Division of Polymer Chemistry (POLY)

Graphical Abstracts

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POLY 1: Using light to grow materials

Jessica R. Lamb¹, Ke Qin¹, Jeremiah A. Johnson¹,², jaj2109@mit.edu. (1) Chemistry, Massachusetts Institute of Technology, Boston, Massachusetts, United States (2) Koch Institute at MIT, Cambridge, Massachusetts, United States

We introduced a strategy for the controlled insertion of monomers and crosslinkers into trithiocarbonate-based polymer networks using light. This process allows one to convert a parent material into progeny materials with diversified functionality. To make this “living additive manufacturing” concept practical, increasingly robust and efficient photopolymerization methods are required. Toward this end, we have recently developed an efficient visible-light mediated polymerization of acrylates that proceeds under ambient atmosphere with no exogenous catalysts or reagents. The details of this reaction will be described, and its application to living additive manufacturing of gels for biomedical applications will be introduced.
Our laboratory is involved in the use of biological systems as models for the elaboration of new concepts at the interface between organic, catalysis, macromolecular, supramolecular and biological sciences by using self-assembling non-biological monodisperse macromolecules as building blocks. These concepts are subsequently used in the design of nanostructures, and functional complex systems by following the first biological principles “structure determines function”. This lecture will first discuss the methodology developed and used in the design and synthesis of libraries of self-assembling building blocks via structural and retrostructural analysis. Subsequently the use of these building blocks for the elaboration of non-biological chiral complex systems
Light offers precise, tunable, and external spatiotemporal control over molecular reactivity. In polymer networks based on dynamic covalent bonds, these changes in reactivity can be translated into macroscopic responses. My lab has designed crosslinks that allow us to tune the thermodynamics and kinetics of dynamic covalent bonds with light, including visible light. When incorporated into polymer networks, these crosslinks allow photocontrol of time-dependent properties. I will discuss our progress towards elucidating the molecular mechanism underlying these macroscopic changes, and applying these designs to hydrogels and vitrimers.
POLY 4 Instructed-assembly to form supramolecular polymers for controlling cell fates

Huaimin Wang, Zhaqianqi Feng, Hongjian He, Jiaqing Wang, Bing Xu, bxu@brandeis.edu. Brandeis University, Waltham, Massachusetts, United States

Instructed-assembly (iAssembly or iA) refers to the formation of ordered superstructures of molecules (e.g., supramolecular polymers) as the consequence of at least one trigger event (e.g., a enzymatic reaction). As a biomimetic process that induces phase/morphology transition, iA has emerging as a powerful approach to form supramolecular polymers for a range of potential biomedical applications, including molecular imaging, cancer therapy, and tissue engineering. This talk introduces the general concept of iA of small building blocks in the context of cells and illustrates how to form supramolecular polymers for applications. By mainly describing the representative examples of supramolecular polymers and its applications in complex environment, such as cells, and providing the perspectives of their future development, we intend to show that, as a multiple step molecular process, iA offers a facile mean to explore the emergent properties of supramolecular polymers and the relevant dynamic molecular processes to control cell fates.

Comparison of a type of instructed-assembly (e.g., EISA) with self-assembly.
POLY 5: Amplifying fluorescent sensors based on molecular systems with extended electronic delocalization

Evgueni E. Nesterov$^{1,2}$, een@lsu.edu. (1) Department of Chemistry & Biochemistry, Northern Illinois University, DeKalb, Illinois, United States (2) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States

Chemo- and biosensors based on fluorescent conjugated polymers and oligomers benefit from the greater detection sensitivity due to amplification of the electronic perturbations produced by analyte binding. This amplification stems from the exciton-transporting properties of the conjugated systems. General sensor design paradigms utilize the concept of analyte binding to cause a perturbation of the local energy gap which changes the fluorescent properties of the polymer sensor. In this presentation, recent examples from our laboratory showing development of amplifying fluorescent sensors utilizing various molecular and mesoscale systems will be discussed. These new designs expand the generality and universality of the signal amplification concept in conjugated polymers, and can be used to construct amplifying turn-on and ratiometric fluorescent sensors for various practically useful analytes.
Efforts in using reactive vapor deposition to create functional polymer films on nontraditional substrates will be described. Vapor coating methods allow for rough and/or fragile substrates to be nondestructively coated with a variety of polymer films. To date, various off-the-shelf garments, commercial textiles, threads/yarns, plant leaves, flower petals, porous membranes, and micropatterned Si/SiO2 substrates have been conformally coated with either electronic-polymer or polyacrylate films. Selected technologies created using vapor-coated fibers, textile and plant matter will be described, including touch-sensitive textiles for interactive electronics; smart elbow braces for movement sensing; textile triboelectric generators that convert small body motions into stored energy; wear-, wash- and ironing-resistant conductive cloths that generate heat with a small applied voltage; thread/yarn supercapacitors that can be sewed or knitted into garments for wearable and portable energy storage; and flexible electrodes for bioimpedance spectroscopy.
Phosphorescent materials are enhancing and broadening the usefulness of organic compounds in a wide variety of applications including OLED, photovoltaics, and optical sensors. Of the emissive materials employed in OLEDs and SSL, phosphorescent compounds produce much higher efficiency devices than those based on fluorescent emitters by utilizing spin-parallel electrons and emitting photons from the decay of triplets. Organo-metallic compounds are thus often doped into organic hosts to impart a phosphorescent pathway into otherwise triplet-forbidding carbon-based materials. However, phosphorescence from metal free, purely organic, compounds is almost always either strictly forbidden or only extremely weakly allowed, leaving pure organics undesirable for room-temperature phosphorescence. In our recent development of highly emissive and metal-free purely organic phosphorescence materials, directed intermolecular heavy atom effects are uniquely implemented in aromatic carbonyl molecules to promote spin-orbit coupling and suppress vibrational dissipation. Color tuning by electron density modulation, molecular engineering to prevent collisional energy dissipation, highly sensitive oxygen sensors, and prototype PhOLED have been demonstrated. Molecular design strategies and applications of purely organic phosphors will be discussed.
Atom Transfer Radical Polymerization (ATRP) has been successfully used to grow uniform very densely grafted chains by from flat, concave and convex solid substrates using covalently anchored initiators. Densely grafted polymer chains were also prepared from organic macronitiators to form molecular brushes, functional networks and multiarm stars.
POLY 9: Chain growth polycondensation via substituent effects for the synthesis of functional rigid rod polymer brushes

Stephen G. Boyes¹, sboyes@mines.edu, Frederick C. Prehn¹, Caleb Reese¹, Shubham Vyas¹, Alison Kennedy². (1) Colorado School of Mines, Golden, Colorado, United States (2) Case Western Reserve University, Cleveland, Ohio, United States

The modification of surfaces with polymers is a field that has fascinated chemists and physicists for over half a century due to the unique ability of polymers to control interfacial properties. Indeed, surface modification using polymers has been directly responsible for both the expansion and improvement of existing technologies and the development of new technologies. Of the many different surface modification techniques available, polymer brushes have received considerable attention and they have been used in applications ranging from sensors to smart coatings. To date, polymer brush research and applications have been essentially limited to polymers prepared via living chain growth polymerization techniques involving vinyl-based monomers. However, recently researchers have established a need to develop polymer brushes based on aromatic polymers for application in areas such as tribological coatings, reverse osmosis membranes, and biosensing. This presentation will expand on exciting work from the group and discuss new research into the use of substituent effect chain growth polycondensation for the preparation of functional aromatic polyamide brushes, with a focus on the factors influencing brush growth, structure, and functionality, and a discussion on the applications of these novel polymer brush systems.
POLY 10: Macromolecules with programmable shape, size, and chemistry

Damien Guironnet¹, damien.guironnet@gmail.com, Dylan Walsh², Charles E. Sing³, Simon Rogers¹, Matthew Wade¹, Sarit Dutta¹. (1) Chemical and Biomolecular Engineering, UIUC, Urbana, Illinois, United States (2) UIUC, Sun Prairie, Wisconsin, United States (3) Chemical and Biomolecular Engineering, University of Illinois, Savoy, Illinois, United States

Bottlebrush polymers are branched polymers with high branching density all originating from a linear backbone. The “flexible rigid rod” behavior of these polymers provides unique physical properties and unusual emergent behaviors (ex. super soft elastomers, drug delivery and self-assembling systems) which has gain much attention recently. Thus far bottlebrush polymers have been limited to linear cylindrical shape. Herein, we present a reactor engineering strategy to control the shape of bottlebrush polymers by using a combination of two controlled polymerization synthesis bottlebrush with any axisymmetric shape. One controlled polymerization synthesizes the arms of the bottlebrush (ring opening polymerization) and the other polymerizes the backbone of the bottlebrush (ring opening metathesis polymerization). Theoretical derivations, in conjunction with a numerical model, are used to aid in the design and characterization of the shaped macromolecules. We have further characterized the materials through atomic force microscopy (AFM) as well as rheology. Rheological data is further correlated back to Brownian dynamics simulations. This methodology provides a unique opportunity to study the impact of macromolecules shapes.
Thermo-responsive bottlebrush polymers are synthesized by a novel grafting-to, radical coupling method with no small molecule synthesis involved. With this method, we demonstrate that bottlebrush polymers with molecular weight in the millions of g/mol can be easily prepared using either homopolymer or block copolymer side chains. More importantly, the dynamic bonds resulting from our radical coupling reactions, which link side chains and backbones of bottlebrush polymers synthesized by our method, are thermo-reversible at elevated temperature. Exploiting this dynamic feature via a simple annealing process with no extra synthetic step involved, the grafting density of bottlebrush polymers can be tuned post-synthesis with the bottlebrush regime going from loose bottlebrush to dense comb and potentially to loose comb with increased annealing. Such materials provide the opportunity to study grafting density-property relationships in bottlebrush polymers with other factors held constant. Thus, besides a facile synthetic pathway, our method also provides a platform for advancing the scientific understanding and technological applications of bottlebrush polymers through incorporated dynamic chemistry. Characterization of bulk and confined properties of our resulting bottlebrush polymers will be described, and implications for achievement of novel nanostructures will be given.
POLY 12: Molecular polymer brush templating for compartmentalized hybrid materials and soft matter

Markus Muellner\textsuperscript{1,2}, Markus.muellner@sydney.edu.au. (1) Key Centre for Polymers and Colloids, School of Chemistry, The University of Sydney, Sydney, New South Wales, Australia (2) The University of Sydney Nano Institute, Sydney, New South Wales, Australia

An application-focused design of materials is expected to overcome many limitations in current materials and biomedical sciences. The possibility to precisely engineer at the nanoscale enables the synthesis of materials with tailored chemical composition and physicochemical properties. Advances in synthetic polymer science have further nourished the fabrication of complex and functional polymer nanomaterials. Within this space, molecular polymer brushes (MPBs) form a unique class of materials that are extremely powerful in molecular templating,\textsuperscript{1} self-assembly,\textsuperscript{2,3,4} and nanomedicine.\textsuperscript{5} Molecular brushes, are one-dimensional nanostructures consisting of polymer chains densely tethered onto a polymer backbone. The grafting density of polymer chains eventually becomes so high that the chains become crowded and stretched, leading to their typical cylindrical shape. Due to the shape-persistent nature, the extraordinary spatial dimensions and the tuneable architecture, molecular brushes offer new opportunities in nanomaterials synthesis using bottom-up fabrication, and provide access to nanostructures that are difficult to yield from linear copolymers or otherwise. Exploiting their cylindrical shape and multiple individually separated compartments and functionalities, these materials and their analogues may be applied as particulate templates\textsuperscript{1,6} and nanocarriers.\textsuperscript{5}

Molecular polymer brushes find application in various fields. For example, they can provide a one-dimensional scaffold (AFM on the left) for the fabrication of uniformly structured soft and shaped polymer nanoparticles (cryo-TEM on the right). Scale bars are 100 nm.
Our group recently reported a method to produce polypentenamer macroinitiators through ring-opening metathesis polymerization (ROMP) with a high degree of synthetic control over target molar mass and low dispersity. These macroinitiator can be subsequently "grafted-from" in near quantitative fashion using atom-transfer radical polymerization (ATRP) to produce a unique bottlebrush (BB) morphology with elastomer segments between graft sites. Although we used thermodynamic principles of equilibrium ROMP to produce these macroinitiators, we can now use the same principles to depolymerize the BB backbone and "release" the grafts in a nearly completely reversible fashion. Such outcomes will be discussed in addition to continued investigation on the properties of this BB morphology.
POLY 14: Amphiphilic double-brushes as stabilizers of hydrophobic solutes

Margarita Herrera-Alonso, margarita.herrera@gmail.com. Chemical and Biological Engineering, Colorado State University, Fort Collins, Colorado, United States

We describe the use of amphiphilic double-brushes as general stabilizers of a variety of hydrophobic solutes. Through control over side-chain ratios and backbone length, macromolecular brushes bearing poly(ethylene glycol) [PEG] and poly(D,L-lactide) [PLA] side chains were shown to effectively stabilize hydrophobic solutes in uni- or multi-molecular aggregates and different morphologies, largely influenced by the physicochemical properties of the solutes.
POLY 15: Ultrasound-induced chain scission of the dendronized polymers: The effect of side chains on the mechanochemical degradation

Ki-Taek Bang, bkt1988@nate.com, Gregory I. Peterson, Tae-Lim Choi. Chemistry, Seoul National University, Seoul, Korea (the Republic of)

Polymer mechanochemistry has attracted much attention since the mechanical force can induce the chemical reaction to the polymer which cannot be initiated by heat, light, electric and chemical reagent. It allows the researchers to develop unique functional materials such as force sensors, self-reinforcing materials. However, there is still a lack of understanding of the fundamentals that determine the mechanochemical reactivity of a polymer chain. One of the most important questions is that how does the side chain size affects the mechanochemical response of the polymers. To exploit the side chain effect, we focused on the dendronized polymers bearing well-defined dendritic side chain, which can be tuned at the molecular level by the proper design.

In the presentation, I'll describe the synthesis of the dendronized polymer composed of the polyphenylene dendron and their degradation behaviour. The systematic studies using the series of the well-defined dendronized polymers revealed that the size of the side chain affects the degradation rate of the polymers. We found the unexpected relationship between the molecular weight of the dendron and the degradation rate. Furthermore, the degradation kinetics and multi-angle laser light scattering (MALLS) analysis showed that the chain extension caused by bulky side chains plays an important role in the mechanochemical response of the polymers.
POLY 16: Quantification of polypropylene degradation as a function of depth in recovered ocean plastics

Sara V. Orski, sara.orski@nist.gov, Kathryn Beers, Viviana Rodriguez C.. Materials Science and Engineering Division, NIST, Bethesda, Maryland, United States

In marine ecosystems, plastics are initially exposed to abiotic degradation in the form of photo-oxidation by UV light, thermodegradation, and hydrolysis, where low molar mass fragments can then be further degraded by microorganisms. In order to understand the extent, ecological effects, and lifetimes of waste plastics in marine environments, it is necessary to quantify how these synthetic polymers degrade under natural environmental conditions and the variability in degradation conditions among materials of different sizes, surfaces areas, differing commercial compositions and formulations. Herein, we report systematic measurements of polypropylene fragments recovered from Kaupo Beach in Oahu, Hawaii to determine changes in chemical composition, molar mass, molar mass distribution, intrinsic viscosity, and short and long chain branching content within each fragment as a function of depth from the outer surface. Polypropylene samples were sectioned, and resultant slices were characterized by x-ray photoelectron spectroscopy (XPS), high temperature size exclusion chromatography (HT-SEC) with tetra-detection, and differential scanning calorimetry (DSC). Polypropylene sections within the same parent fragment all demonstrated a clear decrease in the number and weight average molar masses, a broader molar mass distribution, a high degree of oxidation, and greater incidence of foreign chemical elements relative to materials sampled from the internal material core. Among all polypropylene fragments measured, molar mass decreases were predominately due to chain scission, as very little long chain branched content was observed by differential viscosity measurements. This research can be used to aid the marine scientific community for sampling plastic marine debris, by providing them with alternate techniques of identification, quantitative degradation measurements, and (ultimately) information to develop predictive quantitative models of polymer degradation pathways and kinetics in marine ecosystems.
Although polymerization of traditional vinyl monomers proceeds by chain addition with the creation of carbon-carbon bonds, some cyclic monomers bearing vinyl or exomethylene groups can be polymerized by a radical pathway through a ring-opening mechanism. Radical ring-opening polymerization (rROP) thus combines the advantages of both ring-opening polymerization and radical polymerization, that is the production of polymers having heteroatom and/or functional groups in the main chain together with the robustness, the ease of use and the mild polymerization conditions of a radical process. Cyclic ketene acetals (CKA) were reported by Bailey and coworkers in the 80s as suitable monomers for rROP. This monomer family was then extensively studied as a way to produce similar polymers to classic aliphatic polyesters, but through a radical pathway. This technique has been recently rejuvenated by the possibility to copolymerize CKA with classic vinyl monomers, leading to cleavable functions into the copolymer backbone. This led to a broad range of novel (bio)degradable materials suitable for a large scope of applications.

We aim at using some biomass-based diols to prepare cyclic ketene acetal monomers that have the advantage to be polymerized by a radical mechanism. This will lead to new materials and it is also possible to copolymerize CKA with traditional vinyl monomers to introduce degradable biomass-based repeat units onto traditional polymer backbone. In both cases, this approach will decrease the petrochemical based monomer ratio. The introduction of a reasonable amount of biomass-based compound in many polymer matrixes aims at keeping the original properties of many materials but while decreasing their carbon footprint.
POLY 18: Weak link strategies for polymer degradation

Stephen A. Miller, miller@chem.ufl.edu, Steven Shen, Gabriel Short, Justin Smith, Jordan Torgunrud. Chemistry, University of Florida, Gainesville, Florida, United States

The degradation of polymers in the environment is an important topic, given the increased understanding of commercial plastic persistence in the oceans and on land. The slow step of polymer degradation is usually the breakdown of high molecular weight polymers to oligomers and monomers. Only then can true metabolic conversion to carbon dioxide proceed. This presentation will describe various strategies for installing weak links into polymer chains. This weak link strategy facilitates the initial chemical degradation (usually hydrolysis) into oligomers and monomers and is not generally reliant upon microbial intervention. Specific functional groups that serve as weak links include acetals, pyrrolidinone-esters, and aromatic esters. In addition to main-chain weak links, side chain strategies can also facilitate polymer degradation.
Commercially available low density foams for single-use consumer applications are primarily produced from petrochemical feedstocks, often with environmentally unfriendly blowing agents, and have poor end-of-life disposal options. The development of expanded polymeric materials from renewable chemical feedstocks utilizing benign blowing agents to afford materials with improved degradability remains a challenge. Poly(lactide) is a promising candidate as a degradable material for preparing low density foams and has a high affinity for carbon dioxide which can be employed as a relatively non-toxic blowing agent. Unfortunately, poly(lactide) has poor properties in the melt for ideal processing into foamed materials. While previous efforts have investigated the benefits of using chain extension strategies to introduce branching and improve the foaming capability of poly(lactide), these materials have not been well-defined. We demonstrate the use of polymers with chemically well-defined branching, star polymers, enable the preparation of low density poly(lactide) foams with subcritical CO2. Additionally we show the utility of incorporating surfactants with multi-arm star poly(lactide) for formulating foams with tunable densities and surface energies. Finally, the application of these compostable foams is demonstrated as a replacement for current foams used to make decorative flower arrangements, referred to as floral foams, which are petroleum based and non-degradable.
Over the years, the demand and the production of commodity plastics have increased exponentially. On the other hand, this has caused a disturbing amount of plastic waste to be generated. To make things worse, most of these heavily used commodity plastics are derived from non-renewable resources and are non-degradable. One solution to this problem is to synthesize biorenewable or degradable polymers from plant waste material that can replace current commodity plastics. This presentation will describe the synthesis of biopolyesters from sinapic acid obtained from mustard seed meal.
As the second most abundant natural biopolymer, lignin can be a sustainable alternative to petroleum-derived polymers that possess high concentration of aromatic structures. In addition, the natural lignin’s existing multiple functional groups can be used to generate efficient crosslinking in the polymer matrix. This talk will presents a new direction of natural lignin valorization, which utilizes lignin to produce a polycaprolactone network via a straightforward, cost-efficient synthesis pathway. Lignin’s hydroxyl groups of its hyper-branched phenolic structure allow lignin to serve as crosslinking agents. The demonstrated role and behavior of lignin as a natural biomass crosslinker and hard segment compensates for and enhances the mechanical properties of polycaprolactone, a favorable new polymeric material which has high controllability in properties and well-defined chemical structure. The prepared lignin-containing 4-arm polycaprolactone network demonstrates thermally-responsive shape memory behavior. Varying the % weight of lignin revealed that the thermal properties of this crosslinked lignin-polycaprolactone are precisely and conveniently tunable. The role of lignin as a crosslinker presented in this work suggests that lignin potentially can serve as an efficient functional additive for many other polymers in general.
Vegetable oils, phenolic acids, and lignin were investigated as sustainable sources to produce degradable epoxy resins with a reduced environmental impact. Epoxy resins are thermoset polymers widely used in composites, coatings and adhesives, with applications spanning automotive and aerospace industries, structural components, and wind turbine blades, among others. The standard precursor to epoxy resins, the diglycidyl ether of bisphenol A (DGEBA), is derived from petroleum and also has potential harmful health impacts. Lignin, an abundant bioresource, was explored as a source for replacing DGEBA in epoxy resins. Vanillic acid, a byproduct of the chemical degradation of lignin was investigated as a replacement for DGEBA in anhydride-cured epoxy resins. Functionalization of vanillic acid with epoxide groups was carried out through allylation, followed by epoxidation. Epoxidized vanillic acid was subsequently cured with an anhydride curing agent. The resulting vanillic acid-based epoxy resins exhibited high glass transition temperatures and high Young’s modulus, comparable to conventional DGEBA-based epoxy resins. The accelerated hydrolytic degradation of epoxy resins containing degradable ester groups, such as in epoxy resins derived from vanillic acid, plant-sourced phenolic acids, and epoxidized soybean oil (ESO), was explored, to provide additional end-of-life options such as composting. The polymer mass loss was monitored after exposure to a base solution at elevated temperature. The biobased epoxy resins exhibited rapid degradation in the base solution, in contrast to the slow degradation rate of the traditional DGEBA-based epoxy resin. A degradation model was proposed to describe the degradation behavior and degradation products were characterized.
Conjugated polymers are promising materials for flexible electronics and energy-relevant applications due to their combination of semiconducting properties, mechanical flexibility and ease of melt or solution processing. Molecular weight can be a key factor in influencing the nanoscale and macroscale properties of polymer chains including crystal architecture, solubility, phase transition temperatures, rheological response, and charge transport efficacy. These, in turn, have been shown to affect device performance in various devices, including transistors, photovoltaics and light emitting diodes. Nevertheless, accurate characterization of the molecular weight of conjugated polymers remains a challenge. Previous work has demonstrated gel permeation chromatography (GPC), when calibrated with polystyrene standards, underrepresents the molecular weight of polymers such as poly(3-hexylthiophene-2,5-diyl). Thus, absolute molecular weight characterization often relies on nuclear magnetic resonance by quantifying the number of chain ends. This approach is limited to modest molecular weights, due to difficulties in measuring chain ends at high molecular weight; furthermore, chain ends are not always well defined for materials synthesized through polycondensations that are prevalent for the synthesis of leading donor-acceptor alternating conjugated polymers. We show that GPC with an in-line viscometer (universal calibration) can accurately characterize the molecular weight of conjugated polymers. We find that a crucial component of this approach is to measure the differential refractive index, such that we can confirm the solution concentration, and thereby determine minimal loss of material in the system. Molecular weights obtained from universal-calibration GPC are validated using static light scattering and measurements of the intrinsic viscosity in an Ubbelohde viscometer.
POLY 24: nano-FTIR based identification & characterization of polymers at 10nm resolution

Andreas Huber, andreas.huber@neaspec.com, Tobias Gokus, Stefan Mastel. neaspec GmbH, Haar, Germany

Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is a scanning probe approach to optical microscopy and spectroscopy bypassing the ubiquitous diffraction limit of light to achieve a spatial resolution below 20 nanometers. s-SNOM employs the strong confinement of light at the apex of a sharp metallic AFM tip to create a nanoscale optical hot-spot. Analyzing the scattered light from the tip enables the extraction of the optical properties (dielectric function) of the sample directly below the tip and yields nanoscale resolved images simultaneous to topography [1]. In addition, the technology has been advanced to enable Fourier-Transform Infrared Spectroscopy on the nanoscale (nano-FTIR) [2] using broadband radiation (i.e. a mid-IR supercontinuum fs-laser) in the mid-IR spectral range.

Applying nano-FTIR near-field spectroscopy to measure the spectroscopic signature enables identification of i.e. polymers at a spatial resolution given only by the size of the AFM tip at unprecedented sensitivity [3]. For example, nano-FTIR spectroscopy of a self-assembled Polyethylene-Oxide (PEO) monolayer enables unambiguous material identification of sub-micron sized structures by comparing IR absorption lines measured by conventional FTIR with near-field spectroscopic signatures (Fig. 1, right). Chemical mapping at 1123 cm\(^{-1}\) is sensitive to the material-characteristic absorption of PEO, which allows to selectively highlight nanoscale PEO structures with thickness of only 11nm and to differentiate between mono- and bilayer structures (Fig. 1, left).

Results presented demonstrate that nano-FTIR can be an ideal analysis method to characterize complex material systems and to identify polymer materials at the nanoscale spatial resolution and unmatched sensitivity.

