lipogram-based membrane models and can be used for further studies as dimers, trimmers, and tetramers. Highly phosphorylated Tau (HP) has been shown to lose its ability to bind to the surface of a model neuronal membrane and can serve as a control in computational methods. Experimentally and computationally verified available nerve cell lipograms were used in the simulations.
Organic-inorganic semi-interpenetrating networks with orthogonal light- and magnetic-responsiveness for smart photonic gels - Wang, Minghao (Oral Only)

Highly transparent and self-healable solar thermal anti-/de-icing surfaces: When ultrathin MXene multilayers marry solid slippery self-cleaning coating - Niu, Wenwen (Oral Only)

Tough and conductive nacre-inspired MXene/epoxy layered bulk nanocomposites - Wang, Huagao (Oral Preferred)

Curved bismacrocycles: Synthesis, chirality and unexpected photophysical properties - Zhang, Xinyu (Oral Only)

Towards stable high-spin carbon-centered polyradicals: Achieving ferromagnetic coupling in polycyclic heteroaromatic scaffolds - Zhang, Di (Oral Only)

2,6-Azulene-based conjugated polymers: Dipole orientation control and property studies - Xiang, Junjun (Oral Only)

Shape memory polymer-based abnormal temperature detectors - Jia, Jichen (Oral Only)

Subcutaneous power supply by NIR-II light - Lyu, Shanzhi (Oral Only)

Gradually tuning the flexibility of two-dimensional covalent organic frameworks via stepwise structural transformation and their flexibility-dependent properties - Zhou, Zhibei (Oral Only)

Fabrication and applications of hypercrosslinked metal-organic polyhedra membranes - Liu, Jinjin (Oral Only)

Molecular-micron multiscale toughening and flame retarding for polyurethane foams - Zeng, Furong (Oral Only)

Gold catalysts containing interstitial carbon atoms boost hydrogenation activity - Sun, Yafei (Oral Only)

Pit pairs in ginkgo seed shell provide unique mechanical properties - Mao, JiaJun (Oral Preferred)

Teststalation strategy with standardized procedures for programming multiple materials - Tan, Yizheng (Oral Only)

Induction and switching of the single-handed helicity of polyacetylenes with topologically chiral [2]catenanes - Wang, Yu (Oral Only)

Locally rotated chiral molecular tiara with reversible Cpl emissions - Wang, Ranran (Oral Only)

Quick and efficient strategy to impart cellulose-based paper with flame-retardant, antibacterial and antifungal properties - He, Shuangmei (Oral Only)
Virtual Graduate Student Symposium in the Asia-Pacific Region on Polymer Chemistry

Selenium-containing block copolymer for siRNA delivery and synergistic cancer gene-immunotherapy - Xianyu, Banruo (Oral Only)

Host-guest supramolecular polymers based on hypoxia-responsive azocalix[4]arenes and their biomedical applications - Yao, Shun-Yu (Oral Only)

Heteromultivalent recognition by amphiphilic macrocyclic co-assembly - Pan, Yu-Chen (Oral Only)

Arene-persubstituted Cyclotrixylohydroquinoylene and its application in co-crystallization and structure determination - Jiao, Jianmin (Oral Only)

Light-driven ordered transformation of supramolecular host-guest assemblies for largely increasing phosphorescent properties - Liu, Mouwei (Oral Only)

Multifunctional fire-resistant materials with high transparency - Zhang, Lin (Oral Only)

Artificial light-harvesting systems based on cyanostilbene derivatives - Kai, Diao (Oral Only)

Upcycling of thermoplastics into malleable thermosets - Wang, Binbo (Oral Only)

Polymeric topological transformations based on BIS-vinylogous thioester conjugate acceptors - Wh, B (Oral Only)

9,9-Dimethyl dihydroacridine-based organic photocatalyst for atom transfer radical polymerization from modifying “unstable” electron donor - Liu, Yiming (Oral Only)

Polymeric toroids derived from the fusion induced particle assembly of anisotropic bowl-shaped nanoparticles - Gao, Yaning (Oral Preferred)
Organic-inorganic semi-interpenetrating networks with orthogonal light- and magnetic-responsiveness for smart photonic gels

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Living matter has the ability to perceive multiple stimuli and respond accordingly. However, the integration of multiple stimuli-responsiveness in artificial materials usually causes mutual interference, which makes artificial materials work improperly. Herein, we design composite gels with organic-inorganic semi-interpenetrating network structures, which are orthogonally responsive to light and magnetic fields. The composite gels are prepared by the co-assembly of a photoswitchable organogelator (Azo-Ch) and superparamagnetic inorganic nanoparticles (Fe3O4@SiO2). Azo-Ch assembles into an organogel network, which shows photoinduced reversible sol-gel transitions. In gel or sol state, Fe3O4@SiO2 nanoparticles reversibly form photonic nanochains via magnetic control. Light and magnetic fields can orthogonally control the composite gel because Azo-Ch and Fe3O4@SiO2 form a unique semi-interpenetrating network, which allows them to work independently. The orthogonal photo- and magnetic-responsiveness enables the fabrication of smart windows, anti-counterfeiting labels, and reconfigurable materials using the composite gel. Our work presents a method to design orthogonally stimuli-responsive materials.

Schematic illustration of the orthogonally photo- and magnetic-responsive composite gel. a Composite gel prepared by the co-assembly of Azo-Ch and superparamagnetic Fe3O4@SiO2 nanoparticles in a solvent. The solvent cyclopentanone in the composite gel is omitted for clarity. b Fe3O4@SiO2 nanoparticles in the sol of cis Azo-Ch. c Semi-interpenetrating network of Azo-Ch fibers and Fe3O4@SiO2 nanochains. The nanochains exhibit photonic crystal structures, which show structural colors. H is the vector of the magnetic field. d Fe3O4@SiO2 nanochains in the sol of cis Azo-Ch. H is the vector of the magnetic field Copyright © 2023, The Author(s).
Highly transparent and self-healable solar thermal anti-/de-icing surfaces: When ultrathin MXene multilayers marry solid slippery self-cleaning coating