Fig 1. nano-FTIR measurements on a PEO monolayer structure. Chemical mapping at 1123 cm\(^{-1}\) clearly highlights PEO structures (left) and nano-FTIR spectroscopy enables unambiguous material identification.
POLY 25: BODIPY based ultra-low band gap D-A polymer with NIR absorption and emission

Gourav Tarafdar¹, tarafdar.91@gmail.com, Upendra K Pandey¹, Praveen C Ramamurthy²,¹. (1) Interdisciplinary Center for Energy Research, Indian Institute of Science, Bangalore, India (2) Materials Engineering, Indian Institute of Science, Bangalore, India

BODIPY or 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene is a class of organic dyes with excellent optical properties which also can be tuned by chemical modifications on the BODIPY core. In this work we have designed and synthesized four novel D-A (P1 - P4) copolymers with a thiophene fused BODIPY as the acceptor subunit and Benzodithiophene as the donor subunit. Unlike P1 and P2, P3 and P4 have alkylated thiophene as spacer between the donor and acceptor moieties. Synthesis of the polymers were done using standard Stille coupling reactions and yielded high molecular weight polymers. DFT calculations performed on the polymer backbones suggest a great degree of planarity in P1 and P2 which explains the low solubility of the pair as compared to P3 and P4. The extended conjugation in BODIPY core leads to ultra-narrow band gap in the polymers as seen from UV-vis absorption spectra of the polymers. The polymers P3 and P4 show intense charge transfer bands center at ~ 950 nm with the absorption band edge extending beyond 1100 nm suggesting band gaps of ~ 1 eV. The polymers 3 and 4 show large Stokes shift of ~ 200 nm with emission maxima at ~ 1200 nm. The HOMO of the polymers were calculated to be ~ -5.5 eV from cyclic voltammetry studies and hence are stable in ambient conditions. Foster resonance energy transfer (FRET) is observed in blends of these polymers with PTB7 where a complete quenching of PTB7 fluorescence is observed and further studied using Time resolved photoluminescence spectroscopy (TRPL). This suggests potential use of these polymers as acceptor material in NIR absorbing solar cells along with PTB7 donor and in NIR photodetectors.

Absorption and emission spectra of polymers 3 and 4.
Additive Manufacturing (AM), otherwise known as 3D printing, is a growing technology area comprised of a spectrum of processes that allow production of solid objects of virtually any shape via information from a digital source. PAEK polymers such as PEEK, PEKK, and PEKEKK are perhaps the most promising candidates for demanding engineering applications and could enable the use of AM plastic parts in critical environments. Due to their superior properties, some PAEKs are suitable for extrusion-based approaches. Technologies such as Fused Filament Fabrication (FFF) have proven to be successful in incorporating a variety of PAEKs as raw materials. Among these, PEEK is particularly attractive as it allows for a larger processing range and represents the majority of the efforts in this area. Understanding the effects of process conditions is essential to predict the performance of these polymers in critical environments.

This study describes structure-property considerations for PEEK filaments offered commercially for extrusion-based AM processes. Results show that the conditions used during 3D printing, will have a definite effect on the properties of AM parts, including those made of PEEK. Characterization of the physical and viscoelastic properties of a series of PEEK filaments, and their resulting 3D printed parts, suggest changes due to the printing process and the quality of raw materials. Thermal and viscoelastic studies revealed that simple geometry parts made by FFF display different thermal stability and viscoelastic behavior compared to their parent filaments, despite the inherently superior properties of PEEK. Similarly, thermal stability and dynamic mechanical analysis data suggest different behavior in PEEK filaments from various sources, further suggesting contribution of the inherent properties of FFF raw materials to the performance of AM PEEK parts. These observations appear to be critical especially in high demanding environments were PEEK (and other PAEKs) could find a future application.
Polyethyleneimine (PEI) is an amine-rich cationic polymer with a wide array of applications, most notably in drug/gene delivery systems, carbon dioxide capture, the preparation of polymer dots and as a metal ion chelating agent. Emerging applications have been propelled by advancements in polymer modification chemistry. However, despite PEI’s established and expanding utility, characterization of modified PEI has been limited due to a lack of methods available for describing the manner and extent to which modification has occurred. In this presentation, a spectroscopic investigation of acetylated PEI is described. 1D and 2D NMR, FTIR, fluorescence and UV spectrophotometric assays were evaluated for their qualitative and quantitative capacity in elucidating the extent and distribution of modification across the polymer.
We present a family of covalent organic frameworks that have been functionalized with oligo-(ethylene oxide) chains of varying lengths. This functionalization produced materials that exhibit amphidynamic behavior, where the side-chains possess dynamic movement and the framework itself remains rigid. The functional groups include ethoxy (OEt), monoglyme monomethyl ether (OMEG), diglyme monomethyl ether (ODEG), and triglyme monomethyl ether (OTEG) creating four distinct COFs. We studied the amphidynamic behavior of the prepared COFs via crystal modeling, PXRD, and $^{13}$C solid state NMR relaxometry. The contrasting differences in T$_1$ relaxation times highlight the amphidynamic behavior of the functionalized COFs. The difference in length of the side-chains allowed for the determination of amphidynamic behavior with the use of $^{13}$C solid-state NMR relaxation methods.
Poly(3,4-ethylenedioxythiophene) (PEDOT) is certainly the most known and most used conductive polymer because it is commercially available and shows great potential for organic electronic, photovoltaic, and thermoelectric applications. Studies dedicated to PEDOT films have led to high conductivity enhancements. However, an exhaustive understanding of the mechanisms governing such enhancement is still lacking, hindered by the semicrystalline nature of the material itself.

In this communication, we report the development of highly conductive PEDOT films by controlling the crystallization of the PEDOT chains and by a subsequent dopant engineering approach using iron(III) trifluoromethanesulfonate as oxidant, N-methyl pyrrolidone as polymerization rate controller and sulfuric acid as dopant. XRD, HRTEM, Synchrotron GIWAXS analyses and conductivity measurements down to 3 K allowed us to unravel the organization, doping, and transport mechanism of these highly conductive PEDOT materials. N-methyl pyrrolidone promotes bigger crystallites and structure enhancement during polymerization, whereas sulfuric acid treatment allows the replacement of triflate anions by hydrogenosulfate and increases the charge carrier concentration.

We finally propose a charge transport model that fully corroborates our experimental observations. These polymers exhibit conductivities up to 5400 S cm\(^{-1}\), it is to our knowledge the highest value reported so far for PEDOT thin films. It is furthermore combined with a high transparency (> 85% in the visible spectrum) of the thin films. Thanks to these remarkable properties, we were able to fabricate the first all-polymeric transparent film heaters. Excellent performances were achieved in terms of heating rate at low applied bias, cyclability and stability. All these results will be presented and discussed.
The demand for high power and fast-charging lithium-ion batteries motivates the discovery of electrochemically stable next-generation electrolytes. High lithium transference number ($t_{\text{Li}^+}$) electrolytes, in which the current is carried primarily by Li$^+$, are specifically useful in avoiding lithium dendrite growth and catastrophic battery failure at fast cell (dis)charge rates. This contribution will describe the synthesis of lithium bis(nonenylmalonato) borate (LiBNMB) and its polymerization by acyclic diene metathesis (ADMET) polymerization to produce the polymeric salt poly(lithium bis(nonenylmalonato) borate) (P(LiBNMB)) with molecular weights $M_n = 2.7$–$55.4$ kg/mol and dispersities $M_w/M_n = 1.6$–$3.2$. Using cyclic voltammetry, we demonstrate that LiBNMB and P(LiBNMB) solutions in propylene carbonate at $22 \, ^\circ\text{C}$ exhibit remarkably little decomposition after the first cycle upon sweeping between $0$–$8 \, \text{V (v. Li/Li}^+)$. The diffusivities of both the Li$^+$ and the polymeric anions were determined using $^7\text{Li}$ and $^1\text{H}$ pulsed–field gradient NMR (PFG-NMR), from which the transference numbers $t_{\text{Li}^+}$ and conductivities of these electrolytes were determined. Notably, $t_{\text{Li}^+} \geq 0.95$ when the degree of polymerization is greater than $N_n \geq 50$. Electrolyte conductivities were further corroborated using electrochemical impedance spectroscopy measurements. These studies demonstrate that the polymeric salt P(LiBNMB) exhibits high transference numbers even at low degrees of polymerizations.
Materials with magneto-optic (MO) properties have enabled critical fiber-optic applications and highly sensitive magnetic field sensors. While traditional MO materials are inorganic in nature, new generations of MO materials based on organic semiconducting polymers could allow increased versatility for device architectures, manufacturing options, and flexible mechanics. However, the origin of MO activity in semiconducting polymers is far from understood. Our recent studies on semiconducting conjugated helical polymers shed light on understanding the underlying mechanism of intrinsic Faraday phenomenon with its supramolecular structures in organic materials. Polymer magnetism is also investigated with conjugated radical polymers, which reveals the promise of multifunctional conjugated radical polymers as responsive MO materials. The structure-property studies provide insights for the design of next-generation MO materials based upon semiconducting conjugated polymers.
In membrane-based gas separation, the key challenge is developing polymeric membranes that are both highly permeable and selective. Polymers of intrinsic microporosity (PIM) having rigid and contorted backbones provide high free volume elements, which often yield high permeability. Introduction of CO$_2$-philic species such as ionic liquids (ILs) into polymeric systems can be often improved high CO$_2$ selectivity over other light gases (CH$_4$ and N$_2$). The current work outlined to combine the high permeability features of PIMs with large CO$_2$ solubilizing functional groups of ILs, hence, obtaining a novel Ionic-PIM material with synergistic gas separation properties. A newly designed diimidazole functionalized spirobisindane-based diimide monomer was prepared to synthesize various novel ionic polyimides having similar characteristics of polymers of intrinsic microporosity (Ionic-PIM-PIs). These ionic-group-mediated PIM polyimide membranes showed excellent thermal and mechanical properties, making them adequate for gas separation applications. The gas permeation parameters (permeability ($P$), diffusivity ($D$) and solubility ($S$) coefficients) of these Ionic-PIM-PIs were determined using a high vacuum time-lag measurement unit. The CO$_2$ permeabilities versus CO$_2$/light gas selectivities of Ionic-PIM-PIs were then compared to the empirical upper bound of Robeson plot. Unlike other typical high-free-volume PIM membranes, the newly developed Ionic-PIM-PIs can exhibit a high tolerance to free volume collapse because of strong ionic-group interactions in the polymeric main chain. Therefore, we also investigate the effects of ILs composites with this Ionic-PIM-PIs series on the structure and physical properties as well as the gas separation parameters of corresponding composite membranes.
POLY 33: High dielectric constant semiconducting poly(3-alkylthiophene)s from side-chain modification with polar sulfinyl and sulfonyl groups

Chunlai Wang², cxw410@case.edu, Zhongbo Zhang², Sandra Pejic², Ruipeng Li³, Masafumi Fukuto³, Lei Zhu¹, Genevieve Sauve². (1) Dept of Macromolecular Sci Eng, Case Western Reserve University, Cleveland, Ohio, United States (2) Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (3) Brookhaven National Lab, New York, New York, United States

There is growing interest in designing and developing high dielectric constant (εr) organic semiconductors, because they have the potential to further enhance device performance by promoting exciton dissociation, reducing bimolecular charge carrier recombination and potentially enhancing charge carrier mobility via charge-screening. In this study, a new class of semiconducting polymers with high εr, i.e., sulfinylated and sulfonylated poly(3-alkylthiophene)s (P3ATs), were synthesized. Because of efficient rotation of highly polar methylsulfinyl and methylsulfonyl side groups (i.e., orientational polarization), high εr values were achieved for these functionalized P3ATs based on an accurate capacitance measurement using a gold/semiconducting polymer/SiO2/n-doped Si configuration. For example, the εr at MHz and room temperature increased from 3.75 for the regioregular poly(3-hexylthiophene) (P3HT) to 7.4 for the sulfinylated and 8.1-9.3 for sulfonylated P3AT polymers. These values are amongst the highest εr reported for conjugated polymers so far. Grazing-incident wide-angle X-ray diffraction results showed that these polar groups decreased the crystallinity for the polythiophene backbones, and interfered with the long-range π-π stacking in the crystalline structure. Consequently, their optical properties, including UV-Vis absorption and fluorescence, changed in thin films. From this study, the sulfinylated polymer may be promising to provide a balance between high εr and preserving favorable polythiophene π-π stacking structure for device applications.
Epoxy thermosets are highly cross-linked polymer networks are commonly used for high performance load bearing applications within the automotive and aerospace industries to name a few. This is due to their high strength, stiffness and, glass transition temperature, as well as their chemical and moisture resistance. However, wider usage is often inhibited by their intrinsic brittleness directly arising from their crosslinked structure. A range of experimental techniques have been employed to improve toughness through the use of additives and modifiers with varying levels of success. A major challenge however, would be created intrinsically toughen crosslinked networks which do not require the use of any modifiers. This would then provide an opportunity for new composite applications and further drive down the cost of composites particularly for out of autoclave fabrication technologies.

The strategy employed here has been to explore novel epoxy resins containing multi-aromatic structures of varying substitutions, linkages and crosslink densities with a view to promote molecular mobility and the ability to deform under load, with a rigid network structure. Synthesis of multi-aromatic, multi-functional epoxy monomers cured with a variety of different hardeners will be discussed. Structure property and processing relationship will be discussed in terms of the substitution patterns, epoxy functionality and curative. Emphasis will be on the effect of processability, mechanical and thermal properties.
A new family of furan-based thermosetting materials will be discussed. Furfuryl amine (FA) was coupled using aldehydes to form furan di-amine (DFDA) and tetra-amine (TFDA) molecules containing two or four furan rings respectively. These amines form the basis for epoxy, benzoxazine, and polyimide thermosetting systems with unique properties. Furan-based epoxy amine systems were found to possess higher density and Young’s modulus (>5 GPa), as well as higher yield strength (>150 MPa in compression) and high char-yield compared to traditional epoxies. Benzoxazine monomers were synthesized by reacting DFDA’s with a number of phenolic compounds and formaldehyde resulting in solid powders that melt at temperatures ranging between 70°C and 150°C to form low-viscosity liquids. Onset cure temperature varied in the range of 120°C-240°C depending on composition. The resulting polybenzoxazine systems possess T_g’s ranging from 220°C to 280°C and char-yield as high as 70% measured at 800°C by TGA in an inert environment. DFDA was also used to prepare norbornene end-capped polyimides analogous to PMR-15. These materials were found to process high T_g (>330°C) and excellent processability because of low melt viscosity and facile imidization. This family of thermosetting systems could provide additional capability for aerospace applications that require good ambient performance characteristics as well thermal management in extreme environments.
POLY 36: Determining amine reactivities effect on epoxy network formation: Influence of chemical structure and processing conditions on local properties

Jared Bates¹, jared.bates@usm.edu, Jeffrey S. Wiggins², Dhriti Nepal³, Carla Estridge⁴, Hilmar Koerner⁶, Samuel J. Tucker⁵, Vikas Varshney⁷. (1) University of Southern Mississippi, Picayune, Mississippi, United States (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Materials and Manufacturing Directorate, Air Force Research Lab, Beavercreek, Ohio, United States (4) Boeing, St. Louis, Missouri, United States (5) Research & Technology, Boeing, Seattle, Washington, United States (6) Soft Matter Materials Branch, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States (7) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States

The interdependency of epoxy system’s network formation, morphologies, and end properties remains undetermined due to a lack of understanding of primary and secondary amine reactivities. This is impeding the usage of cure path optimization for improving part performance and cost. In the subsequent work, with this motivation, systems consisting of the difunctional epoxide monomer diglycidyl ether of bisphenol F (DGEBF), the tetra functional epoxide monomer tetraglycidyl 4,4’-diaminodiphenylmethane (TGDDM), and a mixture of the two crosslinked with the diamine curing agent 4,4’-diaminodiphenylsulphone (44DDS) all in a stoichiometric epoxide to reactive proton ratio were investigated. were studied in order to begin understanding the different reactivities elicited effect. Standard activation energy (Eₐ) calculations were performed using differential scanning calorimetry (DSC) via the Flynn-Wall-Ozawa method (FWO). However, DSC yields a wholistic view of the cure taking place, lending no insight into specific reactions/molecular conversion. Therefore, corroborative experiments were performed in-situ through near infrared (NIR) spectroscopy to yield detailed information on the individual reactions taking place. Then the nanoscale morphology analysis were done ies were studied through atomic force microscopy (AFM), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM). The morphology was correlated with chemical mapping through nanoscale IR analysis (AFM-IR). Peak force AFM was used for local mechanical mapping of the surfaces. This work illustrates the critical role that chemical composition and processing pathways have on network structures and local properties.
POLY 37: Development of a fundamental understanding of the curing kinetics of benzoxazine/epoxy blends via in situ Fourier transform infrared spectroscopy

Spencer Hawkins\textsuperscript{1,2}, spencerahawkins@gmail.com, Adam Maffe\textsuperscript{4}, Ehsan Barjasteh\textsuperscript{3}, Dhriti Nepal\textsuperscript{2}. (1) Universal Technology Corporation, Dayton, Ohio, United States (2) Materials and Manufacturing Directorate, Air Force Research Lab, Beavercreek, Ohio, United States (3) Mechanical & Aerospace Engineering, Chemical Engineering, California State University Long Beach, Long Beach, California, United States (4) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

Benzoxazines (Bz) are a class of thermoset resins that have been poised to replace traditional aerospace resins such as epoxy (Ep), bismaleimide, and phenolic due to their high glass transition temperature ($T_g$), excellent fire retardancy, small coefficient of thermal expansion (CTE), near zero cure shrinkage, low water absorption, and excellent solvent resistance. Unfortunately, they suffer from higher viscosities than resins used for additive manufacturing and vacuum-assisted resin transfer molding (VaRTM). In order to enhance the $T_g$ of a traditional Bz resin without sacrificing its superior inherent qualities, we blended a Bz resin with epoxy resins of various functionality to alter the network formation during cure. The ratio of Bz and Ep were varied by weight to determine which yielded the highest $T_g$ and lowest viscosity. Furthermore, fourier transform infrared spectroscopy (FTIR) was conducted during cure to identify the crosslinking reaction mechanisms that took place. Currently, there is no fundamental understanding of the crosslinking mechanism in the homopolymerization of Bz, let alone in the copolymerization of Bz/Ep hybrids. Previous studies by a collaborator showed that a significant increase in $T_g$ (~100 °C) and decrease in viscosity (~10\textsuperscript{2} Pa*s) can be obtained by mixing Bz and Ep at 50 wt. %/50 wt. %. To develop a better understanding of the mechanisms responsible for the aforementioned changes in the behavior of the Bz/Ep hybrid, IR spectra were obtained for the neat monomer resins. Next, Bz/Ep blends were fabricated by rotovaping predetermined amounts in a flask at 95 °C, and 60 RPM while under vacuum (50 mbar). The spectra were analyzed by running a Matlab script that identified peaks of particular interest and calculated the concentration of particular chemical bonds based on the Beer-Lambert law. The concentrations were plotted as a function of time and compared between systems.

\[ \begin{align*}
\text{Benzoxazine homopolymerization} \\
\text{Benzoxazine-epoxy copolymerization}
\end{align*} \]

Proposed crosslinking mechanisms for homopolymerization of Bz and copolymerization of Bz/Ep hybrids.
POLY 38: Directly spun, aligned carbon nanotubes and carbon fibre epoxy-based hybrid composites for the potential applications in aerospace engineering

Sameer Rahatekar¹, sameer.rahatekar@gmail.com, Jinhu Chen¹, Kalyan Hazra², Agnieszka Lekawa³, Krzysztof Kozioł¹. (1) School of Aerospace Transport & Manufacturing, Cranfield University, Cranfield, United Kingdom (2) National Composites Centre, Bristol, United Kingdom (3) Warsaw University of Technology, Warsaw, United Kingdom

We have developed new routes of production of hybrid aligned carbon nanotube (CNT) films and Carbon fibre based epoxy composites which can potentially be used in aerospace structures for multifunctional applications. A gas phase chemical reactor was used for continuous production of carbon nanotubes films using a one-step chemical vapour deposition (CVD) based method. The nanotube films based were manufactured using aerospace grade epoxy resin as a matrix and using vacuum bagging and autoclave curing process which is a conventional composites manufacturing technique. The use of continuous carbon nanotube and high-performance epoxy resin using vacuum bagging process allowed to produce nanotube epoxy film composites with a high weight fraction of nanotubes in composites (40wt%). The epoxy and carbon nanotube films showed very good mechanical properties, improvement in the tensile modulus behaviour with unique pseudo-ductile fracture behaviour. The epoxy nanotube film composites also showed excellent electrical properties which conductivity increase well above the requirement of EMI shielding applications. We also manufactured the hybrid composites of nanotube films in combination with carbon fibres using conventional composites manufacturing using vacuum bagging and autoclave curing. The resulting hybrid carbon nanotube films and carbon fibre composites showed excellent surface conductivity which was far superior to that of baseline carbon fibre composites. These hybrid carbon nanotube film and carbon fibre based composites can be used for wide range of aerospace application in EMI shielding, improved electrostatic dissipation, electric energy storage, improved fracture toughness and electrical actuation of composites. Simultaneously, the process is much simpler, inexpensive and easy to upscale for the aerospace composites manufacturing.
The design of next-generation air- and spacecraft necessitates the development of high strength-to-weight ratio materials. Specifically, carbon fiber reinforced polymers (CFRPs) are used to improve aeronautical range of commercial aircrafts, maneuverability of military jets, and payload capacity of space-bound rockets. Polybenzoxazine (BOX) networks represent an appealing new chemistry for CFRPs with the potential to replace traditional epoxy-based matrices due to their excellent shelf-life stability, minimal chemical shrinkage, synthetic modularity, and high performing thermomechanical properties. Low Earth Orbit (LEO) is a notoriously hazardous environment for organic materials due to high levels of ultraviolet radiation (UV) and atomic oxygen (AO). A variety of techniques have been developed to impart UV- and AO-resistance to organic composites, such as the application of coatings or the blending of nanoparticles. More recently though, it has been found that chemical incorporation of passivating functional groups, like phenylphosphine oxide (PPO), into the polymer’s backbone offers greater protection and is a more economical solution than applying and maintaining secondary coatings. Although PPO has been proven in polyimide systems, the viability of PPO-modified BOX for UV- and AO-resistance is not well understood. In this study, phenylphosphine oxide functional BOX (PPO BOX) was synthesized to probe PPO’s effects on network thermomechanical and photooxidative properties, and the protective mechanism of PPO BOX was investigated. This research would provide fundamental knowledge on the network properties of PPO BOX and its behaviour in extreme environments such as LEO.
POLY 40: Moisture adsorption of the benzoxazine-based thermoset matrix for advanced composite applications

Jose Bannuelos¹,³, jose.bannuelos@csulb.edu, Ehsan Barjasteht². (1) Chemical Engineering, California State University, Long Beach, Long Beach, California, United States (2) Chemical Engineering, California State University, Long Beach, California, United States (3) Mechanical Engineering, California State University, Long Beach, Long Beach, California, United States

Benzoxazine resin can be copolymered with low-viscosity epoxy resin to create a processable system with superior thermal properties upon the cure. In this study the hygrothermal aging of Benzoxazine-Epoxy copolymers were investigated. The moisture sorption-desorption behaviors of the bisphenol A-based benzoxazine (BZ-a) copolymered with various bi-functional epoxies were studied by aging the specimens in water bath at: 50 °C, 70 °C and 90 °C. The effects of moisture on the change in the physical, thermal, and mechanical properties of the copolymer systems were investigated by thermogravametric and volumetric analysis, dynamic mechanical analyzer (DMA), and Fourier Transform Infrared Spectroscopy (FTIR), respectively. Results showed that the choice of epoxy affected the swelling, mass adsorption and viscoelastic response of the specimen during exposure. No direct correlation was observed between the Tg and the amount of absorbed water. The complete water desorption of the specimens was performed to investigate potential hydrolytic reaction of the Benzoxazine Epoxy copolymers using FTIR. The results show that pure Benzoxazine absorbs 2.20% less moisture than the epoxy amine system, and the Benzoxazine Epoxy copolymer systems absorbed 1.00% and 1.72% less moisture than the epoxy amine system as well, showing resistivity of Benzoxazine systems to moisture attack even when copolymerized with epoxies.

![Moisture adsorption of benzoxazine/epoxy system at 70 °C](image1)

![Moisture adsorption of benzoxazine/epoxy system at 90 °C](image2)

Model-based Moisture adsorption Prediction: \[ \frac{M_t}{M_\infty} = 1 - \exp\left(-7.3\left(\frac{Dt}{h^2}\right)^{7.5}\right) \]
Carbon fiber reinforced thermoplastic (CFRTP) composites are a platform material for structural applications due to their lightweight, chemical resistance, and high fracture toughness. However, the chemical inertness of the CFRTP surface hinders the material's ability to robustly bond to form structural assemblies. Low temperature plasma treatments of CFRTP composites have demonstrated their ability to overcome this limitation by creating an activated surface while maintaining the desired mechanical properties within the bulk of the material. A highly active composite surface comprised of ionic and radicalic species is intrinsically unstable, resulting in the degradation of the activation state over time. The ability to determine the activation state of the surface is paramount for quality control of bonded structural assemblies for aerospace and automotive applications. A novel, non-destructive method of characterizing the activation state of plasma-treated polymeric surfaces was discovered using surface potential measurements. Activated surfaces exhibit a characteristic narrow, well-defined surface potential distribution. The narrow peak is hypothesized to be due to the presence of meta-stable radical-ion complexes. Evidence for plasma-treated surfaces being uniformly comprised of radicals and anions is supported by surface potential and contact angle measurements, magnetic force microscopy, and radical scavenging experiments. The radical-anion complexes demonstrated longer lifetimes compared the isolated constituents. Further support for radical-anion complexes was observed via a decrease presence of surface radicals for plasma-treated samples subjected to a charge-neutralization source compared to non-neutralized plasma-treated samples.
Polymers are well-suited additives to control stability, activity, and solubility of enzymes. In most cases, proteins and polymers interact by hydrophobic or ionic attraction forces between polymer backbone and protein surface. This way, the biomacromolecules can be stabilized, inhibited or rendered water-insoluble or even organo-soluble. This usually requires a large amount of polymer mass. Only few examples of specific polymer/protein interactions have been exploited to influence enzyme properties. We have considered poly(2-oxazoline)s (POx) with 2,2'-imino diacetate (IDA) end groups as polymer additives with more specific interactions. For example, the enzyme horse radish peroxidase (HRP) is inhibited by these polymers in a non-competitive way. Thereby, the IDA end group shows a very weak binding to the protein and the polymer collapses on the proteins surface showing an endothermic reaction. In contrast to HRP, the enzyme laccase is inhibited by the IDA terminated POx via a competitive mechanism. All IDA-POx induced inhibitions are fully reversible, opening the opportunity to apply thermo-responsive POx for designing a temperature switchable enzyme inhibitor.

Additionally, the IDA-terminated polymers are suited to form organo-soluble polymer enzyme conjugates (PECs). Dynamic light scattering (DLS) revealed that enzymes, such as lysozyme and HRP, can be molecularly dispersed in organic media after being conjugated with POx-IDA. PECs of larger enzymes, such as alcohol dehydrogenase or catalase, are still forming clear solutions in polar aprotic solvents, but are dispersed in the nanometer scale (diameter of less than 50 nm). In some cases, the organo-dissolved enzyme can be extracted from the organic phase into the aqueous phase practically without losing activity. The enzymes are also found to be active in the dry organic solvents.

Concept of a non-competitive enzyme inhibition by POx-IDA.
A powerful array of strategies are now available for defining the conformation of specified peptoid sequences. In addition, improved computational tools are being developed to reliably model and design peptoid structures capable of addressing a variety of functional objectives. As our vision of peptoid sequence-structure-function relationships becomes increasingly clear, we are able to reliably predict which peptoid sequences can address critical needs in molecular pharmacology. We evaluate some promising concepts for crafting bioactive peptoids, such as the construction of precise multivalent ligand displays and the synthesis of conformationally ordered peptoid macrocycles. We highlight recent advances in developing peptoids as therapeutics for late-stage prostate cancer, including the computer-assisted design of a peptoid macrocycle that abrogates the protein-protein interaction between β-catenin and Tcf in the Wnt signaling pathway. Peptoids may populate an attractive "middle-space" that lies between small-molecule therapeutics suitable for intracellular targets and protein therapeutics capable of binding to broad protein surfaces.
Poly(2-oxazoline) and Poly(2-oxazine) micelles show a highly structure-sensitive solubilization behavior for hydrophobic molecules and drugs. Notably, these systems seem to strongly contradict the common wisdom, like-dissolves-like. In fact, the polymers with a minimal hydrophilic/hydrophobic contrast are much typically found to be more successful in solubilizing molecules of ultra-low water solubility. Here, the influence of the hydrophobic blocks and the drug structure is investigated as well as the effects of drug loading on the therapeutic efficacy in a variety of tumor models.
POLY 45: Amplification of protein detection signal using poly(2-methyl-2-oxazoline) based mixed brushes with switchable properties

Yanmei Wang, wanyanm@ustc.edu.cn. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, China

It was a challenge to determine trace protein with high sensitivity using commercial capillary electrophoresis (CE) equipped with UV-detector. In this work, a mixed polymer brushes coated capillary with switchable protein adsorption/desorption properties was developed and applied for on-line extraction and preconcentration of proteins to enhance the detection sensitivity. Firstly, amine-terminated poly(2-methyl-2-oxazoline) (PMOXA-NH₂) and thiol-terminated poly(acrylic acid) (PAA-SH) were synthesized by cationic ring-opening polymerization and reversible addition fragmentation chain transfer polymerization, respectively. Then, mixed brushes based on poly(2-methyl-2-oxazoline) (PMOXA) and poly(acrylic acid) (PAA) coated capillary were prepared by sequentially grafting of PMOXA-NH₂ and PAA-SH onto fused-silica capillary inner surface through poly(dopamine) as an anchor. The study of electroosmotic flow showed that the inner surface charge of mixed polymer brushes coated capillary is function of the pH value and ionic strength (I) of the surrounding aqueous solution. Afterward, the protein adsorption/desorption performance of polymer coated capillary was investigated by using fluorescence microscope. The results showed that a selected mixed PMOXA/PAA coated capillary could adsorb high amounts of lysozyme, and then most of adsorbed protein could be desorbed upon pH and I change at high speed. This switchable protein adsorption/desorption ability of coated capillary were then used to extract and preconcentrate lysozyme during CE performance. The results displayed that the detection sensitivity of lysozyme in CE with UV-detector could reach to 10⁻⁹ M due to the amplification of lysozyme signal. Finally, this technique was applied successfully to amplify the detection signal of lysozyme existing in hen’s egg, and the detection sensitivity was boosted to a large extent.
POLY 46: Polysaccharide-\textit{graft}-poly(2-alkyl-2-oxazoline) hybrid copolymers: Versatile materials for bioapplications

\textbf{Martin Hruby, mhruby@centrum.cz, Lenka Loukotova, Mariia Rabyk. Institute of Macromolecular Chemistry AS CR, Prague 6, Czechia}

We have prepared a family of modular “molecular toolbox-like” hybrid copolymers polysaccharide-\textit{graft}-poly(2-alkyl-2-oxazoline) by a simple one-pot procedure, consisting of cationic ring-opening polymerization of 2-alkyl-2-oxazoline monomers and subsequent termination with sodium alcoholdate of the corresponding polysaccharide. The prepared copolymers can be further conjugated via terminal double bonds on the grafts (\textbf{Fig. 1}). Hydrophilic monomers were used to fine-tune the final polymer biodegradation rate as well as its cellular uptake, while 2-isopropyl-2-oxazoline was exploited to produce thermoresponsive polymers, suitable for a polymer depot formation after injection of polymer solution into the body. Moreover, the polysaccharide nature plays an important role in the polymer properties – we have used glycogen (fully biodegradable and biocompatible d-glucose-based hyperbranched structure), b-glucan and lentinan (d-glucose-based Toll-like receptor agonist immunomodulators), k-carageenan (anionic thermo- and potassium-responsive immunomodulator) or mannan (DC-SIGN receptor ligand targeting to macrophages and dendritic cells). We have demonstrated the polymer tuneable multistimuli-responsive behavior in aqueous solutions. Furthermore, these polymers were demonstrated to show superior anticancer effects in \textit{in vivo} murine model as local radioimmunomodulators and to be excellent agents for \textit{in vivo} imaging of sentinel lymph nodes or for melanoma imaging.

\textbf{Fig. 1. The example of hybrid copolymer conjugate synthesis.}
POLY 47: Functional bioinspired polypeptoide-based polymers

Jing Sun, jingsun@qust.edu.cn, Yunxia Ni, zhekun shi. Qingdao University of Science and Techonolgy, Qingdao, China

Bioinspired polymeric materials receive considerable attention due to significant advantages. Polypeptoids, also known as poly N-substituted glycines, are a promising class of protein-mimetic polymers, which offer great unique properties for both fundamental research and applications in biotechnology. The chemical structure of polypeptoid is fairly similar to that of polypeptide. The polypeptoid possess identical backbones to the polypeptide, but the side chain is attached to the nitrogen instead of a-carbon. It thus eliminates the inter- and intrachain hydrogen bonding and the chirality in the main chain. The peptoid polymers with high molecular weights and large scale yields can be obtained by ring-opening polymerization technique. Many polypeptoid-based block copolymers have therefore been synthesized and studied. We synthesized a series of functional polypeptoids with stimuli responsive properties by a combination of ring-opening polymerization and click chemistry. For example, the obtained polypeptoids show either LCST-type or UCST-type behaviour depending on the side-chain functionalities. We further reported a facile approach to prepare functional nanostructures such as highly flexible 2D crystalline nanosheets. The obtained bioinspired nanostructures are potential candidates for applications in nanoscience and biomedicine.
POLY 48: POZ™ – poly(2-oxazoline) update on next generation in polymer therapeutics

Randall Moreadith, Rmoreadith@serinatherapeutics.com. Serina Therapeutics, Inc., Huntsville, Alabama, United States

The first poly(2-ethyl-2-oxazoline) (POZ™) polymer therapeutic is entering Phase Ib in patients with Parkinson’s disease (PD), and the design, pre-clinical and clinical results of this candidate drug will be reviewed during this lecture. SER-214 is a twenty kDa ten pendent polymer with ten rotigotine molecules attached employing copper-catalyzed “click chemistry”. In patients that lack sufficient dopamine signaling, continuous drug delivery of a potent dopaminergic agent such as rotigotine provides continuous dopaminergic tone – a long-sought clinical strategy that obviates the phasic "peak and trough" profiles of oral agents. The second molecule in addressing the unmet medical need in PD has entered pre-clinical studies. SER-240 is a POZ conjugate of apomorphine, one of the most potent dopamine agonists known. This product candidate is being developed for treatment of advanced PD patients who have significant periods of “off” time during daily awake periods.

In this lecture I will also provide an update on the pipeline at Serina. SER-227 is a one-time injection of POZ-buprenorphine that may be delivered in the recovery room following surgery. SER-227 is designed to provide immediate (within 1-2 hours) and prolonged (3-4 days) continuous drug delivery of buprenorphine - an analgesic that will also address the opioid epidemic in the US. Finally, I will provide an update on our POZ-cannabinoid programs with special emphasis on SER-228 – a POZ conjugate of cannabidiol (CBD) that provides continuous delivery of CBD. SER-228 will initially be developed for refractory epilepsy, but may also be effective in a myriad of other clinical indications.

SER-214 - A POZ conjugate of rotigotine
Multi-drug resistant diseases are one of the biggest challenges society is facing in the domain of healthcare. Contraction of a multi-drug resistant disease, whether through a microbial infection or the loss of chemotherapeutic effectiveness, results in an extremely poor patient prognosis given the severely limited treatment options. The rapid resistance development in microbes, for instance, has completely eviscerated the current antimicrobial drug pipeline. The resistance development of a variety of cancer cell lines has rendered treatment with a single therapeutic agent completely ineffective. Instead, chemotherapeutic treatments must rely on a bevy of chemotherapeutic agents and chemosensitizers to achieve remission, most often at the cost of the patient’s well-being, owing to significant toxicity.

Traditional, small-molecule drug therapy usually targets highly specific cellular processes or interactions, enabling resistance development through simple mutations in the pathogen’s genome. In contrast, macromolecular therapeutics consist of polymeric assemblies that exhibit selective but non-specific interactions with the pathogen, making resistance development extremely difficult. In fact, macromolecular therapeutic agents developed at IBM have shown no resistance development in the treatment of bacteria and viruses, in preliminary in vitro studies. Additionally, these agents have been found to be highly effective against drug-resistant bacteria and cancer cell lines, while maintaining very low toxicity towards healthy cells. Given these impressive features, macromolecular therapeutics hold significant promise for disease treatment.
Disulfiram (DSF), an alcohol-aversion drug, has been explored for cancer treatment. Copper diethylidithiocarbamate (Cu(DDC)₂) complex formed by DSF and copper ions is a major active ingredient for its anticancer activity. Direct administration of Cu(DDC)₂ is a promising strategy to enhance the anticancer efficacy of DSF. However, efficient drug delivery remains a significant challenge for Cu(DDC)₂ and hinders its clinical use. In this study, we developed a facile Stabilized Metal Ion Ligand complex (SMILE) method to prepare Cu(DDC)₂ nanoparticles (NPs). The SMILE method could prepare Cu(DDC)₂ NPs with different types of stabilizers including 1, 2-distearoyl-sn-glycerol-3-phosphoethanolamine-poly(ethylene glycol) 2000 (DSPE-PEG), D-α-tocopherol polyethylene glycol 1000 succinate (TPGS), methoxy poly(ethylene glycol) 5000 -b-poly(L-lactide) 5000 (PEG-PLA), and other generally recognized as safe (GRAS) excipients approved by the US Food and Drug Administration (FDA). The optimized formulations demonstrated excellent drug loading efficiency (close to 100%), high drug concentrations (increased drug concentration by over 200-fold compared to the traditional micelle formulation), and an optimal particle size in the sub-100 nm range. The anticancer effects of Cu(DDC)₂ NP formulations were determined by multiple assays including MTT Assay, Colony-forming Assay, Calcein-AM/Propidium Iodide (PI) Staining, and others. Cu(DDC)₂ NPs showed excellent activity against drug-resistant prostate cancer cells and other cancer cells. To our best knowledge, the SMILE method provides, for the first time, a simple yet efficient process for generating Cu(DDC)₂ NPs with high drug concentration, excellent loading efficiency, and desirable physicochemical properties. This method could potentially address drug delivery challenges of DSF/Copper based chemotherapy and facilitate its clinical translation.
POLY 51: Block-copolymer-based polyion complexes for utilization of proteins and inorganic nanoparticles

Akihiro Kishimura¹,², kishimura.akihiro.776@m.kyushu-u.ac.jp, Yiwei Liu³, Biplab KC³, Takumi Egashira³, Takeshi Mori³, Yoshiki Katayama⁴, (1) Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan (2) Center for molecular systems, Fukuoka, Japan (3) Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka City, Fukuoka, Japan (4) Kyushu Univ Dept Appld Chem, Fukuoka, Japan

Block copolymers are powerful tools to build self-assembled materials with well-controlled nanostructures, and greatly contribute to rational design of nanostructured functional materials. Herein, we have focused on polyion complex (PIC) formation, which is driven by electrostatic interaction among oppositely charged materials particularly [1]. PICs are characterized by their simple fabrication process, specifically in aqueous media, and have attracted much attention for the self-assembly of biomolecules and colloidal nano-particles toward pharmaceutical and industrial applications. By full utilization of block copolymers consisting of a neutral polyethylene glycol (PEG) chain and charged poly(amino acid) chains, we succeeded in precise tuning of PIC structures at the nanoscopic level as well as stability and physicochemical property tuning [2], which allowed for development of enzymatic nanoreactors for effective bio-imaging, therapy, and biodetoxification [3], and a novel delivery platform for water soluble low-molecular weight drugs [4]. Also, we developed a novel methodology to incorporate functional nanoparticles and proteins into unique PIC nano-architectures, and found some advanced functions, which are helpful for drug delivery applications.
Particulate elasticity and shape are crucial parameter that dictate highly specific biological functions and controlling them allows comprehensive optimization of drug delivery carriers. This talk will focus on pH- and redox-responsive poly(methacrylic acid) (PMAA)-based hydrogel particle of controllable shape and size for on-demand release of drugs in cancer therapy. When conjugated with a hepsin-targeting IPLVVLVPL peptide, these particles exhibit selective affinity to hepsin-overexpressed cancer. We will discuss how the cell type along with hydrogel shape and size controls the cell uptake kinetics and the ultimate extent of internalization. The peptide modification significantly promotes the uptake of the 700 nm hydrogel cubes by hepsin-positive MCF-7 cells due to ligand-receptor recognition but has a negligible effect on the uptake of 2-μm PMAA hydrogels. The selectivity of 700-nm IPLVVLVPL-PMAA hydrogel cubes to hepsin-overexpressing tumor cells is further confirmed by a 3- to 10-fold higher particle internalization by hepsin-positive MCF-7 and SK-OV-3 compared to hepsin-negative PC-3 cells. The integration of an active targeting moiety, pH-sensitivity and redox-triggered degradation into the polymeric networks represents a new platform for efficient delivery of therapeutics. In addition, this work has investigated the interplay of particle size, surface ligand modification and cell type on the interaction between hydrogels and cancer cells, which improves the understanding of carrier design in cancer therapy.
POLY 53: Polymer prodrug nanocarriers for anticancer therapy

Julien Nicolas, julien.nicolas@u-psud.fr. UMR CNRS 8612, Univ Paris-Sud, Chatenay-Malabry, France

We report on the design of a new class of polymer prodrug nanocarriers by using the "drug-initiated" method, which consists in the controlled growth of vinyl polymers from anticancer drug-bearing initiators to prepare well-defined and high drug content polymer prodrug nanoparticles with in vitro and in vivo anticancer activity. This method is robust and versatile as was applied to different drugs including Gemcitabine, Cladribine and Paclitaxel, to different polymers and to different drug/polymer linkers to adjust the drug release kinetics and thus the cytotoxicity. Fluorescent polymer prodrug nanocarriers can also be produced in a similar fashion from a fluorescent dye-bearing initiator. This approach was further developed to yield heterotelechelic polymer prodrugs for drug delivery, imaging and combination therapy.

We also present our recent achievements to confer degradability to vinyl polymers by using controlled radical ring-opening polymerization (rROP) using cyclic ketene acetal (CKA) monomers. In particular, 2-methylene-4-phenyl-1,3-dioxolane (MPDL) was copolymerized with oligo(ethylene glycol) methyl ether methacrylate (OEGMA) or methyl methacrylate (MMA) by NMP to produce well-defined, non-cytotoxic and degradable copolymers. This approach was eventually applied to the "drug-initiated" synthesis of degradable polymer prodrug nanocarriers with tuneable cytotoxicity towards cancer cells (Figure).
Degradable polymers are of significant interest in nanomedicine, where they are frequently used to prepare nanoparticles that can encapsulate drugs and then release them as the polymers break down. Much progress has been made using polyesters such as polylactide and polycaprolactone. However, the ability to control drug release using these polymers is limited as they may degrade more rapidly or more slowly than desired. Many stimuli-responsive polymers have been developed over the past couple of decades, but these polymers typically require many stimuli-mediated events to achieve complete polymer degradation. To address these limitations, we have been developing self-immolative polymers (SIPs), which undergo complete end-to-end depolymerization following the cleavage of a single stimuli-responsive end-cap from the polymer terminus (Fig. 1A). This presentation will describe our group’s development of polyglyoxylate SIPs and their applications in drug delivery. Polyglyoxylates were prepared with end-caps responsive to a wide range of stimuli including light, heat, weak acids, hydrogen peroxide, and reducing agents, many of which are accessible in vivo and are associated with disease states such as cancer and inflammation. Their degradation was studied in solution, as assemblies of block copolymers, in the form of nanoparticles, and as coatings. In each case, the triggered polymers underwent rapid depolymerization whereas the untriggered controls remained quite stable (Fig. 1B). This provided the selective triggered release of drug molecules. The in vitro and in vivo properties of the delivery systems were also evaluated. Overall, these studies have demonstrated that polyglyoxylates have great potential for drug delivery applications.
Aqueous solutions of some amphiphilic block copolymers are known to exhibit sol-to-gel transitions in response to temperature increase. Such thermo-gelling polymer systems have attracted great attention as injectable polymers (IPs) for biomedical applications. We have studied on thermo-gelling systems using biodegradable block copolymers of PEG and aliphatic polyesters\footnote{1}. One of the practical problems for these systems is the short duration time of the gel state in the body. The formed hydrogel tends to revert to the sol state within a short period where a large amount of body fluid exists, because the main driving force of gelation in these systems is a non-covalent hydrophobic interaction. This property is one of the obstacles of biodegradable IP systems for clinical application as implant biomedical materials. We recently reported biodegradable temperature-triggered covalent gelation systems exhibiting longer and controllable duration time of the gel state utilizing thiol-ene reaction\footnote{2}. We synthesized a tri-block copolymer of poly(caprolactone-co-glycolic acid) and PEG (tri-PCG) and attached acryloyl groups on both termini (tri-PCG-Acryl). Tri-PCG micelle solution containing hydrophobic hexa-functional polythiol and tri-PCG-Acryl micelle solution were mixed. The obtained solution was still sol state after mixing, and exhibited an irreversible sol-to-gel transition in response to temperature (Figure). The duration time of the gel state \textit{in vitro} and \textit{in vivo} (after subcutaneous implantation in rat) could be altered from 1 to 90 days just by changing the mixing ratio. We then investigated potential utility of the IP system as drug delivery systems\footnote{3} and other biomedical devices. The IP system showed sustained release behavior of GLP-1 (peptide drug for diabetes) \textit{in vivo} after subcutaneous injection in rats.
Our group currently explores the use of thermosensitive recombinant polypeptides to design safe, self-assembled, targeted drug nanocarriers by solvent-free self-assembly methods. Derived from the natural protein tropoelastin, elastin-like polypeptide (ELPs) are biocompatible, biodegradable and inert thermo-responsive protein polymers. ELPs present a reversible soluble-to-insoluble phase transition behavior (LCST) which can be exploited for solvent-free self-assembly in aqueous solution. Properly designed ELPs can self-assemble into micelles, and be exploited as biocompatible drug nanocarriers, as well as bioactive nano-objects. To avoid tedious molecular cloning steps, our group uses chemical methods to functionalize recombinant ELPs at their chain-ends or along the polypeptide backbone. Chemoselective modifications at methionine residues placed along the ELP sequence are in particular used to introduce various pendant groups to promote drug interaction (e.g., positive charges for encapsulation of nucleic acids).
Polymer-drug conjugation of small molecule chemotherapeutics to highly water-soluble and biocompatible polymers, such as poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC), imparts excellent aqueous solubility, improved pharmacokinetics, and reduced off-target toxicity to those drugs, allowing for an enhancement of antitumor efficacy. A novel polyMPC-based system incorporating temozolomide (TMZ) was developed for the treatment of glioblastoma, a highly aggressive and infiltrative brain cancer. Using a versatile TMZ-methacrylate, well-defined and water-soluble polyMPC-TMZ random and block copolymers were prepared by controlled free radical polymerization over a wide range of drug incorporations (15-50 mole percent TMZ). The aqueous solution assembly properties of the conjugates were investigated by dynamic light scattering (DLS) and transmission electron microscopy (TEM), showing the formation of nanoscale aggregates of the block copolymers. The polyMPC-TMZ copolymers exhibited enhanced solution stability of pendant TMZ moieties in physiological conditions, as demonstrated by UV-vis spectroscopy. Furthermore, polyMPC-TMZ conjugates showed architecture- and drug loading-dependent cytotoxicity in both chemosensitive and chemoresistant glioblastoma cell lines. This polyMPC-TMZ system represents a versatile application of the polyMPC-based prodrug platform which holds promise for future in vivo evaluations.
The lack of scalable and sustainable methods to prepare conjugated polymers belies their importance in many enabling technologies such as photovoltaics, light emitting diodes and field-effect transistors. Accessing high-performance poly(hetero)arene conjugated polymers via dehydration has remained an unsolved problem in synthetic chemistry and has historically required transitional-metal coupling reactions. This talk will discuss our recent efforts developing a dehydration method that allows access to conjugated small molecules and polymers. The resulting materials will also be discussed in the context of the interesting optoelectronic properties they exhibit due to non-covalent interactions along the conjugated backbone.
In this presentation, new advances in the design and synthesis of base-stable, mechanically strong, and synthetically feasible alkaline anion exchange membranes will be presented.
Conjugated polymers possess many exceptional electronic, optical and thermal properties and thus are well suited for organic semiconducting applications, such as solar cells, thin film transistors, and light emitting diodes. Of particular interest is the development of materials with narrow band gaps and broad absorption profiles for use in organic solar cells. Since the properties of organic semiconductors can be readily modified through chemical synthesis, we have turned our attention towards the design and synthesis of novel building blocks. Recently we have synthesized monomers based on the electron-rich benzo[1,2-b:4,5-b']difuran (BDF) and naphtho[2,1-b:6,5-b']difuran moieties. Our work on the synthesis and properties and utility of these polymers will be presented.
POLY 61: Matchmaking in catalyst-transfer polymerization

Anne J. McNeil, ajmcneil@umich.edu. Chemistry, University of Michigan, Ann Arbor, Michigan, United States

Living, chain-growth methods for synthesizing conjugated polymers have the potential to access to new materials with varying sequences, lengths and end-groups. In practice, however, expanding these methods to structurally complex monomers has been limited. One reason is that the polymerization mechanism relies on the catalyst to reliably ring-walk over the p-system without undergoing unproductive pathways (e.g., trapping, insertion or dissociation). Recently, we have begun identifying the most significant unproductive pathways using the computational methods. This information is then used to play “matchmaker” by designing a specific metal/ligand combination that can bypass the unproductive pathways. This approach, as well as applications of the new materials that can now be accessed, will be highlighted in this talk.
POLY 62: Using ROMP to prepare polymers with controlled structures

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

Ruthenium based initiators of ring opening metathesis polymerization (ROMP) allow the controlled polymerization of a cyclic olefins. Strained olefins can be polymerized in a controlled fashion to provide high molecular weight polymers of controlled dispersity. Over the past several years, these initiators have been used to prepare brush-block polymers of extremely high molecular weight. Block systems spontaneously phase separate into well-ordered structures. At sufficient molecular weights, the systems are photonic crystals that reflect into the IR. The systems are robust enough to make multiblock systems. These systems allow the control of the structure to yield materials with precisely designed structures for numerous applications and to study structure function relationships. Recent advances have been made in the study of the role of brush density of structure and in the synthesis of cyclic polyolefins.
The Sydlik group is developing functional graphenic materials (FGMs) that inherently induce osteogenesis in vitro and in vivo. Specifically, our modified Arbuzov reaction installs polyphosphate on the GO backbone with control over a variety of bioinstructive counter ions (Ca$^{2+}$, K$^+$, Li$^+$, Mg$^{2+}$, or Na$^+$). Ca$^{2+}$, Li$^+$, Mg$^{2+}$, and PO$_4$-$^3$. These ions are known to be inducerons, or small ions that encourage the osteogeneic differentiation of stem cells. Further, we have shown that CaPG induces osteogenesis in vivo in a mouse model. Additionally, we are refining the Claisen reaction to produce Claisen graphene (CG) that attaches stable, cell instructive moieties at the surface. We are also developing the Mitsunobu reaction to occur with GO in very mild conditions to attach sensitive small molecules and growth factors known to promote osteogenesis to the graphenic backbone. Attachment occurs via hydrolytically labile covalent bonds that enable the covalent controlled release from Mitsunobu graphene (MG). The Sydlik group collaborates with Dimension Inx, to produce free standing, porous scaffolds with 90% FGM content, using poly(lactide-co-glycolide) as a binder. These 3D printed FGM scaffolds use the power of chemistry to direct the biological healing response.
In this award address, I will describe some themes from my research in the design and synthesis of polymers. Much of my interest over the years has been captivated by electronic polymers and in our early investigations we created complex systems with integrated receptors that enabled sensing properties and the templated synthesis of complex systems. More recently we are focused on magneto-optical properties of these materials and elucidating the structure property relationships of these materials. Rigid bicyclic ring systems has also been an area of interest and we first identified the ability of these materials to create free volume in polymer films. The applications of these latter materials are multidimensional and these designs are now the basis of the highest performance gas separation materials and ion conducting membranes. I will highlight our recent work the gas and ion transport using polymer designs that create intrinsic free volume.
POLY 65: Striving for perfection: “Defect”-free brush polymer networks for improved metrology

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

Polymer networks are a ubiquitous class of materials applied across many disciplines, functioning as soft, highly modular solids with a huge variety of tunable properties. Extremely soft networks have been of particular interest for biomedical applications but are challenging to achieve in the bulk due to the presence of entanglements. By employing a network with a brush architecture, entanglements can altogether be avoided without the need for a solvent, and networks with mechanical properties comparable to biologics can be realized. Here, we both demonstrate a brush polymer network platform using ROMP and extend the potential application space of brush networks to art conservation. The ROMP-based networks were formed using a grafting-through approach, by copolymerizing mono- and di-norbornene functionalized poly(n-butyl acrylate) macromonomers with varying molecular weights and molar ratios. By tuning these handles, brush networks with moduli varying from 1 – 20 kPa and varying mesh sizes were studied and employed as a route to improved fracture metrology. Moreover, due to the extreme softness of this class of materials, analogous PDMS brush networks were studied for their ability to make conformal contact with model rough surfaces with dimensions relevant to those found in works of art and cultural heritage objects. Softer networks were found to improve conformal contact, which in turn was correlated with improved cleaning efficiency. Due to their unique architecture, brush polymer networks offer insight into important fundamental physics as well as potential use in a variety of applications.
POLY 66: Film surface fluctuation dynamics and surface segregation in the limit of dense branching

Mark D. Foster, mdf1@uakron.edu. Univ of Akron, Akron, Ohio, United States

The manner in which the surface height fluctuations of melt films of polystyrene vary with thickness for thin films has been found to vary sensitively with the branching architecture of the chain. This can be seen particularly in the case of a series of comb-branched polymers for which the architecture varies from that similar to a star to that of a densely branched comb. The surface height fluctuations of melt films of densely branched comb polystyrenes of thicknesses greater than 55nm and at temperatures more than 23 °C above the $T_{g,bulk}$ can be rationalized using a hydrodynamic continuum theory (HCT) known to describe melts of linear and unentangled cyclic chains. Film viscosities ($\eta_{XPCS}$) for three combs inferred from fits of the HCT to X-ray Photon Correlation Spectroscopy (XPCS) data are the same as bulk viscosities ($\eta_{bulk}$) measured with rheometry. For the comb most like a star polymer and the comb closest to showing bulk entanglement behavior, the deviation between the observed behavior and that expected from the HCT is greatest. However, this deviation is still smaller than that seen for less densely branched polystyrenes. The smaller magnitude of the deviation for the most densely grafted combs is due to a lack of interpenetration of the side chains when branching is very dense. While data of relaxation time versus $T$ for cyclic chains virtually collapse to a single curve when $T_{g,bulk}$ is accounted for, that is not the case for combs. $T_{g,bulk}$ and specific chain architecture both play important roles in determining the surface fluctuations.