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Solar anti-/de-icing can solve icing problems by converting sunlight into heat. One of the biggest problems, which has long been plaguing the design of solar anti-/de-icing surfaces, is that photothermal materials are always lightproof and appear black, because of the mutual exclusiveness between generating heat and retaining transparency. Herein, we report a highly transparent and scalable solar anti-/de-icing surface, which enables the coated glass to exhibit high transparency (>77% transmittance at 550 nm) and meanwhile, causes a >30 °C surface temperature increase relative to ambient under 1.0 sun illumination. Such a transparent anti-/de-icing surface can be fabricated onto a large class of substrates (e.g., glass, ceramics, metals, plastics), by applying a solid omniphobic slippery coating onto layer-by-layer assembled ultrathin MXene multilayers. Hence, the surface possesses self-cleaning ability to shed waterborne and oil-based liquids thanks to residue-free slipping motion. Passive anti-icing and active de-icing capabilities are, respectively, obtained on the solar thermal surface, which effectively prevents water from freezing and simultaneously melts pre-formed ice and thick frost. The self-cleaning effect enables residue-free removal of unfrozen water and interfacially melted ice/frost to boost the anti-/de-icing efficiency. Importantly, the surface is capable of self-healing under illumination to repair physical damage and chemical degradation. It is believed that the substrate-independent and self-healable MXene-SOPS coating, which has unprecedentedly achieved the feat of unifying high transparency and excellent solar thermal properties, will find a wide range of practical outdoor applications for anti-/de-icing, self-cleaning, and anti-smudge purposes, in the fields of civil construction, automobile, power networks, photovoltaics, wind power, and aeronautics.
A long-standing quest in materials science has been the development of high fracture toughness epoxy resin composites used in numerous applications. Inspired by the layered structure and high fracture toughness of the nacre, here, we report the development of tough and conductive MXene/epoxy layered bulk nanocomposites employing the freeze-casting technique. We enhanced the orientation of freeze-casting MXene lamellar scaffolds by annealing treatment. The interfacial interactions between MXene lamellar scaffold and epoxy matrix through surface chemical modification resulted in a synergistic effect for improving the mechanical properties. Tailoring the interlayer spacing of MXene nanosheets to a critical distance resulted in the nanocomposite fracture toughness about eight times higher than that of pure epoxy, surpassing other epoxy nanocomposites reported to date as well. Our nacre-inspired MXene/epoxy layered bulk nanocomposites also show high electrical conductivity that provides self-monitoring capability to the structure integrity and exhibits an excellent electromagnetic interference shielding efficiency with 28 dB in the range of 8.2 - 12.4 GHz. Our proposed strategy of refining the orientation by annealing and interfacial modifications to improve epoxy fracture toughness could provide a new avenue for fabricating high-performance nanocomposites.

Figure 1. Natural nacre and the preparation of conductive nacre.
Curved bismacrocycles: Synthesis, chirality and unexpected photophysical properties

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Cycloparaphenylene nanorings are representative macrocycles composed of para-connected benzene rings, which can be regarded as the smallest segment of carbon nanotubes. In recent years, novel topological structures based on carbon nanorings such as bismacrocycles have been successfully synthesized, which have attracted extensive research due to their novel photophysical properties and supramolecular behaviours. In 2021, we report the precise synthesis of a highly strained all-phenylene bismacrocycle, termed conjoined (1,4)[10]cycloparaphenylene (SCPP[10]), and this structure was confirmed by scanning tunneling microscope imaging. In addition, we studied the supramolecular interaction behavior between SCPP[10] and [6,6]-phenyl-C61-butyric acid methyl ester, demonstrating the formation of a peanut-shaped 1:2 host-guest complex. Recently, we successfully synthesized a novel chiral bismacrocycle (SCPP[8]) with dual-emissive property. The luminescent behavior of SCPP[8] shows unique characteristics of both aggregation-induced emission (AIE) and aggregation-caused quenching (ACQ) effects, inducing tunable emission from cyan to red including near white-light emission. In addition, SCPP[8] displays enhanced circularly polarized luminescence properties due to AIE effect. Furthermore, we have also achieved the synthesis of a series of bismacrocycles with different sizes. These conjugated bismacrocycles exhibit interesting size-depended properties and novel excitation-dependent emissions.
Towards stable high-spin carbon-centered polyradicals: Achieving ferromagnetic coupling in polycyclic heteroaromatic scaffolds

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Open-shell polycyclic aromatic hydrocarbons (PAHs) are a promising class of functional materials due to their unique photo-electro-magnetic properties and structural diversity. Of particular interest are polyradicals exhibiting high-spin states and strong ferromagnetic (FM) couplings, which hold the potentials for applications including organic magnets and quantum information technologies. But due to the high chemical reactivity, achieving a high spin state in carbon-based radicals is more challenging than in heteroatom spin centers. So far, most of the radicals reported with intramolecular ferromagnetic coupling are based on the $m$-phenylene moiety.

This work presents a series of stable high-spin polyradicals through incorporating diarylmethyl radicals into aza-PAH scaffolds. The aromatic cores of the resulting molecules can be considered a novel type of FM coupling unit, characterized by extended conjugated areas and resonance structures. Both experimental and theoretical investigations demonstrate that the designed diradical (DR) and triradical (TR) possess high-spin ground states. Based on the electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID) measurements, the energy gaps between the low-spin state and high-spin state ($\Delta E_{\text{LS-HS}}$) are determined. Notably, both DR and TR exhibit air-stability, which can be attributed to the successful molecular design strategy that involves the incorporation of nitrogen atoms and sterically hindered substituents at the spin-sharing sites. The optimal stability of DR and TR allow their thorough structural and magnetic property characterizations.

Figure 1. Design of ferromagnetic coupling moieties.
**2,6-Azulene-based conjugated polymers: Dipole orientation control and property studies**

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Conventional building blocks for organic conjugated polymers contain mostly alternant aromatic rings, such benzene and thiophene. Nevertheless, non-alternant frameworks can be present in structures, often leading to unusual electron configurations, molecular orbital characteristics, and physicochemical properties. One seminal example is azulene. Azulene, an isomer of naphthalene, has a fused structure of five- and seven-membered rings, the non-alternant structure endows it with a large inherent dipole moment of 1.08 D, non-mirror-related frontier molecular orbitals, anti-Kasha's fluorescence, and proton responsiveness. Therefore, azulene-containing molecules and polymers generally have unique physicochemical properties and great potential in the fields of (opto)electronics, energy, sensor and imaging, disease diagnosis and therapy, etc. However, controlling the dipole orientations of 2,6-azulene units in the conjugated polymer backbones is still a great challenge so far due to the difficulties in monomer design and synthesis. Herein, we present the successful control of dipole orientations of 2,6-azulene units in two types of conjugated polymers (PAzEs and PAzVs) via standard palladium-catalyzed coupling reactions. The proportions of 2-6, 6-6, and 2-2 connected segments in the regiorandom copolymers were determined by $^1$H NMR spectra. These polymers exhibited ambipolar semiconductor characteristics in organic field effect transistors and acid-responsiveness, which distinguished them from the corresponding benzenoid polymers. The structure-property relationship studies indicate that the incorporation of 2-2 and 6-6 connected segments into the conjugated backbones could enhance microstructural order and thereby led to higher charge carrier mobilities.
In many cases, high temperature signifies danger. High ambient temperature may result in equipment failure, fire disaster may cause casualties and environmental resources destruction. The occurrence of the fire accident that caused by abnormal temperature is usually accompanied by a significant temperature change or heat release. Shape memory polymers (SMPs) are one of suitable choices for temperature detection because of their unique programmability, sensitivity to temperature, and rapid shape change ability. Based on shape memory polymers, we have constructed two kinds of intelligent conductors for abnormal temperature detection in different scenarios. Firstly, we fabricated a cross-linked polycaprolactone network, and based on its shape memory property and subsequent electroless deposition process, we prepared a smart conductor with ability of switching between non-conductive and conductive at low and high temperatures respectively. Outdoor experiments presented that this electrically “OFF-to-ON” conductor could effectively respond to a fire and play a crucial role in early fire alarming under simulated fire scene. The finite element analysis simulation results further prove the advantages of this material over the traditional thermocouple in detecting temperature changes. Furthermore, we developed a novel shape memorized current collectors which could successfully brake battery thermal runaway at battery internal overheating status. Unlike traditional current collectors made of commercial copper foils, the shape memorized current collector was made of a micropatterned shape memory micron-sized film with copper deposition. The shape memorized current collectors displayed ideally conductive at normal temperatures and turned to be insulative at overheating temperature. Following this principle, the battery consisting of the shape memorized current collector could run normally at temperatures lower than 90 ˚C while it quickly achieved self-shutdown before the occurrence of battery combustion and explosion.
Subcutaneous power supply by NIR-II light