We have also considered the effect of the dense branching on surface segregation in blends of linear and comb-branched polystyrenes. The comb-branched chains are strongly preferred at the surface and the experimentally determined surface segregation can be compared with self-consistent field theory calculations.

Surface fluctuations vary as the density of grafting varies.
The functionalization of inorganic and organic surfaces by highly branched, functional polymer adsorbates enables a fine tuning of the interfacial physicochemical properties and allows one to determine the interaction of the modified support with the surrounding environment. This is valid on metal oxide surfaces, where graft copolymers featuring different compositions and side chain topologies can assemble forming biopassive and lubricious interfaces. Alternatively, from similar inorganic substrates, bottlebrushes with controlled molar mass and side chain length can be grown exploiting controlled radical polymerization (CRP) methods, enabling a broad modulation of steric stabilization of the surface, and tuning its biopassivity and nanotribological properties.

The design concepts and functionalization strategies applied for model inorganic materials can be additionally enlarged to complex tissue surfaces such as articular cartilage, where highly branched, biocompatible copolymers can replace structurally similar biomacromolecules responsible for protection and lubrication of the underlying tissue.

In this contribution, the influence of polymer architecture and composition on the fabrication and properties of graft copolymer- and bottlebrush-based interfaces will be discussed, bringing the above-mentioned cases as examples of highly-technologically-relevant applications.
POLY 68: Enthalpy and entropy-driven segregation of mixed bottlebrush polymers in linear polymer matrices

Hao Mei¹, hm11@rice.edu, Travis Laws², Jiabei Li¹, Adeline Mah³, Gila Stein², Rafael Verduzco¹. (1) Dept of Chemical and Biomolecular Eng, Rice University, Houston, Texas, United States (2) Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Knoxville, Tennessee, United States (3) Materials Science and Engineering, University of Houston, Houston, Texas, United States

Bottlebrush polymer additives in linear polymer matrices spontaneously segregate to surfaces and interfaces driven in part by the branched architecture and high density of side-chains. Prior work has primarily focused on athermal blends, where the composition of the bottlebrush side-chains matches that of the linear matrix. Here, we investigate segregation of bottlebrush polymers with mixed and random copolymer side-chains in a linear polymer matrix and utilize time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to elucidate the distribution of bottlebrush polymers as a function of thermal annealing time, linear polymer molecular weight, and side-chain composition. Specifically, bottlebrush polymers with mixed polystyrene (PS) and polymethyl methacrylate (PMMA) side-chains were synthesized and analyzed in blends with both linear PS and PMMA. For comparison, bottlebrush polymers with styrene-co-methyl methacrylate side-chains were synthesized and analyzed in blends with both linear PS and linear PMMA. Bottlebrush additive segregate to film interfaces (film-air and film-substrate) as additives (10 wt %) in both linear PS and linear PMMA matrices. Bottlebrush polymers segregate to film interfaces more strongly with increasing linear matrix molecular weight, and segregation is strongest after casting and prior to thermal annealing. With thermal annealing, the surface segregation of bottlebrush polymers with random copolymer side-chains disappears while that of bottlebrushes with mixed side-chains is stable. We hypothesize that this is driven by the stronger repulsive enthalpic interactions between the bottlebrush side-chains and linear polymer matrices. This study provides insight into the phase behavior of mixed bottlebrush polymers with and linear polymers and demonstrates that bottlebrush polymers with mixed composition side-chains can be used to tailor properties of film interfaces.
Good interfacial compatibility is the key to realize the full potential of metal-organic framework-based mix matrix membranes for gas separation. Here we report a new approach that uses polyimide brushes covalently grafted on the MOF surface to engineer the MOF-polymer interface. Benefiting from the strong brush-brush interaction, polyimide grafted MOF particles can form a stand-alone membrane at near 90 wt% MOF loading without the assistance of polymeric matrix. Compared to traditional mixed-matrix membranes, the modified membranes exhibit significantly improved ductility, reduced interfacial tearing phenomenon under shear force, decreased matrix chain mobility, and improved plasticization resistance against CO₂. Most importantly, with increasing MOF loading, only the modified membranes exhibit a simultaneous increase of selectivity and permeability for CO₂/N₂ and CO₂/CH₄ separation, following the trend predicted by the modified Maxwell model.
Attaching mesogens to block copolymer backbones (BCP) can result in a rich interplay of self-assembly on multiple length scales, and provides new opportunities to control nanostructure development in the resulting liquid crystalline (LC) materials. At the same time, the bottlebrush motif leads to interesting new structure and dynamics in homopolymers and block copolymers alike, relative to traditional linear polymers. Here, we explore the structure and properties of two different bottlebrush BCPs in which one component of the system is a mesogen-containing side chain. In the first case, the BCP is derived by sequential ring-opening metathesis polymerization (ROMP) of poly(lactide) and mesogen-containing macromonomers. In the second case, the system is a bottlebrush realized by ROMP of a mesogen-containing oligodimethylsiloxane (ODMS) diblock macromonomer. We examine in detail the influence of mesogen type, mesogen spacer length, backbone molecular weight, side-chain molecular weight, mesogen attachment functionality, and overall chain topology, on the structure and properties of the systems in question. Despite the steric hindrances associated with the densely grafted norbornene backbones, both systems form well-ordered microphase separated nanostructures in all cases studied. However the phase diagram of the liquid crystalline (LC) bottlebrush derived from ODMS/mesogen based diblock macromonomers deviates sharply from traditional coil-coil BCPs, while that of the lactide-mesogen system shows little deviation. We discuss opportunities for applications of these unique materials in BCP lithography and as shape memory materials, based on their ability to form ordered nanostructures readily at sub-10 nm lengthscales, their propensity for surface-induced ordering and the use of magnetic fields to direct the orientation of their self-assembled structures.

Bottlebrushes formed ROMP of 1,2 or 3-mesogen containing diblock macromonomers exhibit highly ordered birefringent optical textures.
Molecular bottlebrushes are branched polymers with very high graft density which results in very rigid backbones. This conformation results in very large entanglement molecular weight ($M_e$) and very low elastic modulus, which could be used to produce super-soft elastomers. Despite the growing interest in bottlebrush polymers, very few studies have been devoted to their linear viscoelastic response, whereas, to our knowledge, no study has been reported on their extensional rheology or their response to cold-drawing. We synthesized a series of ultra-high molecular weight (UHMW) α-olefin molecular bottlebrushes by organometallic coordinative insertion polymerization of 1-alkenes with lengths ranging from 8 to 18 carbons. The molecular weight of these polymers are in the order of a few million g/mol, which allows accurate measurement of their rubbery plateau modulus ($G_N^0$) and their $M_e$ values. The latter is an increasing function of the side chain length ($N_{sc}$) and takes values ranging from 25 kg/mol (for poly(1-octene)) to 115 kg/mol (for poly(1-octadecene)). These UHMW bottlebrush polymers have sufficient melt strength to perform extensional rheology measurements using commercial extensional rheometers. Bottlebrush chain alignment was measured using a novel method that combines the use of extensional rheometry with time-resolved SANS. Those measurements were used to confirm the direct correlation between strain hardening and bottlebrush chain alignment, both in the melt and in the semi-crystalline state. In situ WAXS and SAXS reveal that chain alignment is concomitant of self-assembly of the bottlebrush molecules into hexagonal packed cylinder phases induced by uniaxial extension. This work reports the first direct evidence of strain-induced alignment and packing of molecular bottlebrushes and their relation with the macroscopic rheological and mechanical responses.
Graft block polymers containing poly(4-methylcaprolactone)-b-poly(±-lactide) (PMCL-PLA) side chains and high PLA content were synthesized with the aim of producing tough and sustainable plastics. The graft block polymers exhibit a 20x increase in toughness over PLA homopolymer while maintaining a high elastic modulus. However, these materials experienced physical aging and became brittle over time. For short aging time, \( t_a \), the samples were ductile, where shear yielding was the primary deformation mechanism. A double yield phenomenon emerged at intermediate \( t_a \) involving crazing followed by shear yielding. At long \( t_a \) the samples eventually became brittle and failed at relatively small strain following crazing. PLA content strongly governed the time to brittle failure, where a PLA homopolymer graft polymer embrittled in 1 day and an 86% PLA graft block polymer embrittled in 35 days. Architecture was also a significant factor in increasing the persistence of ductility of linear block polymers: a linear triblock aged three times faster than a graft block polymer with the same PLA content. Pre-straining the graft block polymers also significantly toughened the PLA materials. Physical aging was eliminated in the pre-strained polymers, which remained ductile even at very long \( t_a \), past 60 days. The pre-strained graft block polymers also demonstrated shape memory properties. When heated above \( T_g \) the stretched polymer rapidly returned to its original dog bone shape and completely recovered the original mechanical properties of the unstrained materials. These results show that graft block polymers can be used to make tough, durable, and sustainable plastics, and demonstrate the importance of studying the mechanical performance of materials over a wide range of timescales.
Microplastics (MPs) are < 5 mm sized plastic particles that are now ubiquitous in oceans and rivers. A combination of physical, chemical, and radiative (UV light) processes degrade large plastic materials into small fragments (MPs and even smaller nanoplastics) and leach chemical by-products. Once small (< 5 mm), MPs become highly mobile, can adsorb other pollutants (such as DDT, PCBs, dioxins), and can be ingested by biota where MPs can have direct effects on an organism or bioaccumulate. The study of MPs began in the 1970s, but has seen a recent resurgence after 2004. During the past 15 years, studies of MPs have focused on marine environments with less than 4% of studies focused on freshwater systems. More recent work is showing that MPs in freshwater systems can be found in concentrations just as high as in marine environments although much less is known about their transport, fate, and affect in freshwater systems. Of the MPs studies in freshwater systems, the focus has been on looking for MPs in sediments on the bed of rivers and streams. MPs are small, lightweight particles that should behave most similarly to non-cohesive fine sediment and therefore follow similar transport and deposition pathways and processes. As such, one should expect to find much higher concentrations of MPs in floodplains than on the bed of rivers and streams. In this research, soil samples were collected downriver of plastic point sources including sediments and floodplains. MPs were separated from the soil by size and density. Larger amounts of MPs were found in the floodplains. The average particle size and distribution suggested a variety of degradation processes including mechanical and photo-oxidative. Fourier transform infrared (FTIR) spectroscopy indicated that the MPs contained depolymerized and oxidized polyolefins and other commonly found packaging polymers.
Poly(lactic acid) is the best known biorenewable polymer. It can be synthesized from a number of starting materials including corn starch, sugarcane, and cavassa root. In 2017, PLA was the third largest produced biobased plastic behind poly(ethylene terephthalate) and polyamides; however, it is not biodegradable. Previous studies have shown some degradation is possible under specific conditions but not in purely aqueous environments. To combat this poor degradation, we have incorporated a hydrophilic, biobased comonomer during polymerization of L-lactide. These copolymers have an increased hydrophilic composition, helping to draw water into the polymer to facilitate degradation.
Among the many factors that influence polymer degradation in aqueous environments, hydrophobicity represents an important contributor. Based on a combined experimental and computational investigation, this presentation will elucidate a hydrophobicity trend for oxygen containing functional groups frequently encountered in monomers and polymers. As such, octanol-water partition coefficients (LogP) values for polymers and models compounds were instrumental in establishing a trend for functional groups with 1 to 3-oxygen atoms.
A new synthetic route for bio-based, highly-thermostable polyamides with a rigid N-substituted pyrrolidone ring from salts of various diamines and a biomonomer itaconic acid, which was mass-produced by the fermentation of *Aspergillus terreus*, was developed. We used monomer-salts composed of itaconate anions and aliphatic diamino cations. These salts converted into polyamides through the aza-Michael addition, followed by intramolecular cyclization with condensation to create the pyrrolidone ring in the polymer main-chain in the presence of sodium dihydrogen phosphate. The polyamides showed molecular weights ranging over 28 000 and Tg values over 87 °C higher than those of conventional nylons. The itaconic-acid derived polyamides showed a ring-opening reaction under the ultraviolet irradiation in water and the resin showed a photo-corrosion and additionally in-soil-corrosion.
Combination therapies – or drug ‘cocktails’ – are often employed to combat diseases such as cancer, HIV/AIDS, and multi-drug resistant (MDR) bacteria; and although effective, the drug combinations can be incredibly toxic and invasive. Nano-based drug delivery systems can be advantageous in this regard since the toxic drugs can be shielded inside the nanomaterial and off-target toxicity issues can be reduced. However, it is still a major challenge to find a one-size-fits-all drug delivery vehicle that can be loaded and unloaded with any combination of small-molecule drugs without having to change the chemistry significantly each time a new clinically relevant combination is needed. My research group has recently developed functional macrocyclic monomers that possess selective drug binding sites that can encapsulate a wide range of drugs through specific interactions and can be linked together via ring-opening metathesis polymerization to make multi-block copolymers. These multi-block copolymers can be crosslinked non-covalently to make nanoparticles, and the resultant delivery vehicle represents a universal platform for combination therapeutics that my group is investigating as a treatment against MDR bacteria and different types of cancer.
Polypropylene has been extensively utilized as an implantable biomaterial since shortly after it was commercialized in the 1960s. Material characteristics like strength, flexibility, chemical stability, biocompatibility, ease of manipulation, and manufacturability contribute to its ubiquitous use as a biomaterial for applications including hernia repair, pelvic organ prolapse, stress urinary incontinence, and general surgery. Although mesh made from stabilized polypropylene has been a common and successful surgical tool for decades, its widespread use coupled with developments in surgical approaches and materials characterization capabilities has refocused attention onto the in vivo performance of these products. Polypropylene’s hydrocarbon backbone is resistant to hydrolytic and proteolytic degradation; however, the tertiary carbon bond is known to be susceptible ex vivo to oxidation under specific conditions. Various groups have documented an observable ‘crust’ by scanning electron microscopy (SEM) after explantation of polypropylene mesh, sometimes hypothesizing that the crust is degraded polypropylene that is evidence of in vivo oxidation. This presentation will focus on chemical, physical, and thermal characterization of non-oxidized, intentionally oxidized, and explanted polypropylene in a comprehensive approach to assess and demonstrate the oxidative stability of polypropylene meshes for in vivo use.
POLY 79: Chemo-enzymatic synthesis and free radical polymerization of renewable acrylate monomers from cellulose-based lactones

Florian Diot-Néant²,¹, floriandiotneant@chem.ufl.edu, Enita Rastoder¹, Stephen A. Miller¹, Florent Allais². (1) Chemistry, University of Florida, Gainesville, Florida, United States (2) Chaire ABI - AgroParisTech, AgroParisTech, Reims, France

The exponential production of petroleum-based polymers and the increasing proliferation of plastic residues in the oceans have raised concerns regarding our impact on the environment and our intensive consumption of non-sustainable materials. Let alone the necessity to develop greener processes, the depletion of fossil resources is a severe issue that needs to be addressed. New alternatives using lignocellulose have been explored to access valuable bio-based synthons such as (S)-γ-hydroxymethyl-α,β-butynolide (HBO) that can be readily obtained from cellulose-derived levoglucosenone. In this work, HBO and (S)-γ-hydroxymethyl-α,β-butyrolactone (2H-HBO) were subjected to a Candida antarctica type B lipase-mediated transesterifications in presence of methyl methacrylate to form (S)-γ-hydroxymethyl-α,β-butynolide methacrylate (HBO-m) and (S)-γ-hydroxymethyl-α,β-butyrolactone methacrylate (2H-HBO-m), respectively. Co-polymerizations with methacrylamide (MAA) and methylene-γ-valerolactone (MGVL) were then performed via free radical polymerization process in an attempt to both increase solubility and improve thermal properties. The resulting high molecular weight co-polymers exhibit a broad range of Tg (94 °C - 187 °C) depending on the incorporation ratio of the co-monomers. Inspired by the synthesis of MGVL, THP-2H-HBO was α methylenated to produce methylene-tetrahydropyranyl (S)-γ-hydroxymethyl-α,β-butyrolactone (M-THP-2H-HB). This novel monomer was then co-polymerized with methyl methacrylate giving material with molecular weight up to 44 kDa and high thermal properties.
POLY 80: Insight into cartilage supramolecular structure and biological function

Ferenc Horkay, horkayf@helix.nih.gov, Peter J. Basser. Section on Quantitative Imaging and Tissue Sciences, National Institutes of Health, Bethesda, Maryland, United States

Cartilage is a connective tissue that provides a smooth, lubricated surface for articulation and facilitates the transmission of loads with a low frictional coefficient. In diseases, such as osteoarthritis, the mechanical properties of cartilage (e.g., its compressive resistance and load-bearing ability) are reduced due to changes in both the chemical composition and the physical properties of its macromolecular constituents. Cartilage proteoglycans (PGs) exhibit a hierarchical bottlebrush structure at multiple length scales. We investigated the hierarchical structure of cartilage PGs and their roles in cartilage function using an array of complementary experimental techniques, including osmotic swelling pressure measurements, small angle neutron and X-ray scattering measurements (SANS and SAXS), light scattering and atomic force microscopy. We proved that aggrecan and its complexes with hyaluronic acid (HA) exhibit microgel-like behavior. The small size and dispersed character of the microgel particles ensure rapid response to sudden changes in external forces, e.g., in shock absorption. Under compressive load, microgel particles deswell and release lubricating fluid, reducing the friction of movement within the joint. An unexpected feature of PG assemblies is their insensitivity to the presence of calcium ions. Over the length scale range (10 – 500 Å) explored by SANS, SAXS and light scattering, no detectable structural change occurs, even at ionic strength (0.2 M) which is much higher than the physiological concentration range. Such stability is a prerequisite for the function of cartilage in bone formation.

Figure 1. Variation of the elastic and osmotic moduli as a function of the position in mouse cartilage sample.
Carbon dioxide chemistry has attracted much attention from the scientific community due to global warming associated with positive carbon accumulation. CO₂ capture and sequestration (CCS) from fossil fuel combustion represents a critical component of efforts aimed at stabilizing greenhouse gas levels in the atmosphere. On the other hand, CO₂ is very attractive as an environmentally friendly feedstock for making commodity chemicals, fuels, and materials.

Porous organic polymers (POPs) have distinctive properties such as large surface areas, low skeleton density, good physicochemical stability and flexibility for rational design, showing quite promising potential for efficient CO₂ adsorption and transformation, especially POPs with CO₂-philic functionalities. Our group focused on CO₂ activation and chemical conversion into value-added chemicals, to construct reaction media composed of ionic liquids/water (organic solvents or compressed CO₂), design various reaction pathways and realize controllable synthesis of micro- and mesoporous organic polymeric materials functionalized with “CO₂-philic” groups (fluoro-, nitrogen-, phosphine-containing groups or ionic ones). Progresses have been made about regulating the structures and morphologies of materials by reaction medium; In addition, bifunctional catalysts have been prepared via immobilizing transition metal complex/nanoparticles onto the as-prepared polymers; CO₂ adsorption capacity, activation and catalytic activity of the resultant materials have been investigated, ultimately realizing efficient CO₂ conversion under mild conditions; The synergistic effects between the functionalities within the backbone, metal catalytic center and porosity nature have been uncovered, getting deeper insight of physical, chemical and catalytic characterization of the porous organic polymers and establishing reliable scientific basis for CO₂ utilization.
POLY 82: Synthesis of morphology-tunable functional porous polymers from diblock copolymers hyper-cross-linking self-assembly strategy

Xu Yang, xy100904087@163.com, Kun Huang. School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, China

Functional porous polymers have been received great attention due to their potential applications in the fields of biomedical applications, gas storage, gas/liquid separations, and catalysis. Especially, the existence of cavity spaces in porous materials can substantially increase accessibility of the active sites by enhanced diffusion, resulting in overall efficiency increase. Such porous polymers usually possess an interconnected pore structure and the morphologies of pore structure and properties of the supports can be controlled during fabrication. However, it is worth noting that the most of the reported researches are focused on the preparation of disordered porous structure, and reports on the synthesis of functional porous polymers with special morphology from diblock copolymers remain rare.

Here, we report on a hyper-cross-linking self-assembly strategy for preparation of various functional porous polymers based on different diblock copolymer precursors (Scheme 1). For the polylactide-b-polystyrene/4-diphenylphosphinostyrene (PLA-b-P(S/DPPS)) and the polylactide-b-poly(N-vinylcarbazole) (PLA-b-PNVC) diblock copolymers, the PLA is chosen as the chemically degraded domain and the DPPS or NVC not only plays as the cross-linkable monomer but also serves as the functional groups for binding the metal species for efficient heterogeneous selective hydrogenations or capturing the radionuclide iodine-129. These great performances could be attributed to the advantages of the 3D honeycomb-like or hollow spherical structure, which allows the accessible active heteroatom sites to be efficiently exposed toward reactants or contaminant. Thus, we believe this new strategy may open a window for the preparation of porous organic polymers with special morphologies and various functionalizations for potential applications including energy storage, adsorption, separation, and catalysis.

Scheme 1. Fabrication of honeycomb-like and hollow spherical functional porous polymers via hyper-cross-linking self-assembly strategy from diblock copolymers.
Novel fluorescent conjugated polymers were synthesized by a Suzuki polycondensation reaction, with high yields and low polydispersities achieved through optimization of the reaction conditions. The photophysical properties of the resulting high quantum yield, highly conjugated polymers were investigated, both as well-dissolved solutions in chloroform and as nanoparticle suspensions in water. A number of these polymers have Stokes shifts of over 100 nm and demonstrate different fluorescent properties in aggregated verse non-aggregated states. Preliminary studies on these polymers suggest they could be used for the detection of common bisphenols, including bisphenol A (BPA), bisphenol F (BPF), and bisphenol S (BPS).
The desirable material properties of vinyl polymers, such as polyolefins, have made them ubiquitous in the world today. Unfortunately, they have proven to be highly resistant to various chemical recycling methods and those known methods and processes are plagued with poor selectivity and harsh conditions. Polar vinyl polymers, such as poly(methyl methacrylate) (PMMA), on the other hand, have been shown to depolymerize to virgin quality monomer under pyrolytic conditions (450 °C). Previously we have reported various polymerization methods to synthesize polar vinyl polymers based on biomass-derived cyclic analogs of linear MMA which showed superior materials properties to PMMA, offering a more sustainable alternative to the petroleum-based PMMA. In this study, we have investigated the chemical recyclability of such renewable polar vinyl polymers and achieve a high recovery yield of the pure monomer, attributed to the cyclic ester structure of the polymer repeat unit. The results of these studies, along with the mechanistic insights and catalytic selection for the chemical recycling, will be discussed.
Cellulose nanocrystals (CNCs) are highly crystalline rod-like nanoparticles that can be isolated from a variety of renewable cellulosic materials. CNCs have gathered a lot of attention as an important green nanomaterial due to their inherent properties, such as high crystallinity, low density, high elastic moduli and high aspect ratio. In this work, CNC was isolated from *Miscanthus x. Giganteus* stalks and functionalized with carboxylic acid groups. Polymethacrylate polymer was synthesized via activators regenerated by electron transfer atom transfer radical polymerization and grafted to the functionalized CNC. The modification ratio was determined by thermal gravimetric analysis, and the polymer-grafted CNC exhibited thermal response in ionic liquid at around 45°C.
POLY 86: Side-chain flexibility competes with hydrogen bonding on properties of supramolecularly crosslinked polyesters

Qianhui Liu1, ql17@zips.uakron.edu, Chao Wang3, Yuanhao Guo3, Abraham Joy2. (1) Polymer Science, The University of Akron, Akron, Ohio, United States (2) Dept of Polymer Science, University of Akron, Akron, Ohio, United States (3) Department of Polymer Engineering, The University of Akron, Akron, Ohio, United States

Hydrogen bonded polymers are of great interest owing to their reversible and dynamic nature of interactions, from which many unique and fascinating functions are achieved. Most of the interesting properties in polymers with secondary amide group, like nylons and proteins originate from the formation of hydrogen bonds. The studies on these materials usually are focused on the impact introduced by hydrogen bonding interactions, whereas the effect of chain flexibility is often neglected.