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Implantable medical devices are wished to be recharged via contactless power transfer technologies. Second near-infrared (NIR-II, 1000~1350 nm) light, which is estimated to be a superior electromagnetic window for wireless power transmission relative to widely investigated visible light and radiofrequency waves (300kHz ~ 300GHz), has a transmittance through skin tissue that is 10 times higher than that of visible light and similar to that of radiofrequency waves. Moreover, its maximum permissible exposure power density of tissues is 1.0 W cm⁻², which is much higher than that of visible light (~0.2 W cm⁻²) or radiofrequency waves (~0.01 W cm⁻²). Despite the deep tissue penetration of NIR-II light, it has rarely been considered for clinical CPTs due to the limited efficient energy conversion scheme caused by poor exciton separation.

Herein, we invented a NIR-II light CPT technology that combined photothermal and thermoelectric conversion to achieve an appreciable output power. The device was further equipped with a selective absorption coating and rational thermal management to ensure higher energy conversion efficiency of NIR-II light and reduce hyperthermia effects on surrounding tissues. Such a photo-thermal-electric converter generated an output power as high as 195 mW when covered by excised tissues, offering advantages of non-invasion, high output power, negligible biological damage, and deep tissue penetration. In an in vivo demonstration, the output power of a packaged converter placed in the abdominal cavity of a rabbit reached 20 mW under NIR-II light irradiation through the rabbit skin with a thickness of 8.5 mm. This value was sufficient to recharge an implanted high-power-consumption wireless camera and transmit video signals out of the body in real-time.
Gradually tuning the flexibility of two-dimensional covalent organic frameworks via stepwise structural transformation and their flexibility-dependent properties

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Flexible covalent organic frameworks (COFs) are intriguing for their dynamic properties distinctive from rigid counterparts but still suffer from limited accessibility. Especially, controlling flexibility of COFs is challenging and the impact of different flexibility on properties of COFs has rarely been unveiled. This article reports stepwise adjustment on flexibility of two-dimensional COFs, which is realized by the designed synthesis of rigid COF (R-COF), semi-flexible COF (SF-COF), and flexible COF (F-COF) through polymerization, linker exchange, and linkage conversion with a newly developed method for reduction of hydrazone, respectively. Significant difference in breathing behavior and self-adaptive capability of the three COFs are uncovered through vapor response and iodine capture experiments. Gas sorption experiments indicate that the porosity of F-COF could switch from "close" state in nitrogen to "open" state in carbon dioxide, which are not observed for R-COF and SF-COF. This study not only develops a strategy to adjust the flexibility of COFs by tuning their linkers and linkages, but also provides a deep insight into the impact of different flexibility on properties of COFs, which lays a foundation for the development of this new class of dynamic porous materials.

Diagram for the stepwise transformations from the rigid COF to semi-flexible and flexible COFs through linker exchange and linkage conversion, respectively.
Fabrication and applications of hypercrosslinked metal-organic polyhedra membranes

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Metal-organic polyhedra (MOPs) have solution processability and modifiable active sites. They can connect with polymer through covalent or coordination bonds to enhance the binding force between fillers and polymer and overcome the shortcomings of traditional polymer membranes, such as the contradictory relationship between permeability and selectivity (trade-off effect), single functionality, etc. We construct MOP-cored crosslinking networks by hierarchical post-assembling, named hypercrosslinked MOPs, and successfully prepared a series of new hybrid membranes. By modifying the amino groups on Zr-MOPs and using MOPs as co-monomers to participate in the polymerization, a hypercrosslinked membrane with the polyimine through covalent bonds was formed. The membranes maintain the characteristics of the polymer matrix (flexibility, processability, etc.) and obtain many attractive properties, such as significantly improving the mechanical properties, giving selective separation performance of gas/liquid phase, self-healing, antibacterial activity, high lithium ion conductivity, etc. In addition, the Cu-MOPs or Rh-MOPs with unsaturated metal coordination sites can also act as crosslinking points to crosslinking with a cellulose-based polymer that modifies iminazole groups by coordination bonds. Owing to the dynamic properties of coordination bonds, the hybrid membranes not only show excellent self-healing and shape memory properties but also have solution processability and can be used as 3D printing ink. The introduction of MOPs also endows the membrane with excellent hydrophobicity, which can be applied to hydrophobic and anti-corrosion coatings. The hypercrosslinked MOPs membrane can solve the problems of traditional mixed matrix membranes and proposes a new method for preparing organic-inorganic hybrid membranes which has universality and can be customized. It provides a new direction of development for MOPs and membrane materials.
Molecular-micron multiscale toughening and flame retarding for polyurethane foams

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Globally, the frequent fires caused by polyurethane foams (PUF) have raised an urgent demand for fire-safe PUF materials. Existing flame retardants, however, always damages the cross-linking networks of PUF, leading to severe deterioration of the dynamic fatigue resistance and toughness. Facing this dilemma, we demonstrate a facile strategy for fabricating phosphorus-based multiscale energy dissipation networks to engineer PUF with superior toughness and fire safety. The designed mono-hydroxyl flame retardant facilitates the in-situ construction of multiscale networks during foaming by employing their polarity/reactivity nature, which consists of molecular scale pendant groups with toughening mechanisms and microscale particles with compatible interphase/reinforcing mechanisms. Notably, the synergistic multiphase networks enable PUF to have an outstanding capability to redistribute/dissipate external stress. Consequently, the resulting flame retardant PUF exhibits greatly improved strength/toughness (+92%) and high deformation recovery ratio (97.3%), avoiding the fragility caused by conventional crosslinked networks or rigid fillers. More phosphorus species with high-energy radical scavenging abilities in gas, given by hydroxymethyl diphenylphosphine oxide (DPM), endow PUF with higher flame-retardant efficiency, which is quite challenging for the other two with P-O bonds. The resulting PUF achieves rapid self-extinguishing with low addition of 1.8 wt% DPM, far superior to previous counterparts. This work provides a new enlightening strategy for dramatic improvement in toughness and fire safety of foams, based on synergistic energy dissipation networks spanning molecular and micron scales, showing obvious superiority for application prospects.
Gold catalysts containing interstitial carbon atoms boost hydrogenation activity

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Gold was once considered one of the least reactive metals. How can one improve the activity and selectivity of Au catalysts? Can the electronic structure of Au be expressed in one parameter? The study adopts a carbon inverse doping strategy to obtain C-Au interstitial solid solution catalysts supported on ordered mesoporous carbon. The electronic properties of Au nanocatalysts are highly related to the neighboring atoms carrying electrons in the lattice, which contributes to the electron transfer or redistribution at Au sites. The d electron gains at Au sites due to interstitial C in the solid is linearly related to the activation entropy associated with the adsorption configuration and energy of the substrate and TOF value. The electron gains of 0.192 of Au for the C-Au-1.6/OMC catalyst is much higher than that of the well-known Au/TiO₂ catalyst, showing an almost three times higher turn-over frequency (TOF=670 h⁻¹) value than the latter in the chemoselective hydrogenation of the nitro group in 3-nitrostyrene. This strategy paves the way for optimizing noble metal catalysts to give an enhanced hydrogenation catalytic performance.
Pit pairs in ginkgo seed shell provide unique mechanical properties