We studied the design and development of polyesters containing one ester-propyl group (P(1EP)), one amide-propyl group (P(1AP)) and two amide-propyl groups (P(2AP)) in the side chain. The results showed that P(1EP) and P(2AP) had the lowest and highest $T_g$, respectively. P(2AP) displayed the highest Young’s modulus and shortest elongation at break among the three materials at room temperature. The hydrogen bonds functioned as physical crosslinks, which strengthened the material and limited chain mobility. Interestingly, we observed that at higher temperature ($T_g + 50 \, ^\circ C$), the rheological study showed that P(2AP) had the shortest chain relaxation time, as well as the lowest zero shear viscosity and moduli. The results indicate that there is a competition between side-chain flexibility and hydrogen bonding interaction. The addition of the second amide-propyl group in the side chain improves processability at higher temperature due to the low viscosity, yet gives better mechanical properties at room temperature.

We will discuss the structure property relationships for this class of materials and how to achieve desirable material properties by modulating environmental conditions like temperature, humidity, and selecting the number of amide groups in the side chain.
Siloxane surfactants have been widely explored in the context of cosmetic and technical applications due to their environmental sustainability and easy accessibility. Especially polyether-siloxanes have been well established as an alternative to expensive and persistent fluorosurfactants for the stabilization of water-in-CO₂ microemulsions due to their low surface tension and high solubility in supercritical CO₂.

Several well-defined polyol-siloxane surfactants were successfully synthesized by anionic ring opening polymerisation of ethylene oxide. A variety of alcohols was used as initiators to achieve multifunctional chain ends such as allyl- or hydroxyl moieties. Addition of 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) to terminal double bonds via hydrosilylation led to an amphiphilic structure of the polymer. By copolymerization of ethylene oxide with propylene oxide or 2-isopropylidene glyceryl glycidyl ether (IGG) the solubility and consequently the surface-active behaviour of the surfactants can be tailored. By (block)copolymerization with different ratios of allyl glycidyl ether (AGE), leading to a differing siloxane content, a variation of the HLB value and thus adjustable thermal properties and micellization behavior was achieved. All surfactants were characterized by ¹H NMR, SEC, MALDI ToF, DSC, TGA, CMC, DLS, and TEM measurements.

Example structure of the polyol-siloxane surfactant Gly-P(EGₙ-co-GGₘ)-b-(AGE-HMTS)ₚ.
Classical radical polymerization has led to the creation of robust materials such as Styrofoam and Plexiglas, which have made significant impacts on modern society. A fundamental element of this process is the creation of polymers with non-degradable, all-carbon backbones. A method to alter this paradigm has long existed through radical ring-opening polymerization (rROP). This method is attractive, as it enables new types of functional groups to be incorporated into the backbone of radical polymers, such as esters, that permit degradation; however, poor reactivity with many important monomer families (styrene, acrylates, and acrylamides) has limited the adoption of this polymerization strategy in next-generation materials. In this work, we have developed a new class of rROP monomers that uses a thiocarbonyl as a reversible radical acceptor to overcome classical issues of monomer reactivity and compatibility with living polymerization techniques. Further, the modular design of the thionolactone monomer allows for easy structural modifications to tune the stability of the propagating radical species. This has resulted in a versatile method to copolymerize challenging monomer families and yields thioester copolymers that are chemically and photochemically degradable.
POLY 89: Additive manufacturing for air force applications: Design and characterization of advanced inks and filament feedstock

Hilmar Koerner, hilmar.koerner@outlook.com. Composites Branch, Air Force Research Laboratory, WPAFB, Ohio, United States

Due to the attractive opportunities in prototyping, parts reduction and complexity enabled capabilities, additive manufacturing of metals, polymer-based materials and composites has seen a significant boost over the last five years. Despite the advancement in AM, current off-the-shelf materials are very limited in property space and do not exhibit the properties necessary for demanding applications, such as aerospace or automotive applications in which durability, thermo-oxidative stability and low creep under extreme conditions (high temperature, humidity, oxygen) are key requirements. This presentation will showcase several routes that lead to feedstock materials that match properties of current state-of-the-art chemistries used for conventional polymer matrix composites, including selective laser sintering, fused deposition modeling and direct-write processes. For example, newly designed resin systems allow 3D printing of parts with service temperatures well above 300°C and excellent thermo-oxidative stability. Synthesis, formulation, feedstock development and 3D printing of these new materials and their thermo-mechanical properties and structural and dynamics evolution during printing will be presented.
The demand for new, advanced polymers for 3D printing continues to increase as the potential of the process to design and produce structures with desirable material properties for specialized applications is realized. Molecular dynamics simulations are an important approach to assist in understanding of polymers in general, and characterization and determination of the structure/property relationships for polymers used in 3D printing will also benefit from this approach. As well as the properties of the final material, properties of the melt are of considerable importance. Molecular simulation algorithms can be used to determine the properties of polymer melts formed during 3D printing processes and to analyse which molecular structural features are most important. It therefore has potential to provide fundamental understanding of the processing of the materials.

A property of considerable interest is the viscosity which can be determined using molecular dynamics simulation at equilibrium or far from equilibrium, as well as bulk or confined systems. It is challenging to accurately calculate polymer viscosities due to their dependence on the length of the polymer, its shape and also because there are multiple relaxation times to consider. The results are also sensitive to the force-fields used to model the polymer interactions. In this presentation we will consider how well different methodologies perform. Due to limitations on computer time and memory, bulk systems are modelled as relatively small periodic simulation cells. In the first part of this presentation we will discuss how this minimum system size varies with the length of a polymer. We will also discuss viscosities of typical polymers of interest in 3D printing and compare the results of different algorithms, molecular structures and force fields. The convergence of the results and their ability to reproduce experimental trends and values at a range of typical temperatures will be discussed in this presentation.
Frontal polymerization (FP) is a promising curing strategy that substantially reduces manufacturing burdens by employing the enthalpy of polymerization of the monomer to provide the energy for materials synthesis, rather than requiring an external energy source. In FP, a solution of monomer and latent initiator is heated locally until the initiator is activated towards the polymerization of the monomer, producing heat from the polymerization, which further drives the reaction. The autoactivation process produces a propagating reaction wave that rapidly transforms the available monomer into polymer. This talk will discuss the use of FP for additive manufacturing of multifunctional thermoset polymers. Thermose set polymers and composites present significant challenges for additive manufacturing due to the required speeds of printing in comparison to the time required for the curing reaction, relaxation of the printed ink, interfacial bonding of the printed layers, and integration of high aspect ratio fibers, among many other factors. Our recent research has demonstrated that FP offers a unique capability to print neat thermosets as well as particle and fiber reinforced composites.

Our printing approach is based on the frontal ring-opening metathesis polymerization of endo-dicyclopentadiene (DCPD) using a thermally activated ruthenium catalyst. Tuning of the inhibitor concentration of the DCPD or the addition of nanoparticle allows access to a range of rheological profiles between low-viscosity liquid and free-standing elastomeric gel – all of which frontally polymerize upon thermal activation. The gel is amenable to 3D printing by extruding from a print head and frontally polymerizing immediately upon exiting the nozzle, allowing for the simultaneous freeform printing and curing of thermosets. We are developing computational models to guide the processing by relating the deposition speed to temperature, flow rate and rheological properties such as viscosity. Matching the print head velocity to the front velocity allows for the manufacture of freeform complex architectures not possible with traditional additive manufacturing approaches.
A complete understanding and design of polymer chemistry and material design requires access to molecular characteristics. A realm of structural variations exist if macromolecules are involved. Already for linear polymers there is the variation of length, copolymer composition and monomer sequences. For branched polymers this is even further complicated with the location of the branching points and the composition of the branches. In the present contribution, it is highlighted that a combination of advanced modeling and experimental analysis allow to characterize polymers at the molecular level. Main focus is on poly(2-oxazoline synthesis), including the model-based design the of synthesis conditions toward well-defined functional copolymers in view of e.g. polymer therapeutics and hydrogels. Both low and high chain length polymers are covered. A future outlook toward complex topologies such as network polymers is also provided.

Example of model-based design toward well-defined functional copolymers: low and high average chain length: left and right
Matthias Barz, barz@uni-mainz.de. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

Polypept(o)ides have been defined by my group as copolymers in which a polypeptoid, e.g. polysarcosine (N-methylated glycine), is combined with polypeptide segments. While a hydrophilic polysarcosine block can provide “stealth-like” properties (reduced protein interaction and non-immunogenicity), proteinogenic amino acids, e.g. lysine, glutamic acid, (homo)cysteine, etc. introduce the desired chemical functionality. Therefore, polypept(o)ides allow for the synthesis of functional nanoparticles completely based on endogenous amino acids.

Over the last years several polymer architectures like (multi) block copolymers and graft copolymers have been synthesized and characterized with the goal to develop functional systems for various application.

In this lecture I would like to report on the recent progress of polypept(o)ide based materials and their application in different fields of polymer research. A strength of polypept(o)ides is their high biocompatibility and functionality, which allows for various applications in diagnosis and therapy. Together with a very robust and scalable synthesis important requirements for biomaterials are met, which will lead to the first clinical phase 1 study of these materials in 2019.
POLY 94: New stimuli-responsive materials via the Spontaneous Zwitterionic Copolymerisation (SZWIP) of 2-oxazolines

Kristian Kempe, kristian.kempe@monash.edu. ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Monash Institute of Pharmaceutical Sciences, Monash University, Melbourne, Victoria, Australia

The spontaneous zwitterionic copolymerization (SZWIP) is a relatively unknown polymerization technique, which provides access to (predominantly) alternating copolymers. Despite its versatility and the availability of a large range of compatible monomers it has only recently gained renewed attention. The SZWIP is believed to occur via a zwitterionic intermediate that is formed upon the reaction of an electrophilic (Me) and nucleophilic monomer (Mn) without the addition of a catalyst or initiator. Depending on the monomers chosen the SZWIP enables the straightforward synthesis of different degradable polymers such as poly(amino ester)s, poly(ester amide)s and poly(phosphoester)s.

Motivated by literature from the 1970s we started to explore the potential of the SZWIP for the synthesis of “(bio)degradable poly(2-oxazoline)s”. In this presentation, our latest efforts in the synthesis of functional polymers based on SZWIP of cyclic imino ethers (CIEs) and acrylic acid will be discussed (Figure 1). We found that under optimal conditions telechelic alternating oligomers can be prepared, which can be employed as macromonomers in redox-initiated RAFT polymerisations. The modularity and functionality of the NPAE macromonomers provide access to dual responsive comb polymers of varying hydrophilicity and enables their post-polymerisation modification via amidation reactions. Moreover, we carefully identified the different species obtained by the SZWIP and based on organic model compounds evaluated their contribution to the polymer properties.

![Figure 1. Functional oligomers obtained by SZWIP.](image-url)
POLY 95: Straightforward route to new poly(2-oxazoline)s via acylation of well-defined polyethyleneimine

Ondrej Sedlacek, on.sedlacek@gmail.com, Richard Hoogenboom. Department of Organic and Macromolecular Chemistry, Ghent University, Gent, Belgium

Herein, we describe a method for the synthesis of new poly(2-alkyl-2-oxazoline)s (PAOx) based on poly(2-ethyl-2-oxazoline) (PEtOx). A well-defined linear polyethyleneimine was first prepared from PEtOx by controlled acidic hydrolysis of its side-chains followed by re-acylation with different carboxylic acids. The described synthetic protocol is universal and can be extremely versatile, especially for PAOx that are difficult to prepare by conventional cationic ring opening polymerization due to the monomer interference or degradation. To demonstrate the versatility of this protocol, we synthesized a series of new “superhydrophilic” PAOx containing side-chain ether groups with potential in the biomaterials science, a series of high molar mass poly(2-methyl-2-oxazoline)s, as well as different thermosensitive poly(2-dialkylamino-2-oxazolines).
α-Amino acid N-thiocarboxyanhydrides (NTAs) are much more stable than the corresponding N-carboxyanhydrides. The syntheses of NTAs are done in open-air and do not need phosgene or its derivatives as a starting reagent. Amines initiate their controlled ring-opening polymerizations (ROPs) to produce well-defined poly(amino acid)s.

Hydroxyl groups are much less active than amine initiators. Certain nucleophiles including water, phenol and alcohol do not affect NTA ROPs. In this presentation, we demonstrate the controlled ROPs of amino acid NTAs in the presence of water and the mechanism of water involved in polymerization. Commercially available solvents are able to used for NTA ROP without purification, which releases the burden to dehydrate solvents in the synthesis of poly(amino acid) materials. As an application, diblock copolymers of polyDOPA-b-polysarcosine chelate iron cations to be used as a MRI contrast agent.
As one of the most promising alternatives to poly(ethylene glycol), poly(2-oxazoline)s do not offer yet the same broad functionalization scope. Particularly, chain-end functionality is highly desirable when it comes to modify surfaces or create advanced macromolecular architectures.

In this presentation, new routes for the preparation of heterotelechelic poly(2-oxazoline)s will be discussed. Both alpha- and omega functionalizations will be described. First, by employing protected initiators, we show that is possible to produce poly(2-ethyl-2-oxazoline)s (PEtOx) with maleimide or thiol alpha functionalities. These are then exploited for further chain-end modifications, protein conjugation, as well as for surface patterning. Secondly, direct termination of the active chain end during cationic ring-opening polymerization affords omega functionality. This route enables the introduction of azide, dithiobenzoate, and norbornene moities, which were subsequently utilized for the synthesis of various PEtOx-stabilized (functional) nanoparticular architectures, such as crosslinked star micelles, crew-cut micelles, nanofibers, and nano/microvesicles.
POLY 98: Development of a two-dye-system based on PMMA-graft-OEtOx graft copolymers

Irina Muljajew\textsuperscript{1,2}, irina.muljajew@uni-jena.de, Christine Weber\textsuperscript{1,2}, Ulrich S. Schubert\textsuperscript{1,2}. (1) Laboratory for Organic and Macromolecular Chem, Friedrich-Schiller-University Jena, Jena, Germany (2) Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany

A library of PMMA-graft-OEtOx graft copolymers was synthesized via reversible addition-fragmentation chain transfer (RAFT) copolymerization of methyl methacrylate (MMA) and oligo(2-ethyl-2-oxazoline)-methacrylate macromonomers\textsuperscript{[1]} of varying degree of polymerization. The PMMA-graft-OEtOx graft copolymers comprised a hydrophobic poly(methyl methacrylate) (PMMA) backbone and hydrophilic oligo(2-ethyl-2-oxazoline) (OEtOx) side chains and, thus, self-assembled into micellar structures in water, enabling the encapsulation of a hydrophobic cargo.\textsuperscript{[2]} Depending on the degree of grafting (DG) and the side chain DP (9% \textless DG \textless 34%; 5 \textless side chain DP \textless 24), the graft copolymers encapsulated different amounts of the hydrophobic dyes Disperse Orange 3 and Neutral Lipid Orange (NLO). Through post polymerization modification of the end group, a hydrophilic dye was introduced yielding a two-dye-micelle system. Through well-considered choice of the dyes it was possible to investigate the uptake and excretory procedures of the loaded micelle \textit{via} intravital laser scanning confocal microscopy \textit{in vivo} (lipophilic NLO (\(\lambda_{\text{em}} = 577\text{ nm}\)), hydrophilic DY-654 (\(\lambda_{\text{em}} = 677\text{ nm}\)), both in ethanol). In addition, the influence of the polymer architecture on the micelle properties was studied in detail including thermo-the responsive behavior and the aggregation behavior \textit{via} turbidimetry, dynamic light scattering, nuclear magnetic resonance spectroscopy, and analytical ultracentrifugation.
POLY 99: Synthetic and compositional control of multicomponent copolymers to promote drug solubility, bioavailability, and delivery

Theresa M. Reineke, treineke@umn.edu. Chemistry, University of Minnesota, Vadnais Heights, Minnesota, United States

Synthetic polymers have enabled amorphous solid dispersions to emerge as a strategy for overcoming poor solubility and bioavailability of intractable drugs via oral administration. In such formulations, polymeric carriers generate and maintain supersaturation of drugs via noncovalent interactions, which serve to increase the apparent drug solubility upon dissolution and enhance gastrointestinal absorption and oral bioavailability. In this work, we use controlled polymerization to create a family of multicomponent copolymers containing numerous functional groups that promote hydrogen bonding and hydrophobic interactions with several drug structures such as phenytoin and nilutamide. Through systematic characterization and screening we show that macromolecular design parameters with comonomers significantly improve efficacy by using: i) one monomer to serve as a precipitation inhibitor that discourages drug recrystallization and ii) another comonomer to provide hydrophilicity and solubility of the hierarchical system. Systems that maintained drug supersaturation in amorphous solid dispersions were identified with molecular-level understanding of noncovalent interactions using NOESY and DOSY NMR spectroscopy. Through this approach, effective polymers have been discovered that promote high drug solubilization and in vivo efficacy such as Poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide) (poly(NIPAm-co-DMA)). In vitro dissolution tests and in vivo pharmacokinetics of select spray-dried dispersions created via this approach have shown polymer chemical composition and solubilization performance relationships, which will be discussed in detail.
POLY 100: MMP2-sensitive tumor-targeted drug delivery and sensitization

Lin Zhu, lzhu@tamhsc.edu. Texas A and M University College of Pharmacy, Kingsville, Texas, United States

Low tumor specificity and multidrug resistance (MDR) are two unmet issues for many anticancer drugs. In this talk, we will introduce a simple, effective strategy for concurrent tumor-targeted drug delivery and sensitization of resistant cancers to anticancer treatments using our newly developed matrix metalloproteinase 2 (MMP2)-sensitive self-assembling polymeric efflux inhibitor as a drug carrier. On several cancer models, including cancer cells, three-dimensional multicellular spheroids, and tumor-bearing mice, we demonstrated that the assembled MMP2-sensitive micelles could effectively carry and deliver various hydrophobic anticancer drugs to cancer cells. More important, the polymers/micelles could inhibit P-glycoprotein mediated drug efflux and sensitize the MDR cancers to anticancer therapeutics. Our in vitro and in vivo results suggested that the MMP2-sensitive polymers might have great potential to be a multifunctional nanocarrier for tumor-targeted drug delivery and therapy.
POLY 101: Organic-inorganic nanohybrid as magnetically navigated nanocarrier for biologicals

Yoshihiro Sasaki¹, sasaki@bio.polym.kyoto-u.ac.jp, Riku Kawasaki¹, Ryousuke Mizuta¹, Naoya Kinoshita², Kazunari Akiyoshi¹. (1) Kyoto University, Kyoto, Japan (2) Tokyo Medical and Dental University, Tokyo, Japan

With properties such as multifunctional specificity and potency, proteins have great promise as therapeutic agents. Despite their great promise, protein pharmaceuticals face many development challenges relating to instability and delivery issues, especially for intracellular applications. Therefore, systems for “protein transduction”, that is, intracellular delivery of functional proteins, are needed. A number of nanocarriers have been described for protein therapeutics, including cationic lipids, polymers, nanogels and organic nanoparticles. On the other hands, few studies have investigated attachment of proteins to magnetic carriers because of the need to preserve innate protein structure and function. We have developed a novel protein transduction system enabling efficient intracellular delivery of functionally active proteins. Our technology is a hybrid combination of iron nanoparticles with a nanogel protein carrier inspired by the “catch and release” mechanisms of molecular chaperones. Through hydrophobic interactions, proteins are sequestered within the polymer matrix of nanogels, to be later released in a functional form via protein–protein exchange mechanisms. We showed that embedding the iron nanoparticles within the nanogel not only shielded the cytotoxic properties of these particles, but also enabled the hybrid nanogel to be magnetically directed to the target cells. We demonstrated several promising properties of this magnetic nanogel chaperone (MC) hybrid when complexed to a variety of model proteins. We further showed that the enzyme, when delivered to HeLa cells, could convert a nontoxic prodrug to a toxic agent, proving that, once delivered to the cytosol of target cells, galactosidase was released in its active form.

Figure 1. Schematic representation of magnetically navigated protein transduction by nanogel with iron oxide nanoparticle.
Dendrimers comprised of heterogeneous polymeric segments (e.g., hydrophobic and hydrophilic) afford multiple properties in a single molecule. Such dendrimers are described as “Janus type” and can be obtained by coupling two dendrons—possessing chemically different properties—to a single core. A unique property exhibited by these Janus dendrimers is the formation of various types of nanoparticles in aqueous media, depending on the ratio between the heterogeneous polymeric segments. However, lack of synthetic feasibility has hindered the widespread adoption of Janus dendrimers in drug delivery literature. In addition, they suffer from poor solubility and cytotoxicity—limiting clinical application. Alternatively, linear-dendritic block copolymers (LDBCs) combine the advantageous properties of dendritic polymers with that of linear copolymers to afford nanomaterials with superior mechanical properties. Herein, we report the analysis of a library of polymers analogous to Janus dendrimers, known as Janus linear-dendritic hybrids composed of a hydrophilic polyamidoamine (PAMAM) dendron covalently linked to a hydrophobic polyester. This combines the advantages regarding drug uptake and release of dendritic systems with the synthetic accessibility and precise molecular weight control of traditional polymerization techniques. Within the study, heterobifunctional groups were incorporated at the hydrophilic block to investigate the interfacial behavior of the nanoparticle surface and towards providing several biological advantages such as efficient cell penetrating ability. In conjunction with microscopy (e.g., TEM and AFM), spectroscopic and light scattering techniques afford evidence of nanoparticle formation. The mean diameters of the nanoparticles formulated at concentrations of 1-10 mg/mL ranged between 30-300 nm. The size of the nanoparticles depend on the formulation method employed. Results of the study suggest materials applicable as next generation drug delivery systems.
We have shown that radical-mediated thiol-ene chemistry provides a robust and simple platform for amorphous polyanhydride synthesis, and that the cross-linked products have low moduli of elasticity and degrade quickly (a 1 cm³ cube degrades within a few days), although the erosion kinetics of these materials are non-linear and appear more complicated than other surface-eroding materials. In comparison with traditional approaches to polyanhydride synthesis that are based on polycondensations, radical polymerization approaches have many advantages, a primary one being that various monomers are simple and readily available. Conventional radical polymerization of methacrylates and vinyl monomers are widely practiced and is the method of choice for the production for many commodity plastic materials. Radical-mediated thiol-ene/yne polymerizations of polyanhydrides also have low susceptibility to oxygen, low shrinkage, and uniform cross-link density and because thiol-ene/yne polymerization occurs via a step-growth mechanism, the degradable anhydride functionality resides in the main chain, rather than a side chain, which reduces the molecular weight of the degradation products compared to materials synthesized by chain growth polymerizations. From an application point of view, our studies indicate that drug delivery from polyanhydrides is typically dictated by erosion kinetics rather than diffusion. We have also shown that these polyanhydrides have low toxicity towards several cell types, and therefore are good options for therapeutic release devices.
POLY 104: Using grafted functional polyesters for drug delivery systems

Joerg Kressler, joerg.kressler@chemie.uni-halle.de, Karsten Maeder. Martin-Luther-University Halle, Halle (Saale), Germany

Different methods for syntheses of functional polyesters based on glycerol or different sugars using Candida antarctica lipase B (CAL-B) are discussed. It is outlined that vinyl endgroups of the polyesters might lead to crosslinked polymers after introducing functional groups to the polyesters via Michael addition. A series of grafted polyesters is produced using different saturated and non-saturated fatty acids having different volume fractions of hydrophobic side chains and also hydrophilic poly(ethylene glycol) side chains are grafted. The hydrophilic-lipophilic balance (HLB) of grafted polyesters is tailored by changing the degree of grafting of hydrophilic and hydrophobic side chains. Polymers are characterized by NMR spectroscopy, differential scanning calorimetry, gel permeation chromatography, and X-ray diffraction. Furthermore, the self-assembly of the graft copolymers and their use as steric stabilizers for cubosomes are investigated. The ternary phase diagram of the system glycerol monooleate (GMO) / water / graft copolymer is studied in detail by SAXS and WAXS measurements. The occurrence of different crystallographic cubic phases and their stability for drug delivery systems is discussed in detail. Furthermore, the linear polyester poly(glycerol adipate) (PGA) was covalently grafted with indomethacin. An interfacial deposition method was employed for the preparation of nanospheres with narrow particle size distribution and the nanoparticles are studied by zeta potential measurements, dynamic light scattering, cryo-electron microscopy and nanoparticle tracking analysis. Cell viability tests were carried out and the cytotoxicity tests using different cell lines showed low toxicity and low hemolytic activity for all samples. A slow and controlled release profile without any burst was observed over 15 days. Thus, the nanoparticles have the potential to improve the therapy of inflammation and related diseases.
Negative-staining electron micrographs of (a) 0.1 wt% dispersion of poly(xylitol adipate)-g-stearic acid15 and (b) 0.1 wt% dispersion of poly(D-sorbitol adipate)-g-stearic acid10.