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Most of the widely studied natural structural materials, such as wood, bones, and abalone shells, have highly anisotropic mechanical properties. Although highly anisotropic structures can effectively achieve external toughening, this mechanism depends on the direction of crack propagation. Here, we have analyzed the unique structure of ginkgo seed shells, which have excellent resistance to crack propagation in different directions. Ginkgo seed shells are tightly bound together by a large number of polygonal sclereids with thick cell walls. The inner secondary wall of the sclereids contains elongated pipes known as pits. These pits extend from the central cavity of the cell to the intercellular layer, forming a "pit pair" structure with the pits of adjacent sclereids. This unique structure makes the fracture toughness $K_{IC}$ of ginkgo seed shells in all directions about 1.26 MPa m$^{1/2}$, which is equivalent to the $K_{IC}$ of wood and bone. This high toughness is due to the unique mechanism of “pits guide crack propagation”. When a load is applied, the cell wall adjacent to the intercellular layer in sclereids will delaminate or tear to resist crack growth. This work providing a theoretical foundation for the preparation of complex isotropic bionic nanocomposites in the future.
Tesstalation strategy with standardized procedures for programming multiple materials

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The development of new methods to program two-dimensional (2D) planes into three-dimensional (3D) structures is of great importance. Planer 2D structures can be produced on a large scale and stored compactly until deployment, while the transformed 3D structure can serve multiple functions. Several emerging methods have been proposed, including origami, kirigami, buckling, printing, and pre-strain. These methods either enable the production of previously impossible models or simplify the preparation of existing shapes.

Innovative ideas to manipulate the stress in materials inspire novel methods to program the shape of materials. These methods require either stress manipulation or specific devices, such as printers or projectors, to integrate the pattern for each production unit, which limits their production speed and scale. However, if only standardized components, and non-pattern input are required in the programming process, while still achieving complex structures in multiple materials, the programming method would be easier to advocate and more suitable for large-scale production.

In this context, we developed a simple "tessellation" strategy by embedding standardized hexagon components onto planar materials. And complex structures or functions can be achieved after applying uniform compression and irradiation in seconds. The standardized hexagon component and planar material can be easily mass-produced, and the programming procedure requires only flat polymethyl methacrylate (PMMA) plates and non-patterned light sources. Thus, the programming process can be easily scaled up. By utilizing the metathesis of the Se-Se dynamic covalent bond, a planar material can be programmed into 90° bending in 30 seconds. Complex structures such as paper cranes can be achieved by combining each bending with different directions in a single programming process. The method is also highly versatile and can be integrated with liquid crystal elastomer (LCE) or shape memory polymer (SMP) to realize actuation and transformation when needed. Therefore, our work presents a standardized procedure to realize complex structures in multiple materials, showing great potential in mass production.
Induction and switching of the single-handed helicity of polyacetylenes with topologically chiral [2]catenanes

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As a typical dynamic helical polymer, phenylacetylene (PA) can adopt preferred-handed helical conformations in the presence of optically active groups in side-chain pendants, which has been widely applied in chiral recognition, sensing, catalysis and so on. Up to now, diverse chiral sources with different types of chirality such as point chirality, axial chirality, planar chirality, and helical chirality have been employed for the induction of single-handed helicity of polyacetylenes. However, the use of topologically chiral compounds as chiral sources has not yet been achieved.

Based on our recent research interest in topologically chiral [2]catenanes that could adopt multiple chirality expression upon external stimuli, poly[2]catenanes with polyacetylenes (PAs) as the main chain and topologically chiral [2]catenanes as the side-chain pendants were designed and synthesized for the first time. The CD investigations revealed that PAs adopt preferred-handed helical conformations depending on the topologically chiral [2]catenanes as pendants. Furthermore, the precise regulations of the transfer from the topological chirality to the helical chirality were achieved by switching either the co-conformation of the [2]catenane pendants or the main chain pitch lengths. It is worth noting that the preferred-handed helix and the stimuli-response properties of the resultant poly[2]catenanes were almost not disturbed by the additional point chirality unit within the [2]catenane skeleton. These results demonstrate the successful construction of not only the first topologically chiral poly[2]catenane, but also a multiple stimuli-responsive CD switch, thus providing a promising platform for the construction of novel chiral materials.
Locally rotated chiral molecular tiara with reversible CPL emissions

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Chiroptical materials capable of emitting circularly polarized luminescence (CPL) have been gaining intensive interest for their wide applications in fields of materials. In this work, a locally rotated molecular tiara \( \text{Py}_5\text{P}_5 \), in which five bulky pyrene units locate at one rim of \( \text{Py}_5\text{P}_5 \), and five small methoxy groups at the other, is designed. The planar chiral skeleton of \( \text{Py}_5\text{P}_5 \) can make five pyrene units being ordered in asymmetrical manner to arise the CPL emission from pyrene excimer, and the small methoxy groups rim in the other can ensure the interconversion between \( pR \)- and \( pS \)-conformers of \( \text{Py}_5\text{P}_5 \) freely via local rotation. Thus, both left-handed and right-handed CPL may emit from pyrene units of \( \text{Py}_5\text{P}_5 \) stacked in the asymmetrical order with a high \(|\gamma_{\text{lum}}|\) up to \( 1.28 \times 10^{-3} \) under the induction of chiral amino acid derivatives. It is the first observation that both right-handed and left-handed CPL from pyrene excimer can be arisen from a single molecule by adding the simple chiral guests.
Quick and efficient strategy to impart cellulose-based paper with flame-retardant, antibacterial and antifungal properties

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Development of a flame retardant, antibacterial, and antifungal paper is important in many fields, such as industry and cultural communication. However, how to achieve these features simultaneously using a quick and effective method is still a challenge. Herein, novel flame retardant, antibacterial, and antifungal paper materials are prepared based on handmade papers (HMPs), poly-hexamethylene biguanide (PHMB) and sodium polyphosphate (PSP). Driven by the hydrogen bonding and electrostatic interactions, PHMB and PSP can be assembled into micro-nano particles and deposited on the surface of HMPs although a facile dip-treating technology, which can endow the paper with high flame retardancy, antibacterial and antifungal performances. When directly exposed to flame, the PHMB/PSP layers can promote the formation of a char layer and give the paper a self-extinguishing property with LOI value of 34.5%. Attributed to the presence of the biguanide groups of PHMB, the treated paper materials exhibit good antibacterial activity against S. aureus (>99.99%) and appreciable fungal resistance against T. viride (Grade 1). More importantly, the treated paper materials show no obvious change in appearance and color compared with the pristine one. Featuring mild conditions and easy and fast processability, this strategy is promising for applications in cellulose-based paper materials with antifungal and fire-safety requirements, presenting certain advantages in the protection of various paper-based materials.
The blockade of immune checkpoints has emerged as a promising strategy for cancer treatment. However, the antitumoral immune response is impeded by overexpression of checkpoint receptors on tumor cells, which greatly limits their clinical application. In this study, we designed a diselenide bond containing block copolymer that self-assembles into nanoparticles capable of delivering siRNA targeting programmed death-ligand 1 (PD-L1) to tumor sites. Exposed to 660 nm laser irradiation, the encapsulated photosensitizer generates reactive oxygen species (ROS), which oxidize the diselenide bond to seleninic acid, facilitating PD-L1 siRNA release and silencing the checkpoint receptor PD-L1 effectively. Simultaneously, the oxidation product seleninic acid blocks the expression of another checkpoint receptor, human leukocyte antigen E (HLA-E). Therefore, the nanocomplexes can synergistically activate natural killer (NK) cell mediated antitumoral activity. Our in vitro and in vivo results indicate that the selenium-containing nanocomplexes can effectively enhance the immune-modulating activity of NK cells by blocking dual immune checkpoints. This study provides a promising strategy for the development of combined cancer gene-immunotherapy.
Host-guest supramolecular polymers based on hypoxia-responsive azocalix[4]arenes and their biomedical applications

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Stimuli-responsive supramolecular polymers (SPs) based on host-guest interactions have attracted intensive research interest in recent years. Currently, exploitation of specific guest which can response to external stimuli is the main approach to construct stimuli-responsive host-guest SPs. Most functional guests such as drugs and dyes, however, fail to manifest stimuli-responses, which hinders the development of SPs for broader application. Herein, we developed two water-soluble azocalix[4]arenes (SAC4A and Naph-SAC4A) for the construction of novel stimuli-responsive supramolecular polymers, since azocalix[4]arenes possess not only excellent hosting abilities towards a wide range of guests (in either 1:1 or 1:2 complexing stoichiometry), but also unique hypoxia-responsive property. For SAC4A which can bind guests in 1:1 stoichiometry, we prepared a dimeric azocalix[4]arene (D-SAC4A) and a glutathione (GSH)-responsive ditropic camptothecin (D-CPT) as the building block for the preparation of stimuli-responsive SPs. A dual-responsive SP with superior antitumor therapeutic efficacy was obtained by 1:1 host-guest polymerization in water. Subsequently, we developed a naphthalenesulfonic acid modified azocalix[4]arene (Naph-SAC4A), which manifested excellent 1:2 hosting abilities to a wide scope of dyes in water with high binding constants ranging from $10^{14}$ to $10^{16}$ M$^{-2}$. Furthermore, we demonstrated that Naph-SAC4A can serve as a hypoxia-responsive noncovalent linkers in the construction of both linear SPs and crosslinked supramolecular hydrogels.
Heteromultivalent recognition by amphiphilic macrocyclic co-assembly

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The highly efficient recognition of biomacromolecules, which play important functions in the life system, is of great significance for the effective regulation and intervention of life processes. However, it is quite challenging to selective and strong binding of biomacromolecules because of their large size, flexible conformation, and presence of multiple and diverse binding sites. Traditional recognition strategies, including monovalent, heterotopic, and multivalent, don’t fit well with biomacromolecules. Accordingly, the heteromultivalent recognition is highly on demand. However, building an artificial heteromultivalent receptor is quite difficult through covalently molecular design because of the tedious synthesis as well as the requirement of precise control over the spatial arrangement of binding sites. We have proposed a supramolecular approach to heteromultivalent recognition by co-assembling two macrocyclic amphiphiles into one ensemble. A series of model peptides were employed to verify the positive cooperativity of two types of macrocyclic amphiphiles. Moreover, the dynamic feature of self-assembly endows the co-assembly with self-adaptability to better match the binding sites of macromolecular guests. The co-assembly has been engaged in several biomedical applications. 1) The co-assembly was applied to recognize β-amyloid (Aβ) peptide and inhibit its fibrillation, therefore, can potentially act as a novel anti-Aβ therapeutic agent for Alzheimer’s disease. 2) The co-assembly was applied to recognize melittin and sequester its toxicity, therefore, can be employed as a supramolecular antidote for melittin poisoning. The co-assembling components can be easily replaced, and the co-assembling ratio can be subtly tuned if needed. We believe the co-assembled heteromultivalent recognition strategy is amenable to various biomedical applications.
A crown-shaped cyclofervatrylene (CTV) analogue with persubstituted arene units, namely cyclotrixylohydroquinoylene (CTX), was synthesized from tetrasubstituted o-xylohydroquinone. Importantly, a series of CTX derivatives were prepared by introducing second bridged methylene and phenylphosphine oxide, at the middle rim, referred to as CTX[CH₂] and CTX[P(O)Ph], respectively, with the completely locked crown conformation, leading to the formation of unique C₃-symmetric Chinese censer-shaped pocket structures. It’s surprising to found that CTX[P(O)Ph] exhibited perfect co-crystallization capacity with various small organic molecules. Up to now, CTX[P(O)Ph] was co-crystallized with 26 oil samples (guest molecules) successfully and their structures could be solved finely. With the aid of CTX[P(O)Ph], the guest molecules were well-ordered with full occupancy in co-crystal structure. In most cases, at least one guest structure without any disorder could be observed and squeeze program didn’t need to be used. Absolute configuration was also assigned reliably for chiral molecules in this method.
Light-driven ordered transformation of supramolecular host-guest assemblies for largely increasing phosphorescent properties

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The construction and transformation of supramolecular assemblies's topological morphorlogies is an important means to achieve well-defined nanostructures and precise control of material functions at the molecular level. However, the traditional light-induced structural transformation of supramolecular assemblies suffers from the problems of low transformation efficiency, insufficient molecular structure characterization and research on the kinetic process during the transformation process. Here, we covalently linked hexathiobenzen molecules(HB-OH), which undergo a strong conformational transition upon photoexcitation, to β-cyclodextrin to obtain a light-responsive assembly motif (HB-β-CD), whose topological morphology can change from a one-dimensional linear structure to a worm-like structure when illuminated its aqueous solution, and then the transformation of the assembled structure during the illumination process was finely characterized by cryo-electron microscopy, circular dichroism spectrometer, etc. Compared with the HB-β-CD aqueous solution without irradiation, the film prepared by mixing the HB-β-CD aqueous solution with irradiation and PVA has longer phosphorescence lifetime. In addition, the film also has good water vapor resistance, which successfully solves the problem of twisted dye molecules doping in PVA hard to obtain long lifetime and the susceptibility of PVA-based phosphorescent films to water vapor.
Multifunctional fire-resistant materials with high transparency