**POLY 105: Next-generation opioid antidotes: Covalent nanoparticles for the delivery of Mu opioid antagonists**

Andrew Kassick¹, Michael Feasel², Benedict Kolber³, Nestor Tomycz¹, **Saadyah Averick¹**, saadyah.averick@ahn.org. (1) Neuroscience Institute, Allegheny Health Network Research Institute, Pittsburgh, Pennsylvania, United States (2) Edgewood Chemical Biological Center, Edgewood, Maryland, United States (3) Biology, Duquesne University, Pittsburgh, Pennsylvania, United States

The rise of synthetic opioids has highlighted the need for new long acting opioid antidotes. Currently available antidotes to reverse an opioid overdose (e.g. naloxone) have short pharmacokinetic half-lives due to rapid metabolism in the liver. Due to the relatively long circulatory times of synthetic opioids such as fentanyl a phenomenon known as renarcotization may occur. The short half-life of these antidotes requires multiple repeat doses to reverse a synthetic opioid overdose. We present a novel polymer based drug delivery system that incorporates a high loading of naloxone into a polymer nanoparticle with zero order sustained release to act as a long acting opioid reversal agent.
In cancer immunotherapy, cytotoxic T cells (CTLs) induced by injection of cancer vaccine attack cancer cells. However, to escape from immunity, cancer cells spontaneously suppress the expression of cancer antigen that is essential for CTL recognition. Therefore, if the cancer antigens are presented on the cellular surface, CTLs can attack the cancer cells again. It is known that CD44 which is one of hyaluronic acid (HA) receptors is excessively expressed on cancer cells. Therefore, HA chemically modified with the antigen is expected to specifically deliver the antigen to cancer cells via CD44. In this study, to restore the CTL response for cancer cells, we prepared the conjugate consisting of HA and antigenic proteins and evaluate the CTL response. HA, a linear polysaccharide, was formed by alternating D-glucuronic acid (GlcUA) and N-acetyl-D-glucosamine (GlcNAc) units (Figure 1). Because the glucuronic acid has a carboxylic acid, we tried chemical modification with ovalbumin (OVA) by a dehydration condensation reaction. The reaction was evaluated by UV measurement of gel permeation chromatography. Since HA is no UV absorption and OVA has absorption at 280 nm, the reaction can be judged from the change in elution time of OVA (Figure 2). After the reaction, the peak for OVA shifted to an earlier elution time. Therefore, OVA increased the molecular weight by conjugating with HA. The splenocytes, which are immunized with OVA and adjuvant, mixed with cancer cells treated with HA-OVA conjugate secreted cytokines such as IFN-g which shows Th1 type immune response. This result indicates that the replacement of weak antigenicity with strong antigenicity can be a novel strategy for cancer vaccine.
POLY 107: Poly(2-alkyl-2-oxazoline) conjugates of doxorubicin bound via pH-sensitive hydrazone linker: Synthesis, in vitro, and in vivo evaluation

Ondrej Sedlacek¹, on.sedlacek@gmail.com, Alexandra Van Driessche¹, Martin Hruby², Bruno De Geest¹, Richard Hoogenboom¹. (1) Ghent University, Ghent, Belgium (2) Institute of Macromolecular Chemistry AS CR, Prague 6, Czechia

Within the presented project, we designed and synthesized a new delivery system for the anticancer drug doxorubicin based on a poly(2-ethyl-2-oxazoline) (PEtOx) carrier with linear architecture and narrow molar mass distribution. The drug is connected to the polymer backbone via an acid-sensitive hydrazone linker, which allows its triggered release in the tumor. The in vitro studies demonstrate successful cellular uptake of conjugates followed by release of the cytostatic cargo. In vivo experiments in EL4 lymphoma bearing mice revealed prolonged blood circulation, increased tumor accumulation and enhanced anticancer properties of the PEtOx conjugate having higher molecular weight (40 kDa) compared to the lower molecular weight (20 kDa) polymer. A similar study was performed using the system based on even more hydrophilic poly(2-methyl-2-oxazoline) carrier. Considering the synthetic advantages of poly(2-alkyl-2-oxazoline)s, the presented study demonstrates their potential as a versatile alternative to well-known PEO- or PHPMA-based materials for the construction of drug delivery systems.
Understanding micellization and quantifying drug partitioning and release rates are crucial in the design of micelle-based formulations for therapeutic cargo delivery. Here we present a study of self-assembly of a Pluronic® F127 (PEO₉₀PPO₆₉PEO₉₀) triblock copolymer and its solubilization of three hydrophobic drugs, hydrochlorothiazide (HCT), indomethacin (IND) and paclitaxel (PTX). Using NMR diffusometry, we have quantified diffusion coefficients and relative sizes of different species in aqueous solution, including the polymers, drug cargo molecules and solvent. The cargo partition coefficient is given by the ratio of model drug concentration in the micellar phase to that in the aqueous phase. We are investigating the effects of polymer concentration, drug chemistry as well as drug concentration on cargo partitioning. As the polymer (micelle) concentration increases, the partition percentages of HCT and IND in micelles are also enhanced (figure below). Small-angle neutron scattering (SANS) results on micelle dimensions are in agreement with our NMR observations, which reveals a growth in the micellar core radius and aggregation number in the meantime a decrease in the volume % of the solvent in cores. This facile and non-invasive NMR method allows the measurement of drug distribution in a micellar system and opens opportunities to understand the dynamic processes of drug partitioning and release in micelles.
Photo-stimuli responsive materials are of interest for a broad range of applications, and take advantage of the inherently non-invasive, spatially resolved, and species-selective optical response. We demonstrate here photo-reversible micellization/de-micellization, gelation, and order-disorder transitions in block copolymer/ionic liquid systems. The general strategy involves one block that is well solvated in the ionic liquid of interest, such as poly(ethylene oxide) and poly(methyl methacrylate), and another that has exhibits either UCST (such as poly(N-isopropylacrylamide)) or LCST (poly(benzyl methacrylate)) behavior. A few mole percent of azomethacrylate is incorporated statistically into the temperature-responsive block. Under UV irradiation, the trans to cis photoisomerization of azobenzene significantly increases the solubility of the thermoresponsive block, leading to a structural transition at appropriate concentrations and temperatures. Under visible light, the cis to trans recovery causes the sample to revert to the original state. The progress of the transition is monitored by in situ photo-rheology and scattering techniques.
The rise and promise of artificial molecular machines allow chemists to explore functions in a nanoscale world. In this presentation, following an introduction of the nature of the mechanical bond, I will talk about our recent advances on the design and synthesis of enthalpically and entropically demanding polyrotaxanes and catenanes bearing densely charged units by courtesy of radical chemistry.

Motor molecules in nature convert energy inputs, such as a chemical fuel or photons of light, into directional motion and drive biochemical systems away from thermal equilibrium. The ability to control directional movements of components in molecules under certain stimuli represents significant advances toward future technological applications. Herein, we aim to develop chemically and electrochemically redox-driven molecular pump systems in order to control the exact number of rings installed onto a polymeric chain. We have designed and synthesized polymers bearing two molecular pumps at both termini of polymeric chains, which act as collecting chains for multiple cyclobis(paraquat-p-phenylene) (CBPQT$^{4+}$) rings. We have demonstrated that the enthalpically and entropically demanding polyrotaxanes can be produced through repeating redox cycles using chemical reagents or supply of electricity without generating and accumulating waste products.
Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) in its various modifications has emerged as a versatile toolbox to control and tailor the properties and interactions of interfaces and to enable the synthesis of hybrid materials with unprecedented property combinations. The resulting materials have attracted interest not only because the high-level structural control of the architecture of polymer-tethered surfaces enables tailoring of the interactions, microstructure and properties of particulate-based materials but also because the confinement of chains on surfaces alters the mechanism of termination reactions that limit conventional polymerization processes. This presentation will review recent examples of the application of SI-ATRP for the synthesis of functional polymer materials. Examples to be covered include the synthesis of ultra-high molecular weight polymers, materials for optical applications, thermal interface materials as well as electronic materials. Examples will also been shown to illustrate the potential of surface-initiated polymerization methods to provide model material systems that advance the understanding of the physics of polymer and hybrid materials.
The structure and function of cell-based polymers control the complex bioprocesses that support living systems. Polymer-Enhanced Biomacromolecular Systems use controlled polymer synthetic techniques to enhance the function of biological molecules, cells, and tissues. Tuning and improving biomolecular function by synthetically marrying polymers to biomolecules polymers is dependent on our ability to precisely control the interactions between the biomolecules and the polymers. We have been interested in how to rationally design polymers that transform the activity, stability and even specificity of the biological molecules with which they interact. Inherent to “rational design” is learning how the chemical structure of a particular polymer exerts its influence on the biological molecule. The emerging science of structure-function interactions between polymers and biological molecules is now driving new synthetic processes, generating novel materials and presenting exciting therapies. Biology and chemistry, when working in unison, can solve a variety of societal challenges that require the ruggedization of biology. Controlled polymer synthesis enables the generation of “nanoarmor” polymer shells around a biomolecule that can rationally tailor function. Because the polymer chemistry is tunable, we can take advantage of a large molecular space to confer novel properties on modified biomolecules, cells or even tissues. We have learned how to covalently couple or display multiple small molecule initiators onto a protein surface and then grow polymers from those sites. The technique is so powerful that a single protein-polymer conjugate molecule can exhibit the properties of both the biomolecule and the polymer. We have used stimuli-responsive polymers that respond to external triggers, such as temperature and pH, while maintaining biologic activity. We are even now in a position to grow polymers directly from the surface of cells without sacrificing cell viability. We will outline our progress and the remaining challenges in the design and synthesis of next-generation polymer-enhanced biomacromolecular systems.
Machines of the Future will synergize biomimetic mechanics with artificial intelligence [1]. The ideal actuator should mimic muscle by being passively elastic while also efficiently converting potential energy into mechanical strokes [2]. The ideal body material should mimic skin by being simultaneously compliant and strong to accommodate actuator motion [3]. Further, both body and actuator should adaptively increase stiffness under stress to maintain performance at peak loads. One drawback of biological tissues, however, is that their softness requires water, which is an unreliable engineering material. To overcome this challenge, we have developed a materials design platform that controls mechanical properties of elastomers by engineering brush-like polymer networks [4]. Adaptable to any chemistry, the platform harnesses architectural parameters to encode tissue-mimetic softness, strain-stiffening, and extensibility within single-chemical-component systems. Applying this platform to archetypal poly(dimethylsiloxane) (PDMS), aka silicone, we have precise replicated the mechanical response of biological tissues including ultra-soft adipose, brain, and fetal membrane tissues without using solvent as a material “softener”.

Figure 1. The evolution from a single-parameter linear chain elastomer to multi-parameter brush-like architectures towards the programmable replication of tissue mechanical properties.
This presentation will be focused on the insights into the structural factors governing the high activity of ATRP catalysts such as the family of tris(2–pyridylmethyl)amine (TPMA) derivatives. Detailed analysis of the electronic structure predicted by DFT calculations will be used to assess the donor-acceptor interactions and to elucidate the bonding and electron transfer pathways inferred from the structure of the electronic orbitals. Special attention will be given to the factors assuring the minimal perturbation of the electronic structure in the electron transfer process, and to the importance of these factors in assuring the desirable high catalyst activity. The impact of these findings on processes such as CuI catalyzed radical termination (CRT) and organometallic mediated radical polymerization (OMRP) will be also addressed.
In this presentation, some of our recent work on new catalysts to enable controlled polymerization of conjugated building blocks will be discussed (Figure 1). One of the significant challenges in the living polymerization of conjugated aromatic monomers is the limited substrate scope for this reaction. When trying to incorporate building blocks with sensitive functional groups or electron-deficient moieties, side reactions and undesirable metal-polymer interactions can be detrimental. Analysis of these pathways is critical to circumventing these issues and producing controlled polymerization reactions with building blocks that have found broad use in organic electronic materials. In this presentation, the development of new nickel diphosphine catalysts for Suzuki-Miyaura cross-coupling will be discussed along with our efforts to broaden the substrate scope.

Figure 1. Illustration of catalyst associating to growing polymer chain.
Radical-based transformations, such as dehalogenation and Barton-McCombie deoxygenation, are important in natural and unnatural product synthesis. These reactions are typically mediated by tributyl tin hydride as the radical chain carrier, which is both toxic and difficult to remove from the products. While other heteroatom-based mediators have been proposed, they have significant cost and/or efficiency disadvantages. The discovery of simpler organic chain carriers is desirable but to date has been elusive due to the difficulty in activating carbon-halogen bonds. Herein we show that ATRP-based chemistry can overcome these problems and may even have more general applicability in (cross)coupling chemistry.
Society depends on polymeric materials now more than at any other time in history. Although synthetic polymers are indispensable in a diverse array of applications, ranging from commodity packaging and structural materials to technologically complex biomedical and electronic devices, their synthesis and proper disposal pose important environmental challenges. The focus of our research is the development of routes to polymers with reduced environmental impact. In this presentation, energy-efficient routes to biodegradable polymers from biorenewable resources will be presented.
POLY 118: Designing infinitely recyclable ‘green’ polymers with tailored properties built upon a ‘gene’ for full chemical recyclability

Eugene Y. Chen, eugene.chen@colostate.edu. Chemistry, Colorado State University, Fort Collins, Colorado, United States

The development of chemically recyclable polymers holds real potential towards the ultimate goal of achieving a circular plastics economy. However, to materialize such potential, three challenges must be addressed first: energy cost, depolymerization selectivity, and depolymerizability/performance tradeoffs. Centering on addressing these key challenges, this presentation will update recent advances made in this field, especially the recent discovery of infinitely recyclable plastics, which have yielded feasible solutions and design principles for monomer/polymer structures that can deliver properties and performances for tailored application needs while maintaining complete chemical recyclability under mild conditions.
Polymer blending is a useful technique to vary polymer properties and to generate new products. As the formation of these blends do not usually involve chemical reactions, they may be potentially cheaper, more easily overcome regulatory/safety hurdles, and possibly lead to a faster path towards commercial development. This methodology is particularly advantageous for agro-based materials, where the starting materials are biodegradable, renewable, and eco-friendly. However, careful design and experimentation are needed in order to produce useful products. In this talk, a review is given of the biopolymer blends, including the benefits and the limitations of this methodology. For illustration, specific examples involving protein/protein, protein/polysaccharide, and polysaccharide/polysaccharide blends will be shown, with a particular emphasis on the work that the speaker was involved. In particular, selected biopolymer blends that involve hemicellulose and proteins will be described. Because these biopolymers are soluble or dispersible in water, easy to process, and do not involve the use or generation of toxic substances, they satisfy the requirements of green chemistry. Because the biopolymers used are agricultural products or byproducts, they are affordable and commercially available. Thus, the biopolymer blends represent good examples of affordable green chemistry.

![Figure 1. A simplified scheme for green polymer chemistry, illustrating the formation of biopolymer blends](image)
Atom transfer radical polymerization (ATRP) has been successfully used to covalently attach polymer chains to various biomolecules such as proteins, enzymes and nucleic acids. Preparation and properties of the resulting bioconjugates will be presented.
This presentation describes selected vignettes of research performed by my group towards integrating biocatalytic and chemical routes to develop next-generation affordable green processes and products. ω-Hydroxyfatty acids derived from fatty acids provide a platform of biobased building blocks for polymers, surfactants and other applications. A brief description will be given of an engineered Candida tropicalis strain from which 16 genes were identified and eliminated. The resulting organism provides an efficient route to ω-hydroxyfatty acids. In one example, 14-hydroxytetradecanoic acid (ω-HOC14) was produced from the corresponding acid at 120 g/L and 2 g L⁻¹ min⁻¹. ω-HOC14 was then converted via condensation polymerization to poly(14-hydroxytetradecanoic acid) ($T_m = 96 \, ^\circ\text{C}, M_w=160 \, 000$) that behaves similarly to medium density polyethylene but is degradable in composts. Peptides bring numerous properties of great value such as self-assembly, antimicrobial, adhesion, suppress ice formation and much more. However, their use is limited to applications such as therapeutics due to tedious and high-cost synthetic routes. Protease catalyzed peptide synthesis can be run under aqueous and bulk conditions using amino acid ethyl esters as monomers. Examples will be discussed of protease-catalyzed synthesis of alternating, block and random oligopeptides, applications and future directions. Considering the current state of plastic waste and a general lack of success in plastic recycling with few exceptions, it is imperative that alternative solutions are developed to unlock the latent energy of plastic waste. Our group is beginning to take a more holistic view of potential solutions while current work has focused on poly(ethylene terephthalate), PET, and cellulose acetate, CA. We have been studying powerful hydrolases known as cutinases that can convert PET to its monomers under mild conditions. Biocatalysis also provides access to microbially produced biosurfactants from renewable feedstocks. Our laboratory has studied simple modification chemistry that improves their cost-performance for use in a wide range of applications.
Polyelectrolyte multilayers (PEMUs) are thin films prepared using the layer by layer deposition of oppositely charged polymers on a substrate. The use of these films as membranes provides several advantages such as good ion selectivity and high ionic fluxes. Despite studies of diffusion coefficients and ion transport inside multilayer membranes, little research has been done on the temperature dependence of PEMU permeability to cations and anions. Moreover, the performance has not been evaluated as a function of the stoichiometry of these films. Here, the temperature dependence ion transport of two electrochemically active species, potassium ferricyanide and ruthenium hexaaamine, through a stoichiometric multilayer made from poly(diallyldimethylammonium) (PDADMA) and polystyrene sulfonate (PSS) is reported. The study uses cyclic voltammetry measurements at a rotating platinum disk electrode of a stoichiometric thin film as a function of temperature to show an evidence for a glass transition and obtain more information about the PEMU mechanical properties. It also explores the effect of using oppositely charged probes, as well as probe concentration on glass transition temperature. The results are compared to analogous measurements using dynamic mechanical testing, thus allowing for accurate prediction of a thermal transition based on a new parameter.

Log of the membrane current vs 1/T (K⁻¹). The blue line indicates the glassy regime while the red one indicates the rubbery regime.
Dielectric relaxation studies performed on hyperbranched polyesters (HBPs) with terminal hydroxyl groups have not yet been extended to their dendrimer analogues which require considerable synthetic efforts. The aim of the study is to compare dielectric behaviors of a 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) based second-generation HBP, Boltorn H20, with its dendrimer analogue and study their correlation with hydrogen bonding organization which is affected by structure dispersity and irregularity. In this study, a monodispersed, ideally structured second-generation dendrimer G2 was prepared via anhydride coupling method. FITR and NMR analysis were performed to study hydrogen bonding formation in H20 and G2. Compared with H20, G2 prefers to form hydrogen bonds between hydroxyl groups rather than between hydroxyl and carbonyl groups. Dielectric spectroscopy was employed to study the dipole relaxation and electrical conductivity behavior of both two polyesters. Both polymers exhibit high dc conductivity at low frequency. The conductivity relaxation, contributed by proton hopping along hydrogen bonds, showed non-Arrhenius dependence above $T_g$ and Arrhenius dependence below $T_g$. Higher conductivity and larger decoupling of G2 suggests higher mobility of protons in the system. Molecular dynamic simulation was conducted to analyze the hydrogen bonding organization, and hydrogen bonded chain-like clusters of O–H…O groups were discovered. Higher mobility of proton in G2 can be explained by its higher fraction of long hydrogen bonded clusters which contains more than two hydrogen bonds. This agrees well with the FTIR and NMR results since long clusters can be easily formed between hydroxyl groups.
Microporous polymers and membranes thereof are heavily sought after for their unique ability to discriminate between small molecules and ions in applications such as gas capture, water desalination, and energy storage. This discriminating ability has, in the past, emerged primarily from their unique pore architecture, but less so due to the presence of specific functional groups within. This deficiency is due to the paucity of means to functionalize the pores. Here, I describe our recent efforts in expanding the types of chemical functionalities that can be placed within the pores of microporous polymers, using polymers of intrinsic microporosity and thermally rearranged polymers as platforms. Our approach allows for tailoring backbone designs in advance or post-polymerization, yielding highly selective membranes whose architectures retain their leading-edge permeability.
We are developing the hypothesis that ions can be transported through polymer films by sequestering the ions within nanoscale aggregates that have microphase separated from the backbone polymers. If the ions within these aggregates are sufficiently dissociated from the acid groups, the ion motion will be decoupled from the polymer backbone. We are particularly interested in nanoscale aggregates in various precise polymers, wherein the pendant functional groups are attached to a linear polymer at precise intervals. These precise polymers have remarkable nanoscale self-assembled morphologies. In addition to the layered structures and random percolated structures we have previously reported, we recently identified aggregates with gyroid-cubic and hexagonal symmetry using in situ X-ray scattering to study a precise polyester sulfone synthesized in Stefan Mecking's group. In this talk we will explore how these morphologies influence transport in both bulk and thin film geometries. Conductivity will be measured as a function of microphase separated morphology types, temperature, and the type and amount of added small molecules.

X-ray scattering of a precise polyester sulfone at 30°C and 190°C. Remarkably, this multiblock copolymer exhibits scattering that is consistent with a bicontinuous gyroid structure at low temperatures. The aggregate morphology has hexagonal order at higher temperatures.
High melting aliphatic precision polysulfones were prepared by bulk metathesis polycondensation using a unique, well-defined Grubbs ruthenium catalyst. Contrary to conventional Grubbs catalysis, this one tolerates high temperatures (200°C) that allowed efficient polymerization above the melting point of the semicrystalline polymer. This is a scalable approach to synthesizing high molecular weight precision aliphatic polysulfones, true materials. Note this bulk polycondensation is scalable chemistry, carried out in a manner similar to that for polyester, for example. Presently, we are investigating these precision materials as ion transport membranes.
Controlling the structure and dynamics of ionizable polymer thin films is critical to their many applications. As the chemical diversity within one polymer is increased, controlling the structure and dynamics of the polymer, which is a key to their use, becomes a challenge. Here molecular dynamics simulations are used to obtain molecular insight into the structure and dynamics of thin films of one such macromolecule at the interface with water and propanol. The polymer consists of an ABCBA topology with randomly sulfonated polystyrene (C), tethered symmetrically to flexible poly(ethylene-propylene) blocks (B), and end-capped by a poly(t-butylstyrene) block (A). The compositions of the interfacial and bulk regions of films of the ABCBA polymers are followed as a function of exposure time to water or propanol. Because of the polarity of the water molecules, they selectively associate with the ionic segments and cause significant rearrangement of the surface. With time, ionic groups migrate to the interface in the presence of water. In contrast to water, propanol has a polar head group as well as shorter non-polar tail. This allows it to interact with both ionic and non-ionic segments of the polymer membrane. The penetration of propanol into the membrane is significantly faster than for water. Initially, solvent molecules rapidly penetrate membrane for both water and propanol. The water molecules are predominantly associated with ionic clusters, whereas the propanol molecules associate with both the ionic and non-ionic segments. For both, the presence of solvent results in significant rearrangement of the ionic clusters.
Solvent-free polymer electrolytes have long been sought after for use in rechargeable batteries. The ideal polymer electrolyte would have high ionic conductivity, a high active ion transference number, a wide electrochemical stability window, and chemical stability with the electrodes of interest. Poly(ethylene oxide)-based electrolytes have historically received the most research attention despite cation conduction rates being highly dependent on chain segmental motion. Here we report on non-polyether, cation conducting, polyanion-based electrolytes. Single-ion conducting polymer electrolytes are investigated wherein lithium conduction occurs in ionic domains or aggregates. The effect of polymer design and tethered anion chemistry on lithium transport will be discussed. In addition, novel multivalent cation conducting polymer electrolytes based on polyanions are demonstrated.
Recently, stretchable and flexible solid polymer electrolytes (SPEs) are widely considered as promising materials for the development of next-generation flexible or bendable energy storage devices such as lithium ion batteries and supercapacitors. The main property required for the SPE is to simultaneously show high ionic conductivity and stretchability. Herein, we synthesize poly(acrylic acid) (PAA)-based SPE hydrogels containing lithium countercations and cross-linkable vinyl silica nanoparticles (VSNP) by one step radical polymerization under nitrogen atmosphere as shown in the photograph of Figure 1. The neutralization of PAA with lithium cations allows the SPE to be Li single-ion conductors, and the VSNP nanoparticles play a role in a control of the stretchability and strength of the SPE. The effect of the VSNP nanoparticle content on thermal, mechanical, and ion conduction properties is systematically investigated, using thermal gravimetric analysis, differential scanning calorimetry, dynamic mechanical analyzer, dielectric relaxation spectroscopy (See Figure 1).

**Figure 1.** Ionic conductivity $\sigma_{DC}$ at 293 K as a function of silica nanoparticle content, where $\Phi_{\text{VSNP}}$ is the weight fraction of VSNP. The inset shows the frequency dependence of the in-phase part of conductivity $\sigma^\prime$ (f).
POLY 130: Elastic single-ion conducting polymer electrolyte

**Pengfei Cao**¹, caopengfei686@gmail.com, Bingrui Li³, Guang Yang⁴, Jagjit Nanda², Alexei P. Sokolov³, Tomonori Saito⁴. (1) Chemical Science Division, Oak Ridge National Lab, Knoxville, Tennessee, United States (2) Oak Ridge National Laboratory, Knoxville, Tennessee, United States (3) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (4) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States

Single-ion conducting polymer electrolytes (SCPEs) are well recognized being the advanced electrolyte system with increased energy efficiency and prolonged cell lifetime due to their capability to mitigate electrode polarization and reduce electrolyte loss. Fabrication of stretchable SCPEs will definitely benefit the future stretchable batteries/electronics considering the advantageous electrolyte performance of the SCPE based systems, while no one report the SCPEs with specific mechanical performance. Herein, we will report the fabrication of a series of single-ion conducting polymer electrolyte membranes with high flexibility and stretchability. Polydimethylsiloxane (PDMS) network and polyethylene glycol (PEG) side chains are critical in retaining their satisfied mechanical and electrochemical performance. The investigation revealed that the incorporation of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) plays a significant role in forming the stretchable polymer membranes, which can not only lower the glass transition temperature but also provide additional reactivity. The obtained membranes exhibited 88%-252% elongation before breaks, and the mechanical properties, including Young’s modulus, toughness and tensile strength, are well adjustable by tuning the crosslinking density. Galvanostatic test of the assembled cells using the obtained SCPE member exhibited satisfied cycling performance with capacity retention up to 81.5% after 100 cycles.
POLY 131: Superionic conductive polymer electrolyte for solid lithium-metal batteries with long cycle life

Yu Zhu, yu.zhu@uakron.edu. Department of Polymer Science, The University of Akron, Akron, Ohio, United States

A highly conductive and electrochemically stable dual-salt solid polymer electrolyte (SPE) for high capacity cathode was developed. A phase-diagram approach was adopted to provide rational guidance for achieving a high ionic conductivity (over 1.76 mS/cm at 30 °C). The synergy of combining different salts rendered the SPE a superior electrochemical stability with an electrochemical window from 0 to 5 V (vs. Li⁺/Li) in linear sweep voltammetry and up to 4.15 V in lithium metal batteries (LMBs). The SPE exhibited outstanding long-term stability performance in lithium plating/striping experiments under current densities from 0.08 to 0.5 mA/cm². The solid-state lithium metal batteries (with LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, NCA, cathode) exhibited initial capacities of 165 mAh/g at 0.1 C rate and 113 mAh/g at 1 C rate at 30 °C. The average Coulombic efficiency of solid-state batteries was over 99.99% in the first 1000 cycles at 1 C rate and the capacity retention was 66% after 1000 cycles. In addition, the per cycle capacity fading after the initial 100 cycles was only 0.017 %/cycle. The results demonstrate that the SPE is a promising candidate electrolyte for high energy density solid-state lithium metal battery.
POLY 132: Amino acid-based poly(ester urea)s for soft–tissue repair applications

Nathan Dreger, nzd1@zips.uakron.edu. Polymer Science, The University of Akron, Akron, Ohio, United States

Novel resorbable polymeric materials are needed to address limitations of current synthetic and biologic derived materials for soft-tissue repair. Here we explored a series of L-valine and L-phenylalanine based poly(ester urea)s (PEU)s that possess a variation in monomer diol length, extent of branching, and monomer feed ratio as candidate polymeric materials for soft tissue repair applications. Mechanical properties and in vivo degradation were assessed to determine material properties and inflammatory response. Several processing techniques (compression molding, blade coating, etc.) were employed to develop prototypes for potential hernia-mesh repair applications with the resulting material's biocompatibility under study. To date, PEUs have shown to be promising alternatives to currently employed synthetic and biologic materials for hernia-mesh repair.
Coacervate, suggested as a model for membrane-free protocells, can be a promising route towards the design and construction of synthetic cellular systems, with property of selective encapsulation for a variety of solutes. Here, we developed a simple and versatile post-coacervation crosslink method using thiol-ene click reaction in aqueous media to prepare covalently crosslinked coacervate. The crosslinked coacervate shows a strong stability at extreme low pH values where the uncrosslinked coacervate fully disassembles. The enhanced hydrophobicity within crosslinked coacervate enables it with a higher encapsulation efficiency of bovine serum albumin (BSA), as compared to the uncrosslinked coacervate. Additionally, incorporation of BSA within crosslinked coacervate shows improved efficiency in the stabilization of BSA at low pH.

Investigation of the use of crosslinked coacervate as carrier for enzymes reveals that the enzymatic activity of alkaline phosphatase (ALP) is enhanced compared to the ALP in aqueous solution. The post-coacervation crosslink approach used here expands the range of condition for the utilization of coacervate without disassembly and helps with the protection of encapsulated protein against denaturation induced by extremes of pH as well as with the enhancement of the enzymatic activity of encapsulated enzyme.
Glycosaminoglycans (GAGs) are among the most complex, biologically active biopolymers in nature. The complexity of GAGs greatly impedes their synthesis, thus complicating the structure-property understanding. We design a regiospecific synthetic route to two types of GAG analogs by chemical modification of commercially available, inexpensive cellulose acetate. Cellulose acetate was first brominated, followed by azide displacement to introduce azides. The resulting 6-N₃ cellulose acetate was then saponified to liberate 6-OH groups. Subsequent oxidation of the liberated primary hydroxyl groups to carboxyl groups was smoothly effected by a TEMPO-catalyzed process. Finally, the azides were reduced to amines using an aqueous process, new to polysaccharide chemistry, employing reduction by dithiothreitol (DTT). Alternatively, another process new to polysaccharide chemistry could be employed to convert most of the azides to acetamido groups by reduction with thioacetic acid. In summary, we successfully prepare two GAG analogs, which provides access to GAG analogs that will be of great interest for exploring structure-property relationships in various biomedical applications.

Scheme 1. Synthetic route to two GAG analogs
Thermoplastic elastomers (TPEs) are widely used in electronics, clothing, adhesives and automotive components due to their high processability and flexibility. ABA triblock copolymers, in which A represents glassy endblocks and B the rubbery midblock, are commercially available TPEs. The most commonly used triblock copolymer TPEs contain glassy polystyrene endblocks and rubbery polydiene midblocks. However, commercial TPEs are derived from petroleum. The manufacturing and disposal of petroleum-derived products have undesired environmental impacts, which promotes development of TPEs from sustainable sources. Vegetable oils and their fatty acid derivatives are attractive alternatives to petroleum due to their abundancy and low cost. Our group has previously reported replacing polydienes in commercial TPEs with sustainable polyacrylates derived from fatty acids. However, polymers with bulky constituents, such as the long alkyl side-chains of fatty acid-derived polymers, typically exhibit poor mechanical performance due to lack of entanglements in the rubbery matrix. To improve the mechanical properties, a transient network was incorporated into the fatty-acid derived midblock through hydrogen bonding. Specifically, triblock copolymers containing polystyrene endblocks and a midblock composed of a random copolymer of poly(lauryl acrylate) (derived from lauric acid) and acrylamide (which undergoes hydrogen bonding) were synthesized. Quantitative FTIR analysis confirmed the formation of a transient network. The polymers exhibits disordered spherical morphologies, desirable for application as TPEs. Rheological measurement revealed the order-disorder transition temperature reduced with increasing acrylamide content, beneficial for high temperature melting process. Importantly, triblock copolymers with hydrogen bonding in the matrix exhibited significantly higher modulus, strain at break, and tensile strength as compared to comparable polymers in the absence of hydrogen bonding.
POLY 136: Harnessing imine reactivity for dynamic topological and functional transformations

Michael B. Sims\textsuperscript{3}, mbsims@ufl.edu, Kush Y. Patel\textsuperscript{1}, Mallika Bhatta\textsuperscript{1}, Soma Mukherjee\textsuperscript{2}, Jacob J. Lessard\textsuperscript{2}, Lian Bai\textsuperscript{1}, Brent S. Sumerlin\textsuperscript{3}. (1) University of Florida, Gainesville, Florida, United States (2) Chemistry, University of Florida, Gainesville, Florida, United States (3) Department of Chemistry, University of Florida, Gainesville, Florida, United States

The generation, accumulation, and persistence of plastic waste is one of the most pressing challenges facing polymer science in the 21\textsuperscript{st} century. It is therefore critical that, in designing the next generation of polymeric materials, consideration is given to imparting mechanisms for degradability and/or efficient repurposing. Here, we describe the use of dynamic-covalent imine chemistry to both finely control the rate of architectural degradation and achieve on-demand polymer (re)functionalization. In pursuit of this first goal, we designed a library of hyperbranched polymers containing imine crosslinks to act as model degradable architectures, seeking to leverage the differential hydrolytic stability of \textit{N}-substituted imines to achieve a spectrum of predictable macromolecular degradation rates. As measured by molecular weight reduction, segmented hyperbranched polymers containing hydrazone crosslinks degraded most rapidly, followed by semicarbazone-containing polymers that degraded at intermediate rates, and finally oxime-crosslinked polymers that only exhibited partial degradation on the experimental timescale, similar to trends observed for small molecule imines. We furthermore demonstrated that hyperbranched polymers containing different imines exhibited “hybrid” degradation rates that corresponded to the identities and relative proportions of the incorporated imines, which could prove useful for applications requiring materials with precisely tailorable degradation rates. Next, we utilized enamines — tautomeric isomers to imines — to achieve rapid and efficient side-chain functionalization of \textit{β}-ketoester-containing polymethacrylates. Unlike traditional enamines, those derived from \textit{β}-ketoesters exhibit enhanced stability due to the formation of a hydrogen bond-mediated six-membered ring. Polymers were functionalized in high yields with a broad scope of primary amines under benign conditions, and it was furthermore shown that the installed functional groups could be dynamically exchanged through a subsequent heat-activated reaction utilizing only the desired new primary amine and a small amount of Brønsted acid catalyst.
Reprocessable polymer networks based on dynamic chemistry with concurrent dissociative and associative mechanisms: Judicious design leading to excellent reprocessability

Lingqiao Li, lingqiao.li@u.northwestern.edu, Xi Chen, John M. Torkelson. Northwestern University, Evanston, Illinois, United States

Conventional thermosets cannot be recycled into high-value products because the permanent, covalent cross-links prevent melt-state reprocessing or reshaping. Dynamic, covalent cross-links that have been studied over the past fifteen years offer an avenue to overcome this long-standing challenge in polymer science. Interestingly, reprocessable network materials are rarely reported to have multiple concurrent dynamic mechanisms. Here, we employ either hydroxyurethane or thiourethane dynamic chemistry, both of which are capable of dissociative reversion and associative exchange mechanisms, to produce reprocessable polymer networks. With judicious design of the chemistry, resulting network materials based on either chemistry can achieve full property recovery associated with cross-link density after multiple recycles. Specifically, high boiling point monomers were chosen for hydroxyurethane dynamic chemistry to avoid monomer evaporation during reprocessing; unbalanced stoichiometry was employed in the thiourethane system to suppress side reactions and promote the desired exchange mechanism. The excellent reprocessability achieved in both cases demonstrates the importance of a well-rounded approach to design such dynamic network materials and indicates the potential for developing dynamic polymer networks and network composites that can be recycled for high-value applications.
**POLY 138: Kinetic control of block polymer micelles: Cavitation induced exchange and templates for nanomaterials**

Kayla A. Lantz¹, kalantz@email.sc.edu, Amrita Sarkar⁶,⁷, Kenneth C. Littrell³, Tianyu Li⁴, Kunlun Hong²,⁴, Wessel van den Bergh¹, Nicholas B. Clamp⁵, Morgan Stefik¹. (1) Chemistry and Biochemistry, University of South Carolina, West Columbia, South Carolina, United States (2) Bldg 8610 MS 6494, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (4) Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, United States (5) Exercise Science, University of South Carolina, Columbia, South Carolina, United States (6) Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States (7) Chemical and Biomolecular Engineering, Rensselaer Polytechnic Institute, Columbia, New York, United States

Kinetically trapped micelles are a novel platform for diverse emerging applications from drug delivery, to nanoreactors, and templates for porous nanomaterials. Kinetic control allows micelle size to be decoupled from any subsequent application. However, micelle homogenization and size tuning are inherently challenging due to the high-χN barrier toward chain exchange processes. It was recently discovered that sonication enables switchable exchange where cavitation leads to chain exchange and cessation returns micelles to kinetic entrapment. SANS measurements were used to quantify chain exchange during cavitation induced exchange (CIE). The extent of exchange increases linearly with CIE time and the rate of chain exchange was directly proportional to the polymer concentration. A CIE mechanism is posited that is consistent with these observations and the atypical concentration dependence. The absence of chain exchange is particularly useful when micelles are used as templates. Persistent Micelle Templates (PMT) were recently developed to enable independent control over pore and wall dimensions. PMT relies upon kinetic controlled micelles of constant size where chain exchange is suppressed with solution water content. Typical PMT embodiments involve water-reactive precursors that unfortunately lower the barrier to exchange upon precursor addition. A new approach was developed to overcome this limitation using ex situ hydrolysis. This approach significantly decouples micelle kinetic control from nanoparticle chemistry and expands the range of precursor additions while maintaining PMT control. These works support the size tuning and homogenization of kinetic controlled micelles via CIE and develop subsequent processing chemistries to support robust deployment of these micelles as templates.
The ring-opening polymerization of lactides is a highly sought-after strategy for the generation of functional, biorenewable plastics. We have identified modular catalytic systems comprised of alkoxides and thioureas or ureas that can achieve fast and selective ring-opening polymerizations of lactide. This presentation will describe computational studies that have been performed on lactide ring-opening by these catalytic systems which reveal insights into the mechanism and energetics of lactide polymerizations.
Dow is among the world’s largest manufacturers of Low-Density Polyethylene (LDPE). However, the industry is very competitive with new or modified products emerging on a regular basis. Given the extreme conditions for LDPE production, lab-scale R&D efforts are quite limited and pilot-plants become the smallest scale at which novel materials exploration can take place. Clearly, this leads to much higher R&D costs as compared to the development of other polymers. Hence, computational techniques provide an appealing alternative to experiments for new product development, hypothesis testing and troubleshooting.

In LDPE, there are three general methods to create new products - controlling the molecular weight, branching distribution and comonomer incorporation. To this end, chain-transfer agents, branching agents and monomers other than ethylene are employed. The molecular architecture of each macromolecule will then be determined by the intrinsic kinetics/properties of these reagents as well as the process conditions. Quantum mechanical (QM) methods such as density functional theory (DFT) can be used to elucidate the reactivity of the various reagents at the atomistic level. This information can subsequently be used in kinetic models which will allow for optimization of the process conditions to tailor the polymer morphology in order to reach the desired material targets. Moreover, QM calculations can be utilized to screen a large number of candidates and, ultimately, focus R&D efforts on select few species. Furthermore, understanding reagent reactivity at the molecular level allows for the design of structure-property relationships which narrow the pool of possible functionalities when proposing the next generation structures.

This talk will focus on the development of a QM method for designing the next generation LDPE products. We will demonstrate the accuracy of the approach to obtain rate parameters for a series of well-known molecules from the open literature. In addition, we will show results for a series of chain-transfer and branching agents of potential industrial significance.

Hydrogen abstraction from propylene by a propagating radical
Many industrial polymer projects involve detailed comparative analysis to determine similarities and differences among materials. Projects can include comparisons of multiple lots of a polymer, polymers from various manufacturers, or polymers that represent “good” and “bad” products. The analysis can be performed to determine if polymers are counterfeit, are comparable substitutes for each other, are being manufactured in a consistent manner, if processing is altering the polymer characteristics, and as an important contribution to the determination of root cause of failure, for example. At a high level, analytical methods that address the polymer parameters is a strong approach to address these types of issues that have been cited. In high consequence applications, medical products for example, it is important to have a reliable supply of consistent polymer raw material for conversion to products. And, to mitigate risk associated with disruptions to the supply chain, it may be important to have multiple suppliers.

This presentation describes comparative analysis to compare two sources of polymer raw material and fiber products made from each raw material. Methods of analysis included differential scanning calorimetry, dynamic mechanical analysis, high temperature $^{13}$C nuclear magnetic resonance spectroscopy, and high temperature size exclusion chromatography. These methods of analysis provided detailed characterization of the raw materials and the fiber products made from each raw material. The methods of analysis address the fundamental polymer parameters; composition, molecular weight, stereochemistry, topology, morphology, and additives. Although this presentation discusses specific polymers and specific fiber products the analytical approach and the methods are broadly applicable. The presentation will provide the specific data sets, their interpretation, and the conclusions reached. In addition, general principles will also be presented so that the content can be used for a wide range of detailed comparative analysis polymer projects.

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Blueshift Materials is working to commercialize polyimide aerogels by building on exploratory research by the National Aeronautics and Space Administration (NASA). An aerogel is a synthetic porous solid with very low density. Aerogels were first made using silica, but now there are many polymer systems that have been demonstrated. Aerogels are produced by first creating a solvent swollen gel and then replacing the solvent with air without allowing the pores to collapse. In this talk, we will discuss Blueshift’s history, the structure, properties, and applications of our polyimide aerogels. In addition, we will discuss transition of producing polyimide aerogel thin films from our current low rate product line to our continuous roll-to-roll production line.
Currently, there is a clinical need for useful products that will protect autologous cells while promoting soft tissue repair or wound healing. The limitation with cell injections without an appropriate scaffold leads to the cells leaving the point of injection rapidly; thus, cells exhibit diminished viability due to the injection process. To overcome this limitation, the crosslinking of natural polymers and poly-ethers was utilized to produce a cell-loadable, flowable, biologically-based microgel system for soft tissue regeneration and wound healing. The system allows for the mixture of the patient’s autologous cells with the biologically based microgel. Analyses of the fluid uptake, degradation rate, and rheological characteristics of the rehydrated materials were evaluated, along with the products’ ability to maintain its integrity during self-life stability, to ensure the desired clinical attributes.
POLY 144: Contact lenses: More than meets the eye

Michael R. Clark, mclark4@its.jnj.com. R&D, Johnson and Johnson, Jacksonville, Florida, United States

While the concept of a lens fitting directly on the eye to modify vision dates back to the time of Leonardo da Vinci, it has only been in the last 90 years, with the advent of synthetic polymers, that contact lenses have been practical for widespread use. These initial plastic lenses, made of polymethyl methacrylate, were hard, expensive, and uncomfortable. More recently, soft hydrogel materials have been developed which have both improved patient comfort and manufacturability. Material science research continues to provide breakthroughs in soft hydrogels, such as the introduction of hydrophobic silicones that increase oxygen permeability and provide greater oxygen flux to the cornea. Today a careful balance of physical and chemical properties, including surface wettability, modulus, water content, and others can result in a lens that provides good visual performance and comfort for patients. With a wide array of refractive ocular disorders to treat, including myopia, hyperopia, astigmatism, and presbyopia, the global contact lens market is valued at approximately 11 billion USD and continues to grow.

In this presentation, we will review some of the current state of the art technology as well as potential paths contact lenses may take in the future. Although the technology has already made tremendous strides, future opportunities for greater comfort, improved manufacturability, medical diagnostics, and enhanced vision still exist. As more is learned about the physiology of the eye and the neuroscience of how visual stimuli are processed in the brain, technology will continue to advance and provide improved products for the health and safety of contact lens wearing patients.
POLY 145: Bio-sourced chelating poly(2-oxazoline)s

Helmut Schlaad, schlaad@uni-potsdam.de, Nils Lüdecke. Chemistry, University of Potsdam, Potsdam, Germany

Poly(2-oxazoline)s are an interesting class of bioinspired pseudo-peptide materials for potential applications in for instance biomedicine and materials science. Here, we report on the synthesis and polymerization of 2-(methoxyphenyl)-2-oxazolines based on naturally occurring O-methylated phenolic acids, i.e., draconic acid, veratric acid, and eudesmic acid, aiming at the production of chelating poly(2-oxazoline)s mimicking mussel adhesive proteins. The 2-(methoxyphenyl)-2-oxazoline monomers were synthesized in high yields from the corresponding nitriles and were (co-)polymerized applying conventional and microwave-assisted polymerization techniques.
POLY 146: Green light photoswitchable poly(2-isopropenyl-2-oxazoline) supramolecular hydrogels

Xiaowen Xu¹, Xiaowen.Xu@UGent.be, Valentin Victor Jerca¹,², Richard Hoogenboom¹. (1) Department of Organic and Macromolecular Chemistry, Ghent University, Gent, Belgium (2) Centre of Organic Chemistry “Costin D. Nenitzescu”, Bucharest, Romania

Stimuli-responsive hydrogels formed by supramolecular interactions are very attractive for the synthesis of nanoscale soft materials.¹ Supramolecular hydrogels display unique physicochemical properties such as: water-retention ability, drug loading capacity, biodegradability and biocompatibility.² Moreover, because of the dynamic nature of the noncovalent interactions they have shape memory ability, shear-thinning, and self-healing properties. Supramolecular hydrogels containing photoresponsive groups are particularly attractive, since their properties and functions can be regulated with high spatial and temporal precision, while the dose control can be easily tune up through the variation of irradiation parameters such as: wavelength, time and intensity of light.³⁻⁶ Herein, we report the synthesis of photoswitchable supramolecular hydrogels based on poly(2-isopropenyl-2-oxazoline) modified with pillar[5]arene derivative and tetra-ortho-methoxy substituted azobenzene. Green light irradiation induced the disassembly of the complexes and a gel to sol transition. Studies regarding the release of entrapped therapeutic agents in an on-demand and dose-tunable fashion were also performed.
Amphiphilic block copolymers play an important role in interfacial and colloid chemistry due to possibility of self-assembly processes in solutions especially for encapsulation of poorly soluble drugs. Gradient copolymers have been shown similar self-assembly properties as in the case of block copolymers. They can be prepared by one-pot cationic copolymerization of 2-(m)ethyl-2-oxazoline with 2-aryl-2-oxazolines due to the distinct difference in the rate of polymerization for both types of monomers [1]. Here, we prepared gradient copolymers of 2-(m)ethyl-2-oxazoline and different aromatic 2-oxazolines with the aim to study the effect of type of hydrophobic moieties on size and properties of nanoparticles.

2-(4-Alkylxyphenyl)-2-oxazolines (ROPhOx) represent new type of lipophilic monomers with tunable side-chain flexibility and hydrophobicity. Cationic copolymerization of ROPhOx with 2-ethyl-2-oxazoline led in all cases to the formation of the gradient copolymers. Our results showed that gradient copolymers above 12 mol.% of aromatic moiety are able to form stable nanoparticles with size ranged from 100 to 300 nm [2]. Particle size, shape, and loading capacity of model drugs were dependent on type of aromatic comonomers, composition of copolymers, and used drug.
Poly(2-oxazoline)s -abbreviated as PAOx, POx, or POZ- constitute a versatile polymer class that is experiencing a growing interest as biomaterials.

PAOx are typically prepared in a batch-type process. In the past, this polymerization reaction was a slow process with polymerization times ranging from hours to days. The introduction of microwave synthesizers for the polymerization of 2-oxazolines allowed the application of high reaction temperatures, thereby reducing polymerization times to minute scales. This development revolutionized the poly(2-oxazoline) file, that experienced an exponential growth in terms of publications and patents filed.

However, due to the low penetration depth of microwaves, the use of microwave synthesizers is limited to 1 liter reactors. A different heating source is thus required if larger production outputs are needed. In addition, the polymerization of 2-oxazolines at high temperatures is a highly exothermic process, complicating temperature and pressure control and presenting a safety risk. The polymerization of 2-oxazolines at high temperatures via a batch process in a closed, pressurized reactor thus constitutes a major safety challenge for up-scaling polyoxazoline production.

Previous attempts to develop a continuous-flow production of PAOx using microwave as an energy source resulted in broader molecular weight distributions compared to a microwave-assisted polymerization in batch mode. In addition, the broadening of the molecular-weight distributions seemed to increase with the flow rate.

More recently, the continuous synthesis of PAOx copolymers using a microfluidics reactor was reported, showing encouraging results, although only analytical amounts of product could be produced using microreactors.

In the present contribution, we present the safe upscaling of PAOx production via continuous flow leading to a kg-scale output of polymer with comparable characteristics -composition, molar mass distribution, dispersity- as polymers produced in a batch process. These results pave the way to the safe production of high-quality PAOx in large scale.
POLY 149: Synthesis and self-assembly of carbohydrate-conjugated poly(2-oxazoline)s: Polymer vesicles with molecular permeability towards therapeutic nanofactories

Tomoki Nishimura, nishimura.tomoki.6w@kyoto-u.ac.jp, Naoki Sumi, Yuta Koda, Yoshihiro Sasaki, Kazunari Akiyoshi. Kyoto University, Kyoto, Japan

The rise of nanobiotechnology and the continuously increasing request for more efficient therapeutics has shifted a focus of interest on therapeutic biocatalytic nanoreactors (the so-called ‘nanofactories’), which can enable the conversion of inactive prodrugs into active agents near a target disease site. [1] Polymer vesicles represent potentially suitable compartments for such nanofactories due to their ease of fabrication and functionalization as well as their desirably high stability. However, owing to their thick membranes, their molecular permeability for common drugs is extremely low. Hitherto reported strategies to increase the permeability include e.g. the incorporation of membrane proteins, but all these approaches are complicated and/or not scalable. In other words, a rational molecular design that enhances the molecular permeability remains elusive.

In this study we focused on a hydrophobic polymer that exhibits a lower critical-solution-temperature (LCST)-like behavior, as a potential component for the permeable bilayer membrane. Among others, poly(n-propyl oxazoline)s exhibit LCSTs in the range 35–40 °C and act as a hydrophobic polymer above room temperature. We therefore decided to take advantage of these properties for the construction of intrinsically permeable polymer vesicles.

In the present study, we have developed a new carbohydrate-based initiator system for the ring-opening polymerization of 2-oxazoline to synthesize carbohydrate-conjugated poly(2-oxazoline)s. We have also demonstrated that vesicles can be formed by self-assembly of the resulting polymers, and that these exhibit desirable molecular permeability. The simple approach of this study provides the basis for the development of a new class of permeable vesicles for nanofactories. Additionally, our results are expected to further the development of a broader range of novel nanofactory-based therapies.

Chemical structure of maltotriose-b-poly(n-propyl oxazoline-co-phenyl oxazoline) and a schematic illustration of the self-assembly of the polymer to form polymer vesicles with molecular permeability.
POLY 150: Messenger RNA loaded polyplex micelles having hydrophobic core protective layer composed of thermo-switchable poly(oxazoline) for promoted gene expression

Shigehito Osawa\(^1,2\), osawa-s@rs.tus.ac.jp, Kensuke Osada\(^4,2\), Kazunori Kataoka\(^2,3\). (1) Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Tokyo-to, Japan (2) Innovation Center of NanoMedicine, Kawasaki-shi, Kawasaki-ku, Japan (3) The Univ. of Tokyo, Policy Alternatives Research Institute, Bunkyo-ku, Tokyo, Japan (4) National Institute for Quantum and Radiological Science and Technology, Chiba-shi, Japan

Using messenger RNA (mRNA) as therapeutic nucleic acids is recently highlighted because mRNA is negligible to risk of host-genome integration and the transfection of mRNA to non-dividing cells is easier than that of DNA. These great advantages of the mRNA transfection are derived from mRNA property of expressing the coded gene in cytoplasm; however, mRNA is much more fragile than DNA and quick digestion of the transfected mRNA in cytoplasm limits the longevity of gene expression. We assume that construction of mRNA carrier system having high tolerability against nuclease digestion would promote not only survival of the loaded-mRNA under physiological environment but also the survival in cytoplasm, leading to the increased and prolonged gene expression. Herein, polyplex micelles (PMs) having hydrophobic barrier compartment between hydrophilic shell and the mRNA-loaded core were designed. The PMs were prepared from mRNA and triblock copolymer composed of hydrophilic poly(2-ethyl-2-oxazoline) (PEtOx) segment, thermo-switchable poly(2-n-propyl-2-oxazoline) (PnPrOx) segment and mRNA binding cationic poly(L-Lysine) (PLys) segment as follows: mixing mRNA with the triblock copolymer at temperature below LCST of PnPrOx, and subsequent incubation at physiological temperature, which is above the LCST of PnPrOx. The PnPrOx segment successfully enhanced tolerability against nuclease attack, increased survival of mRNA in cytoplasm, and improved gene expression compared to PMs prepared from diblock copolymer without PnPrOx segment. Moreover, enhancement of the PnPrOx barrier compartment was achieved by adding PnPrOx homo-polymer to the PMs solution before the incubation at the physiological temperature, showing further improved tolerability against nuclease and promoted gene expression. These results suggest forming hydrophobic layer is promising strategy to increase stability of PMs and the increased stability contribute to improve gene expression property of the loaded-mRNA.