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The resistance of materials to environmental damage, such as fire, stress, and microorganisms, greatly limits the safety and life of materials. The use of multifunctional fire-resistant materials provides protection values, effectively improving the high-temperature stability and sustainability for prolonging the service life of the substrate. A major challenge in the fabrication of multifunctional materials is the contradiction between different functions, especially transparency. We have proposed a facile one-step strategy in which fire-resistant and antibacterial functional components are co-introduced into a transparent siloxane-based cross-linking network by sol-gel chemistry, forming an integrated structure, and realizing transparent, flexible, strengthening, fire-resistant, and antibacterial multifunctional protective materials. In our design, on the one hand, the physical-chemical double cross-linking enables poly(organosiloxane) excellent flexibility and strengthening (assisting the paper to promote the vertical tensile stress and strain at failure by 54.5% and 108.3%, respectively). On the other hand, the siloxane network containing phosphorus exhibits high efficiency against fire and microorganisms (antibacterial rate >99%). Once exposed to fire, this material can respond quickly and expand to form a stable heat insulation carbon layer, which can effectively protect various substrates (such as glass and wood) from a 1400 °C high-temperature attack. Notably, the resulting multifunctional material has light transmittance as high as 92% in the visible region, making it promising for buildings, electronic devices, windshields, and other fields.
Artificial light-harvesting systems based on cyanostilbene derivatives

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Luminescent materials in aqueous media through the light-harvesting strategy have attracted significant interest on account of their excellent tunability. In this lecture, we will present generalized methods toward the fabrication of tunable luminescent materials based on cyanostilbene derivatives through light-harvesting strategy in water. Firstly, a cyanostilbene-bridged ditopic ureidopyrimidinone donor (CSU) was designed and synthesized, which can self-assemble into dispersed nanoparticles in water. Fascinatingly, efficient white-light emission can be realized by co-assembling 0.1% DBT into the nanoparticles through a light-harvesting strategy; Secondly, an amphiphilic monomer (CSO), was synthesized which contains a hydrophobic cyanostilbene core flanked by two hydrophilic oligo(ethylene glycol) tails. The CSO molecule can self-assemble into nanoaggregates in water with blue fluorescence and LCST behavior. These nano-assemblies also exhibit thermo-responsive fluorescence and were further used to construct a responsive light-harvesting system. We hope that the present work is expected to mimic the energy funneling mechanism in nature and have potential applications in organic luminescent materials.
Upcycling of thermoplastics into malleable thermosets

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With the promotion of environmental awareness, the environmental pollution caused by scrap plastics has attracted global attention. Upcycling plastics might be a promising means, which transfers scrap plastics into materials with increased performance and functionality. In this way, not only the service life of plastics will be extended but their application fields will be expanded. In our work, several approaches (chain breaking-dynamic covalent cross-linking, cross-linked by hyperbranched polymer, cross-linked by covalent adaptable networks) were developed to cross-link commercial plastics to obtain malleable thermosets. Chain breaking-dynamic covalent cross-linking refers to the process of obtaining multifunctional telechelic polymers through the reactive extrusion of polyols with polyester or polyurethane, based on the transesterification or urethane transesterification, and then cross-linked by epoxy or Isocyanate. The formation of cross-linked networks effectively enhances their thermal/mechanical properties, creep resistance, solvent resistance, and so on. Subsequently, multi-hydroxy hyperbranched epoxy resins enriched with hydroxyl and cross-linking agents were used to cross-link polyurethane. By enriching hydroxyl groups and epoxy, one-step cross-linking is achieved. Finally, based on the dynamic exchange reaction between covalent adaptable networks and linear molecular chains, the transition from blending to cross-linking can be achieved. In addition, all prepared materials can be reprocessed by extrusion or hot pressing. Our work will provide highly efficient upcycling strategies for thermoplastics through dynamic covalent cross-linking.
Polymeric topological transformations based on BIS-vinylogous thioester conjugate acceptors

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Polymer topology determines the dynamic and mechanical properties of materials. For most polymers, the topology is a static characteristic. Rarely can it be manipulated by altering the bonding patterns within the main chain structure and changing the functionality of crosslinking groups. Our research group has proposed a strategy for chemically triggering dynamic topology changes in polymers in response to specific chemical stimuli, a process that can be monitored in real-time through changes in fluorescence intensity. From linear or hyperbranched non-fluorescent polymers, they transform into linear fluorescent polymers or degrade into fluorescent small molecules via amine-disulfide exchange. The controllable and visualizable transition of polymer morphology through fluorescence, along with its degradation, heralds the advent of a new generation of smart materials.
9,9-Dimethyl dihydroacridine-based organic photocatalyst for atom transfer radical polymerization from modifying “unstable” electron donor

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Organic photocatalytic atom transfer radical polymerization (ATRP) has recently become a research highlight. Organic photocatalysts based on phenothiazine, phenoxazine, and phenazine have been reported and exhibited remarkable performance. All of those structures contain two heteroatoms, which makes the oxidative state (i.e., the radical cation) of the photocatalysts stable enough to complete the catalytic cycle. However, despite the similar structure, 9,9-dimethyl dihydroacridine (DHA) was rarely used for constructing photocatalyst due to its unstable oxidative state. DHA is a weak electron donor that was widely applied in blue-emitting thermally activated delayed fluorescence (TADF) molecules. Its weaker electron-donating ability will contribute to a higher energy level of the excited state. Also, the higher oxidation potential of its radical cation will contribute to better controllability due to fast reversible dormancy. In this study, we found that substitution on the active sites of DHA could make it stable enough to be the donor part of a donor−acceptor (D−A)-type photocatalyst for ATRP. Moreover, chemical modification is necessary for both stabilizing the radical cation and improving the controllability in the polymerization process. Further modification was made to construct a rapid equilibrium between initiation and reversible dormancy, and polymerization with quantitative initiator efficiencies was achieved with a polydispersity of 1.14. It is notable that such modification can probably apply to different kinds of electron donors, and various organic chromophores could thus be applied to construct organic photocatalyst with superior performance.
Polymer self-assembly is a powerful tool to fabricate soft nanomaterials with diverse morphologies and functionalities, such as spheres, cylinders, vesicles, toroids, nanorods, tubes, nanobowls, helices, and so forth. As one of the most fascinating structure, polymeric toroids are fascinating soft nanostructures due to their unique geometry and properties. The study of toroidal-shaped nanostructures is very important for understanding many complex biological processes, which have shown potential applications in the fields of nano-reactors, drug delivery and cancer therapy etc. However, the facile preparation of polymeric toroids is still challenging. Herein, we propose a fusion induced particle assembly (FIPA) strategy to prepare polymeric toroids using anisotropic bowl-shaped nanoparticles (BNPs) as building block. The BNPs are prepared in ethanol by the self-assembly of an amphiphilic homopolymer, poly(N-(2,2'-bipyridyl)-4-acrylamide) (PBPyAA), synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. Upon incubation in ethanol above the glass transition temperature ($T_g$) of PBPyAA, the BNPs gradually aggregate to form trimers and tetramers due to the disturbance of the colloidal stability. With the increase of incubation time, the aggregated BNPs fuse with each other and then form toroids. Notably, we find that only anisotropic BNPs can aggregate and fuse to form toroids rather than spherical compound micelles due to high surface energy and curvature at the edge of the BNPs. Besides, mathematical calculations further confirm the formation of trimers and tetramers during the FIPA process and the driving force for the formation of toroids. Overall, we propose a fresh insight for the facile preparation of polymeric toroids by the FIPA of anisotropic BNPs.

figure 1 The self-assembly of PBPyAA to form BNPs and the FIPA of BNPs to form polymeric toroids.
Young Industrial Polymer Scientist Award in Honor of Hayley Brown (Invited)

Advances in free radical ethylene polymerization and copolymerization - Brown, Hayley (Oral Only)

Carbon dioxide sourced functional cyclic carbonates used to prepare macromolecular therapeutics to treat infectious disease and cancer - Hedrick, J (Oral Only)

Enhancing polyolefin recycling with cellulose nanocrystals - Robertson, Megan (Oral Only)

Building approaches at the intersection of biochemistry and computational methods; Developing insights into filtration technology - Lipscomb, Corinne (Oral Only)

Organic catalysts and flow processes for polymer science - Waymouth, Robert (Oral Only)

Catalytic routes to olefin block copolymers - Auyeung, Evelyn (Oral Only)

Reprocessable addition-type networks with dynamic covalent crosslinks: Simple radical-based methods for direct synthesis of recyclable networks and upcycling ethylene-based polymers into recyclable networks - Torkelson, John (Oral Only)

Nanoparticle diffusion coefficients in polymer nanocomposites: Effect of polymer molecular weight, nanoparticle size, and interparticle distance - Winey, Karen (Oral Only)
Advances in free radical ethylene polymerization and copolymerization

Hayley A. Brown, hbrown1@dow.com, Ivan Konstantinov, Zhe Zhou, CJ DuBois, Roxanne M. Jenkins, Cristina Serrat. The Dow Chemical Company, Lake Jackson, Texas, United States

The balance of two key questions defines the parameters of industrial polymer synthesis: what does a polymeric system need to be in order to do what it needs to do, and how do we make that particular system? Answering those questions takes a balance of materials science understanding and synthetic insight, derived experimentally and computationally. Free radical polymerization and copolymerization of ethylene with polar olefinic monomers represents one of the oldest large scale polymerization technologies practiced today, with a range of synthetic interactions that produce complex systems. This talk will review the foundational synthetic chemistry underlying these systems, including efforts to probe and understand them through advanced NMR techniques and computational screening. We will then review the novel synthetic methods derived from those insights to control key polymer molecular weight and compositional dispersity effects. Finally, we will touch on how this synthetic control can be used to enable complex ethylene-based polymer synthesis and use in the modern world.
Carbon dioxide sourced functional cyclic carbonates used to prepare macromolecular therapeutics to treat infectious disease and cancer

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High value specialty polycarbonates are employed in numerous applications, including resins for 3D additive printing, macromonomers for polyurethanes, surfactants, battery electrolytes, and degradable adhesives for medical applications. Driving the growth in use cases are the significant advancements made over the last two decades in improved methodologies for the synthesis of aliphatic carbonates as well as upcycling carbon dioxide (CO2) into high value-added materials. We have recently reported a method to transform 1,3- and 1,5-diols into functional cyclic carbonates without the use of hazardous reagents. Employment of TMEDA was shown to provide selective ring-closure to the cyclic carbonate in the presence of CO2 while minimizing oligomerization and formation of other byproducts. A series of commercial and synthetic 1,3- and 1,5-diols were employed to generate 6- and 8-membered cyclic carbonates with diverse pendant functional groups tuning polymer properties. The ability to tune these functional monomers and subsequent polymers has allowed numerous applications that include drug, gene and cell delivery as well as the use of the polymer as a stand-alone therapeutic including antimicrobials, anticancer agents and antiviral therapies packaged as either micelles, hydrogels or coacervates. Specifically, we address the multi-faceted problem of drug-resistance as well as other important concerns in disease treatment exploiting polymer science to develop novel macromolecular therapeutics for treating infectious disease and cancer.
Enhancing polyolefin recycling with cellulose nanocrystals

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Polyolefins represent the largest contribution to plastic production, use, and generated waste worldwide, yet their recycling rates are low. More efficient methods of recycling polyolefins have been underexplored, due to significant technological, scientific and economic challenges. We are exploring chemical functionalization and processing strategies for converting waste polyolefins to high value materials for advanced manufacturing and use. Cellulose nanocrystals offer unique opportunities as particle additives for enhancing waste plastic properties through reinforcing and compatibilization mechanisms. We have grafted polypropylene to cellulose nanocrystals (CNCs) through melt extrusion, and used the polypropylene-grafted CNCs as additives for blends of polypropylene and polyethylene. Addition of the polypropylene-grafted CNCs to the blends reduced the size of macroscopically phase-separated domains. Impact of the CNCs on the thermomechanical properties of the blends is under investigation.
Building approaches at the intersection of biochemistry and computational methods; Developing insights into filtration technology

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Polymers and chemistry are the foundation for separation technologies used in the biopharmaceutical landscape. Structure-function relationships between chemical moieties and biologics are complex. Computational methods, including simulation and data science methods, can be used to develop insights into these relationships. An example use case will be discussed.
Organic catalysts and flow processes for polymer science

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We have developed new classes of organic catalysts and polymerization processes for the efficient living polymerization of lactone and carbonate monomers. Integration of these catalysts into efficient flow reactors for the programmed synthesis of block copolymer libraries have provided new solutions to challenges in sustainable materials and drug and gene delivery agents.
Catalytic routes to olefin block copolymers

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Functionalized polyolefins are materials that exhibit performance advantages and broader application scope over conventional polyolefins. Methods to prepare functionalized polyolefins on a large scale include processes involving high temperatures/pressures as well as grafting strategies. Further diversification of the polymer design such as the morphology, blockiness, and incorporation of additional monomers requires the development of new processes including catalytic approaches. In this talk, several methods for the preparation of functionalized polyolefins, including those based on Dow’s innovative olefin block copolymer (OBC) technology, will be discussed. These approaches allow for the preparation of novel materials including polar-containing block copolymers that may further expand the range and applications of existing commercial polyolefins.
Reprocessable addition-type networks with dynamic covalent crosslinks: Simple radical-based methods for direct synthesis of recyclable networks and upcycling ethylene-based polymers into recyclable networks

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Polymers enable modern life because of their advantageous properties. Their importance is evident from the fact that at least 800 billion pounds of polymers are produced annually worldwide. While thermoplastics present some challenges for efficient recycling, it is possible to recycle such materials by melt-state reprocessing. In contrast, conventional thermosets with permanent covalent crosslinks cannot be returned to a "melt" state because the crosslinks prevent macroscopic flow. To overcome this limitation, we have designed reprocessable networks with covalent crosslinks that are dynamic at elevated temperature but robustly bonded at use conditions. Research into dynamic covalent polymer networks (DCPNs) have led to some auspicious outcomes regarding recyclability. However, most published studies have focused on step-growth polymer networks with crosslinking reactions between functional groups; there has been little focus on networks made by addition-type polymerization reactions. Here, we will overview studies from our research group that have led to the development of reprocessable addition-type DCPNs which exhibit full recovery of crosslink density after reprocessing. The methods developed by my research group typically involve simple, one-step radical-based reactions, like those used in basic free-radical polymerization of addition-type polymers. We can also use a similar approach with melt-state processing to upcycle spent or waste polyethylene into fully recyclable polyethylene networks. In particular, our dialkylamino disulfide-based dynamic crosslinks have a bond dissociation energy of ~110 kJ/mol, which is low enough to provide for dissociation but high enough to make the dissociation relatively strongly dependent on temperature. Thus, our DCPNs exhibit excellent resistance to creep at temperatures approaching 100 °C. Therefore, our approach overcomes an Achilles' heel of DCPNs – substantial creep at temperatures far below the reprocessing temperature because of the presence of dynamic character in the crosslinks. We will also describe the implications of our research for future developments in polymer networks and network composites.
Nanoparticle diffusion coefficients in polymer nanocomposites: Effect of polymer molecular weight, nanoparticle size, and interparticle distance

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The properties of polymer nanocomposites depend in part on the arrangement of nanoparticles and this spatial distribution can evolve during the fabrication and use of these hybrid materials. One fundamental parameter that impacts the evolution of nanoparticle morphologies is the nanoparticle diffusion coefficient. We apply time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and cross-sectioned trilayer samples to measure nanoparticle (NP) diffusion on micrometer length scales in polymer melts. We fabricate polymer/nanocomposite/polymer trilayer samples and measure the cross section to extract the NP distribution in 3D using ToF-SIMS. After correcting the data for sample tilt, deconvoluting the beam resolution, and integrating the data to extract 1D concentration profiles, we fit the data to extract the diffusion coefficient. The NP diffusion coefficients measured by cross-sectional ToF-SIMS are in excellent agreement with earlier studies using well-established ion beam methods. This method was also employed to measure the polymer trace diffusion coefficients, which were also in excellent agreement with previous results. Having established our ToF-SIMS method as a reliable approach for measuring NP and polymer diffusion coefficients, we study the effects of nanoparticle size and polymer molecular weight to identify the limit of the Stokes-Einstein model for NP diffusion in a polymer matrix and compare to recent theory. We also explore the effect of nanoparticle crowding on nanoparticle diffusion. By adapting ToF SIMS to probe center-of-mass diffusion in polymeric systems, this study opens the door to investigating diffusion in more complex polymer systems and across longer time and length scales relative to alternative methods.
Polymer science and sustainability: A nexus of opportunities – Cheng, H.N. (Oral Only)

POLY Awards Presentation – Haase, Danniebelle I Mathers, Rob I Moore, Levi I Orski, Sara I Guymon, Allan
Polymer science and sustainability: A nexus of opportunities

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Polymer science continues to be a vibrant and productive field for innovation and product development. In recent years, sustainability and green chemistry have become hot topics because of increasing public awareness of climate change, environmental pollution, and earth’s dwindling resources. An increasing trend is to combine polymer science and sustainable green chemistry in order to explore new chemical pathways and develop new or improved processes. The speaker has been actively exploring this area and will show several examples from his work: 1) Use of biobased materials for the development of new chemical pathways and products; these materials can biodegrade and reduce the problem of microplastics; 2) Biocatalysts (e.g., enzymes and micro-organisms) can be effective and biodegradable catalysts for specific chemical and polymer conversions; 3) Application of green chemistry concepts to polymer reactions; and 4) Development of green methodologies for process studies and improvements (such as the use of microwave and ecofriendly solvents). These approaches represent the intersection of polymer chemistry, sustainable green chemistry, and agriculture, and they may provide promising new opportunities for multidisciplinary collaborations and innovations in the future.
POLY/PMSE Plenary & Award Presentation

Allan Guymon
University of Iowa
2023 POLY Chair

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Martin James
Harm Klokk
Kat Knauer
Jessica Kramer

Jinsang Kim
Abigail Knight
Joerg Kressler
Sebastien
Lecommandoux
Frank Leibfarth
Yongfu Li
Corinne Lipscomb
Brian Long
Alexander Lonnecker
Paulomi Majumder
Jeff Moore
Laura Murdock
Leslie Olear
Bradley Olsen
Adriana Osmani
Charles Paul
Michael Petr
Dawanne Poree
Timothy Pruyn
Jeffrey Pyun
Dahui Qu
George Rodriguez
Stuart Rowan
Tonomori Saito
Alice Savage
Carmen Scholz
Colin Li Pi Shan
Ellen Sletten
Brent Sumerlin
Stefanie Sydlik
Ksenia Takhistova
Yujing Tan
Jia Tang
Veda Telfner
Kathryn Uhrich
Shruti Venkatram
Jun Wang
Peter Zarras
Chunxiao Zheng

2023 ACS Award in Pure Chemistry

Julia Kalow
Northwestern University

Recognizes and encourages fundamental research in pure chemistry carried out in North America by young men and women
2023 Fall Poster Awards

Takumi Yamamoto
Tokyo Institute of Technology
“Fluorescent Radical Precursors for Detecting Mechanical Degradation of Polymers”

Nicodemo Ciccia
University of California Berkeley,
“Catalytic C–H amination creates tough, adhesive materials from polyethylenes”

Anna Makar-Limanov
Stanford University
“Towards Chemically Recyclable Resins for Vat Photopolymerization Additive Manufacturing”

Thanks to our Judges and Poster Co-Chairs: Piril Ertem and Xiangyi Zhang

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2023 POLY Graduate Student Travel Award

Kriti Kapil
Carnegie Mellon University

Julio E. Terán
North Carolina State University

To provide funding for graduate students studying polymer science at US institutions to travel to national ACS meetings and present their results
Fall 2023 General Paper Presentation Awards

Keldy Mason, UT Austin
3D printed porous polymer sorbents for cobalt recycling

Oliver Penrhyn-Lowe, U. Liverpool
Transfer-dominated branching radical telomerisation (TBRT): Studying the impact of multi-vinyl taxogen dimensions on the branching behaviour of high molecular weight polymers

Hirogi Yokochi, Tokyo Institute of Technology
Synthesis of bio-based cyclic polycarbonate based on dynamic covalent chemistry

Alexander Oanta, Northwestern
Understanding the effect of zwitterion incorporation on 2DP materials quality

Marshal Allen, UT Austin
Spatial control over mechanical properties of polymer networks from single resin feedstocks

2023 Henkel Award for Outstanding Graduate Research in Polymer Science and Engineering

Chris Delre
University of California, Berkeley
Graduate Advisor, Ting Xu

Recognizes a PhD graduate student or recent graduate who has completed an outstanding PhD thesis in research at a university in the US or Canada

Sponsored by Henkel
2023 Charles G. Overberger International Prize for Excellence in Polymer Research

Uli B. Wiesner
Cornell University

Recognizes and encourages accomplishments of unusual merit in the field of basic or applied polymer science, from researchers from anywhere in the world
2023 ACS Fellows
POLY & PMSE Member Recognition

Jaime C. Grunlan
Texas A&M University

LaShanda Korley
University of Delaware

Theresa M. Reineke
University of Minnesota

Christopher M. Stafford
NIST

Jane E. Wissinger
University of Minnesota

2023 Young Industrial Polymer Scientist Award

Hayley Brown
Dow, Inc.

Recognizing outstanding industrial innovation and creativity in the application of Polymer Science, conducted by young individual scientists
2023 Outstanding Award Recognition
Distinguished Service Award

Michael Meador
NASA Glenn Research Center (Retired)

Recognizes work in enhancing and empowering student chapters & exceptional leadership of POLY in 2020; an extremely challenging year

2023 Herman F. Mark
Polymer Chemistry Award

Robert Waymouth
Stanford University

Recognizes outstanding research and leadership in polymer science