Construction of the polyplex micelles with the hydrophobic barrier and further enhancement of the hydrophobic barrier
Protein-based therapeutics are becoming a major fraction of the world’s approved drug portfolio and are now used to treat a variety of diseases such as diabetes and cancer. Although protein-based therapeutics have high efficacy, selectivity, and minimal side effects, they suffer from premature degradation in vivo, which increases cost of treatment and reduces patient compliance. As a result, numerous studies have been devoted to the development of polymeric carriers to provide controlled release of protein therapeutics. Our lab has developed a library of thermoresponsive polyesters (TR-PEs) inspired by poly(acrylamides) (PAs), polyoxazolines (POx), and thermoresponsive elastin-like peptides (ELPs). A modular synthetic design allows for polyesterification of a variety of N-substituted monomers, yielding a library of high molecular weight TR-PEs, which undergo a reversible hydrophilicity change at a lower critical solution temperature (LCST). The hydrophilic nature of TR-PEs prevents full dehydration above the LCST, resulting in the formation of viscous polymer-rich coacervates. The degradable polyester backbone facilitates quick hydrolytic degradation. These features make TR-PEs ideal carriers for the controlled release of therapeutically useful proteins, whose biological function is dependent on maintaining their native structure. In this work, the ability of these polymers to encapsulate a model protein, fluorescently-tagged bovine serum albumin (FITC-BSA), is illustrated. We present a robust delivery system that is able to efficiently encapsulate proteins without loss of activity and delivery them locally in a controlled manner.
Being present for more than six decades, poly(2-oxazoline)s are in the lucky position to have grown older and wiser. As pseudo-polyamides, these (co-)polymers may be considered in numerous application fields such as high-voltage engineering as well as microelectronics. In such applications, (co-)poly(2-oxazoline)s can replace the well-established polyamides. One major advantage of poly(2-oxazoline)s is a combination of the facts that 2-oxazoline monomers can be polymerized in (pseudo-) living cationic ring-opening polymerizations and that numerous monomers can be synthesized from renewable resources. In more detail: The reaction of ethanol amine with carboxylic acids yields 2-oxazolines, e.g. 2-nonyl-2-oxazoline from decanoic acid (coconut oil) and 2-dec-9′-enyl-2-oxazoline from undec-10-enoic acid (castor oil). The corresponding copolymers such as poly(2-nonyl-2-oxazoline)-stat-poly(2-dec-9′-enyl-2-oxazoline) can be crosslinked with thiols.

This lecture will detail the applicability of poly(2-oxazoline)s as insulators in high-voltage engineering and as additive in blends for the fabrication of polymer surfaces with tunable functionality: The permittivity, loss factor and conductivity of (densely) crosslinked copoly(2-oxazoline)s are in the same range as for polyamides; the complex permittivity, however, decreases with the network density. Hence, the usage of glycol dimercapto acetate (with hydrolyzable ester bonds) as crosslinker limits the applicability of such poly(2-oxazoline)-based resins as insulators to the corresponding composites with nano-scaled fillers, the so-called nanodielectrica (Figure 1). Copoly(2-oxazoline)s with a precisely defined number of alcohol and carboxylic acid functions can be obtained from polymeranalogous reactions of poly(2-oxazoline)s such as the thiol-ene reaction with hydroxyl-functionalized thiols and the hydrolysis of side-chain ester groups. Such copolymers can be blended with non-polar polymers such as polyolefins, yielding polymer surfaces with tailor-made polarity and enhanced adhesion towards other polymers.

Figure 1: Nanodielectrica with non-functionalized and functionalized particles.
Reactive oxygen species (ROS) is known to play a variety of roles at many important event opportunities in vivo. However, overproduction of ROS causes serious adverse side effects in the body. Many drugs have been applied to reduce excessively produced ROS. However, low molecular weight (LMW) antioxidants spread nonspecifically to the whole body and are internalized in healthy cells. Since the organism acquires energy via the mitochondrial electron transport chain, such LMW antioxidants suppress this type of normal redox reaction and cause severe damage to normal organs and the body. In order to improve selective antioxidant properties in vivo, we started to focus on novel design of effective antioxidant drugs. Our concept of drug design is to avoid side effects such as inevitable toxicity of small molecules and to create safe and effective drugs by molecular assembly. To create this concept, we synthesized a redox amphiphilic block copolymer, forms self-assembling nanoparticles in an aqueous media. Our idea is to prevent mitochondrial damage of healthy cells by preventing cellular uptake by self-assembly structure of antioxidant. The nitroxe radical, which is one of the strongest antioxidants, covalently conjugated as a side chain of the hydrophobic segment in the block copolymer were compartmentalized into the solid core of the nano-drug and was named nitroxide radical containing nanoparticles (RNP\textsuperscript{N}). Because RNP\textsuperscript{N} is hardly incorporated into healthy cells, unlike LMW antioxidants, its in vivo toxicity has become extremely low. Since RNP\textsuperscript{N} has pH-sensitive disassembling properties, it collapse at pH-reducing tumors and sites of inflammation. We have confirmed that this particle can be applied for versatile oxidative stress related diseases such as cerebral, renal and myocardial ischemia reperfusion injuries, cerebral hemorrhage, cancer, ulcerative colitis and Alzheimer’s disease and it is promising as a novel antioxidant self-assembling nanodrugs.
POLY 154: Transdermal delivery of polymer nanoparticles via faint electricity

Kentaro Kogure1, kogure@mb.kyoto-phu.ac.jp, Yukio Nagasaki2. (1) Tokushima University, Tokushima, Japan (2) Tsukuba University, Tsukuba Ibaraki, Japan

Skin is the versatile target for macromolecular medicines. However, since stratum corneum is tight barrier of skin, non-invasive transdermal delivery of macromolecules is difficult. Recently, iontophoresis is known as a non-invasive transdermal delivery technology. Iontophoresis can deliver ionic molecules by using faint electricity (0.3-0.5 mA/cm²). Although it has been considered that iontophoresis delivers only small ionic molecules, we succeeded in the delivery of macromolecules and nanoparticles by iontophoresis (Kajimoto et al., Int J Pharm 2011). In addition, we found that faint electricity opens intercellular junction via activation of cell signaling pathway (Hama et al., J Biol Chem 2014). Based on these findings, we examined transdermal delivery of various polymer nanoparticles by iontophoresis. We tried the iontophoresis of antigen peptide-loaded nanogels, which are polymer-based nanoparticle, for anti-cancer vaccination. Iontophoresis resulted in the accumulation of the peptide and nanogels in the epidermis, and subsequent increase in the number of Langerhans cells in the epidermis. Moreover, tumor growth was significantly suppressed by iontophoresis of the antigen peptide-loaded nanogels (Fig.A, Toyoda et al., Int J Pharm 2015). Alternatively, we tried the iontophoresis of redox nanoparticles (RNP) for prevention of UV-induced melanin production in the skin. RNP containing nitroxide radicals as free radical scavengers were previously developed, and shown to be effective ROS scavengers in the body. RNP are therefore expected to be useful for effective protection against UV-induced melanin production. RNP were accumulated in the epidermal layer upon application of iontophoresis. Further, the combination of RNP with iontophoresis decreased UV-induced melanin spots and melanin content in the skin (Fig. B, Shiota et al., Biol Pharm Bull 2017). In conclusion, iontophoresis of polymer nanoparticles, such as peptide-loaded nanogels and RNP, would serve as an effective transdermal delivery system for various skin disorders.

Figure A) Suppression of tumor growth by IP of antigen-loaded nanogel, B) Reduction of UV-mediated melanin production by IP of RNP.
Delivery of hydrophobic photosensitizer (PS) efficiently to tumor or cancer cells is a key step for photodynamic therapy (PDT). Redox-responsive polymeric nanoparticles of amphiphilic macro-photosensitizer has designed and prepared as a prodrug-like pro-photosensitizer (pro-PS) for PDT. PEG chain works as the hydrophilic block and a near infrared (NIR) brominated BODIPY derivative (BDP) PS works as the hydrophobic molecule, and they were linked via the disulfide bond as PEG-SS-BDP, which could be broken for drug release owing to the high GSH concentration inside tumor cells. The amphiphilic PEG-SS-BDP can be self-assembled into polymeric micelles with suitable size (about 110 nm), which is benefit with prolonged blood circulation and enhanced tumor accumulation confirmed by NIR imaging in vivo. The higher efficiency of PEG-SS-BDP nanoparticles (PSSBDP NPs) than non-responsive PDT agent (PEG-BDP) with similar structure was confirmed by both in vitro and in vivo studies, suggesting the advantages of the redox-responsive pro-PS system for improving potential near infrared tumor imaging and photodynamic therapy.
POLY 156: Metabolism-controlled boron delivery systems composed of biocompatible polymers and boronophenylalanine for neutron capture therapy

Takahiro Nomoto¹, nomoto@res.titech.ac.jp, Yukiya Inoue¹, Ying Yao¹, Minoru Suzuki², Kaito Kanamori¹, Hiroyasu Takemoto¹, Makoto Matsui¹, Keishiro Tomoda¹, Nobuhiro Nishiyama¹. (1) Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan (2) Kyoto University, Kumatori-cho, Osaka, Japan

Boron neutron capture therapy (BNCT) is a therapeutic modality for tumors utilizing nuclear reaction of ¹⁰B atoms and neutrons, which generates α particles that can efficiently kill cells. Since the range of the α particle is about 10 µm, selective delivery of ¹⁰B to target tumor cells is critical for successful BNCT. Up to now, boronophenylalanine (BPA) has been extensively investigated as a boron drug in clinical studies, because BPA offers selective accumulation within tumors owing to its structure resembling phenylalanine, which facilitates cellular internalization through LAT1 transporters overexpressed on many tumor cells. However, upon decrease of extracellular BPA concentration, exchange transport mechanism of LAT1 might cause efflux of intracellular BPA. Such efflux may decrease intratumoral boron concentration during irradiation of neutrons, thereby compromising therapeutic efficiency of BPA.

Here, to improve the intracellular retention of BPA and maintain high intratumoral boron concentration, we have developed biocompatible polymers possessing polyol structures that can form reversible bonds with boronic acids. The polymers and BPA could form complexes by simple mixing of these components in aqueous solution, and the complex exposes the phenylalanine structure that is critical for recognition by LAT1. The polymer-BPA complex was internalized into cancer cells through LAT1-mediated endocytosis, and localized in endo-/lysosomes, whereas conventional BPA was localized in cytosol. The polymer-BPA also exhibited prolonged intracellular retention, which may be owing to the alteration of subcellular localization and avoidance of the efflux by LAT1. Importantly, the polymer-BPA revealed significantly enhanced tumor accumulation and retention, and exerted drastic antitumor activity upon irradiation of neutrons (Figure 1). Our polymer-BPA complex should offer great promise in clinical application.

![Figure 1. Antitumor activity.](Image)

The boron drugs were intravenously injected to mice bearing subcutaneous CT26 tumors, and the tumors were irradiated with neutrons 3 h after injection.
POLY 157: Enzyme-Directed Assembly of Particle Immunotherapeutics (EDAPI): A strategy for engineering tumor microenvironments for cancer therapy

**Claudia Battistella**, claudia.battistella@northwestern.edu, **Matthew P. Thompson**, Tomoko Hayashi, Cassandra E. Callmann, Dennis A. Carson, Nathan C. Gianneschi. (1) Northwestern University, Evanston, Illinois, United States (2) University of California, San Diego, La Jolla, California, United States

The cellular and chemical environment within tumors, the so-called tumor microenvironment, plays a central role in the ability of tumors to proliferate and evade immune surveillance. In recent years, medicinal efforts to alert the immune system to the presence of metastatic cancer have led to many new approaches stemming from the development of new small molecule-based drugs, to biological molecules and systems. However, since the systemic administration of these compounds can cause nonspecific immune activation and therefore toxicity, attempts have been made that aimed at the selective delivery and prolonged retention of these therapeutics to desired target tissues. With the aim of reengineering the tumor microenvironment and supporting the immune system in a safe and selective manner, we have developed a homing block copolymer-based particle that targets enzymes that are upregulated in several types of tumors. Upon accumulation into the tumor microenvironment, these immunotherapeutic-loaded nanoparticles undergo a morphological transition from nanoscale spherical-shaped, discrete materials to scaffold like, micron scale assemblies. These newly formed immunotherapeutic depots have the potential to awaken the immune system to attack not only the tumor tissue located both at the main, or primary site of the disease, but also tumor tissue that has metastasized.
DNA is a natural, biocompatible, biodegradable, bioactive, and arbitrarily designable polymer. These features of DNA promise its use as a material for the construction of delivery systems for bioactive compounds. Long double-stranded DNA, such as plasmid DNA, can be used for the delivery of therapeutic genes and anticancer agents, but their tissue distribution, as well as interaction with cells, is hardly able to be manipulated. Nanosized DNA constructs, which can be prepared by using two or more oligodeoxynucleotides (ODNs), can have diverse features from simple double-stranded DNA depending on their structure. Based on this difference, we have developed a variety of nanostructured DNAs with unique features and evaluated their physicochemical, biological and therapeutic properties. We first designed multibranched DNA nanostructures and obtained them with high yield. Tripod-like nanostructured DNA, or tripodna, was effective in increasing the retention of a phosphorodiamidate morpholino oligomer in the systemic circulation after intravenous injection into mice. In addition, cytokine release by unmethylated cytosine-phosphate-guanine (CpG) ODN was significantly increased by its incorporation into tripodna or hexapod-like nanostructured DNA, or hexapodna. We also succeeded in preparing DNA hydrogel by self-assembling of hexapodna with adhesive single-stranded tails. The DNA hydrogel obtained was injectable through a 27-G needle, and immediately regelated after injection. DNA hydrogels constructed with CpG ODNs, or CpG DNA hydrogels, were effective in the stimulation of innate immunity and in the sustained release of biomolecules incorporated into the hydrogels. CpG DNA hydrogel containing an ovalbumin (OVA)-derived antigen peptide significantly retarded the tumor growth in mouse T cell lymphoma EG7-OVA tumor-bearing mice. We also succeeded in incorporating dendritic cells together with the antigen into the hydrogel, which was effective in inhibiting tumor growth. These results indicate that nanostructured DNA is suitable for the in vivo delivery of biomolecules and cells.
Tailorable, non-toxic, PEI-based, nucleic acid delivery systems have been synthesized by covalent modification of the cationic polymer backbone. The modular approach used to prepare these non-viral vectors enables the insertion of controlled amounts of fluorescent labels, toxicity mitigators and cell targeting moieties. This work describes the toxicity and transfection ability of a pair of novel, chemically-related, polymers in three different mammalian cell lines. Fluorescently-tagged polymer and fluorescently-labeled plasmid DNA were used to enable the detailed monitoring of the location and shape evolution of the DNA-delivering complexes within cells via confocal microscopy. Our studies demonstrate that minor differences in the chemical architecture of the functionalized PEIs can have significant effects on cell toxicity, and polymer-DNA aggregate size/charge ratios. The use of fluorescent labels in both plasmid DNA and cationic polymer produced fundamental insights into the effect of polymer structure on its interaction with the polynucleotides and the cell membrane. A better understanding of these interactions will enable the identification of promising pathways towards the development of effective, targeted cationic polymer-based reagents.
Major non-viral polymeric vectors studied for gene therapy are based on polyethylene imine (PEI) because of its high condensation ability and superior transfection efficiencies. Typically high molecular weight (MW) and branched PEI is used to electrostatically condense DNA and produce polyplex nanoparticles in the range of 10-100 nm capable of adsorptive endocytosis. To overcome the stability and low plasma half-life of PEI/DNA polyplex, the hydrophilic polyethylene glycol (PEG) is often utilized to decorate the polyplex surface resulting in "stealth" core-shell micelles. The major drawback of PEI is high cytotoxicity associated with high charge density, which directly relates to the MW. We have developed a new gene delivery system, three layered micelles (3LM) using low MW linear PEI and biodegradable polylactides (PLLA/PDLA).

For localized gene delivery DNA can be encapsulated within a gel forming polymer system; the vector is then implanted or injected within a close proximity to the target site. The 3LM is further formulated into a physical hydrogel by the stereocomplexation mechanism of enantiomeric PLA’s to study as an injectable local delivery system. The dual encapsulation mechanism by electrostatic interaction and solvent condensation to form 3LM allowed large-sized DNA to be efficiently loaded into compact nano-sized particles using low MW low-cytotoxic PEI. The folate-conjugated 3LM showed pH-responsive DNA release, significantly lower cytotoxicity, and successful targeting in activated macrophage and ovarian cancer cells achieving statistically higher transfection. Upon addition of an stereoisomeric micelle solutions to the 3LM, chain exchange between these two micelle population led to co-crystallization of PDLA/PLLA leading to network formation and eventual gelation occurred at ~37°C. Further structural analyses and gene delivery studies indicated that 3LM/hydrogel systems are promising systemic and local delivery systems.
POLY 161: Well-defined poly(ethylene glycol)-b-poly(ε-caprolactone) based diblock polymeric biomaterials for drug and gene delivery

Amin Jafari1, aminjafa@buffalo.edu, Guojian Zhang†, Lingyue Yan2, Mohamed Alaa Mohamed1, Yun Wu2, Blaine A. Pfeifer1, Chong Cheng1. (1) Chemical and Biological Engineering, University at Buffalo (SUNY), Buffalo, New York, United States (2) Department of Biomedical Engineering, University at Buffalo (SUNY), Buffalo, New York, United States

Due to the tunable structures and properties of polymers, polymer-based drug and gene delivery systems hold promise for treating a wide range of diseases in a more accurate and disease-specific manner. In this study, well-defined poly(ethylene glycol)-b-poly(ε-caprolactone) (PEG-b-PCL) based biomaterials were investigated for drug and gene delivery applications (Figure 1). Specifically, the polymeric biomaterials for individual delivery of: (1) doxorubicin (DOX) as an anticancer drug, and (2) plasmid DNA (pDNA) were successfully achieved through the synthesis of functionalized ε-caprolactone monomers, the subsequent preparation of functional PEG-b-PCL diblock copolymers, followed by post-polymerization click modifications. The DOX-containing polymer-drug conjugate (PDC) was obtained by using alkyne-functionalized ε-caprolactone as the starting monomer to prepare the corresponding functional PEG-b-PCL for DOX conjugation. Cytotoxicity study using MCF-7 cells showed that the PDC micelles led to improved anticancer efficacy as compared to free DOX. The PEGylated cationic PCL (CPCL) for pDNA delivery was prepared by using allyl-functionalized ε-caprolactone as the starting monomer to synthesize the corresponding functional PEG-b-PCL for modification with tertiary amine groups. CPCL can readily form nanocomplexes with pDNA via spontaneous electrostatic interactions. At optimal weight ratio of CPCL to pDNA, these nanocomplexes resulted in significant transfection efficiency.

![Figure 1. Conceptual illustration of PEG-b-PCL based drug and gene delivery systems](image-url)
The promise shown by polyethylenimine (PEI) as a non-viral gene therapy vector has been linked with its pH-responsive behavior. As less than half of the amines in PEI are protonated at typical physiological pH, PEI becomes increasingly protonated in acidic environments encountered during the gene delivery process, potentially altering interactions in PEI-nucleic acid complexes and facilitating endosomal release. Despite its importance, the relationship between pH-responsiveness properties of PEI and high transfection efficiencies of PEI-based vectors is not well understood. Here, we use atomistic molecular dynamics simulations to examine how linear PEI depends on protonation to provide a microscopic picture of structural changes in PEI during gene delivery. In general, as PEI transitions from being uncharged to fully protonated, it changes from a compact configuration containing many intrachain hydrophobic interactions to an extended structure. However, the specific behavior underlying this expansion depends on whether the chain is a weak or strong polyelectrolyte, a transition that occurs at a protonation level of ~40%. In the weak polyelectrolyte regime, chain expansion is associated with disruption of most hydrophobic interactions, but, chain stiffness, quantified by the persistence length, is relatively constant. In the strong polyelectrolyte regime, increasing protonation is associated with increasing stiffness and a change in the torsional angle defined by N-C-C-N atoms along the chain backbone. Furthermore, the ionic strength had a stronger effect on the chain size within the strong regime.
POLY 163: Utilizing functional monomers with self-accelerating reactions to explore polymers with new structures and functions

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

Advance in polymer materials is always desiring new polymerization methods that can use inexpensive monomers to achieve better controlled polymer structures and architectures. When selecting the suitable monomers, one of the desiring criteria is that the monomers can involve self-accelerating reactions to efficiently connect building blocks into one macromolecular structure. This presentation discusses our recent interest on utilizing several functional monomers with self-accelerating reaction features for synthesis of hyperbranched polymers with high degree of polymerization, molecular brushes with high grafting density of side chains and linear polymers with high molecular weights with no need of stoichiometric balance of monomers. These polymers are successfully applied as unimolecular nanocontainers for encapsulation and as membrane materials for efficient gas separation of CO₂ from CH₄.

Hyperbranched polymer with high degree of branching

Molecular brush with high grafting density

Linear polymer from step growth with high molecular weight
Block copolymers (BCPs), which consist of two or more distinct homopolymers covalently linked together, have been widely investigated as nanostructured materials for a range of applications due to their ability to self-assemble into a variety of phase-separated nanostructures. BCP nanostructures have been proposed for applications in microelectronics, photonics, separations, and energy conversion. This presentation will focus on the synthesis, self-assembly, and applications of multicomponent bottlebrush BCPs (BBCPs) with precisely defined sidechain sequence. These novel BBCPs provide an architectural platform for achieving independent control of BCP nanostructures and bulk properties. They have been utilized as templates for hierarchically porous carbon, which can be used in supercapacitor electrodes, and as materials for membrane separators with charged nanodomains for use in redox flow batteries. Both of these applications take advantage of the accessibility of ultra-small nanodomains, as well as independently tuned nanostructure and bulk properties enabled by the BBCP architecture.
Polymer networks containing consist of long polymer linked together using crosslinking points. Introduction of dynamic linkers, such as non-covalent or dynamic covalent linkers into a polymer material can give materials with properties such as self-healing, increased toughness and shape memory characteristics. However, there is a delicate tradeoff between desirable dynamic characteristics and also undesirable mechanical instability under load or susceptibility to creep. Therefore, designing dynamic linkers with optimized for dynamic character and performance under ambient conditions is critical to applications of these materials. Small molecule analogues can be used to study the intrinsic dynamic covalent chemistry, providing insights into the performance of these dynamic linkers in a polymer network material. In this project, several dynamic covalent reactions will be explored, including dynamic thiol-Michael chemistry and dynamic exchange of anilinium salts. Detailed mechanistic studies will be presented to elucidate the conditions needed to establish dynamic exchange, and also to guide the design of the underlying polymer material. These mechanistic studies are subsequently translated to polymer networks crosslinked with these same crosslinkers, and insights gained from the small molecule study are used to optimize material properties such as mechanical strength, Young’s modulus dynamic character evaluated through self-healing potential and also stimulus induced malleability and also mechanical stability and creep resistance. In this way a bottom up design of dynamically crosslinked polymer materials is outlined using two representative systems.
Polyelectrolytes are a class of macromolecules containing charged groups. The fields of macromolecular sciences have enjoyed a unique combination of metals and soft organic frameworks in the name of metallopolymers, metal-containing polymers or organometallic polymers. When metallopolymers carry charged groups, they form a class of polyelectrolytes or metallo-polyelectrolytes. This is an emerging area that is particularly well suited for manufacturing functional materials. This presentation will focus on a few unique properties and functions of metallo-polyelectrolytes that conventional organo-polyelectrolytes, do not possess. Particularly I will talk about cationic metallocene-containing polyelectrolytes on the following perspectives: (1) electronic, bonding, and redox properties; (2) functional materials via electrostatic interactions; (3) ion-exchange for transport. A perspective on the critical challenges will be discussed, especially on experimental quantitative analysis and theoretical modeling of ionic binding.
Hypervalent iodine(III) reagents of the type ArIL₂ as well as benziodoxoles, or benziodazols with exocyclic hypervalent I-L bonds (Ar = aryl, L = (pseudo)halide, carboxylate, or tetrazolate) readily undergo ionic and radical reactions, and are very useful in the synthesis of functional polymers with complex macromolecular architectures. For example, many of the mentioned compounds serve as efficient radical initiators as well as chain transfer agents, and have found applications in the preparation of chain-end-functionalized linear or branched polymers. The radicals generated (typically L*, which are the result of the homolytic cleavage of the weak hypervalent I-L bonds) can also be used to modify pre-made polymers containing unsaturation, such as polybutadiene or polyisoprene, or even commodity polymers such as polystyrene. Further, due to the dynamic nature of the hypervalent I-L bonds, polymers containing the structural motif -L-I-L-, are both dynamic and self-healing. The synthesis of linear, branched, and network functionalized polymers as well as polymers containing hypervalent iodine-based building blocks will be described and the properties, and some applications of these materials will be discussed.

L = Cl, Br, N₃, RCO₂, RCN₄; R = H, Cl, alkyl, aryl
The use of deuterium labelling in conjunction with small angle neutron scattering (SANS) provides a powerful method to probe the confirmation of semicrystalline polymers, especially in regard to tie-chain estimation. Although polyethylene is the most widely consumed polyolefin, and such investigations are of great industrial interest, preparation of polyethylene with deuterium labeling has been challenging historically, either not allowing for high degrees of deuteration, or not permitting labeling of selective portions of the polymer chain, such as chain-ends. In this work, we have demonstrated the use of polyhomologation to prepare well-defined polyethylene with a controllable amount of deuteration which is uniform across the molar mass distribution. This initial investigation has been extended to include selective deuterium labeling of chain-ends as well, which will allow for identification of chain-ends in semicrystalline polyethylene by SANS. Furthermore, the deuterated polyethylene produced is hydroxy-terminated, making these ideal candidates for the preparation of functional deuterated polyethylene.
POLY 169: Dynamic-covalent chemistry for functional diversification, vitrimers, and other self-healing materials

Jacob J. Lessard, Michael B. Sims, Luis F. Garcia, Charles P. Easterling, Kyle C. Bentz, Scarlett Arencibia, Daniel A. Savin, Brent S. Sumerlin, sumerlin@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville, Florida, United States

By incorporating reversible covalent bonds within network materials, the traditional delineation between thermosets and thermoplastics can become blurred. This presentation will describe our recent work in using enaminone exchange as a way to access vitrimer materials based on commercially relevant vinyl polymers. Taking advantage of the reversible nature of the bonds that compose the crosslinks, these materials have the advantage of the enhanced solvent resistance and mechanical integrity of thermosets while also allowing reprocessing and healability more typically associated with thermoplastics.
POLY 170: Design of high-precision polymers by multistep synthesis

**Jean-François Lutz**, jflutz@unistra.fr. *Precision Macromolecular Chemistry, Institut Charles Sadron, CNRS, Strasbourg, France*

Synthetic polymers are usually synthesized by two main mechanisms: chain-growth and step-growth polymerizations. Although useful for large scale synthesis, both approaches lead in general to polydisperse samples, in which polymer chains have different chain-lengths. Furthermore, when different monomers are copolymerized via these mechanisms, the formed copolymers exhibit chain-to-chain composition- and sequence-deviations. This differs from biological polymerization mechanisms, in which uniform macromolecules with precisely-controlled chain-lengths, tacticity and monomer sequences are formed. Thus, over the past few decades, polymerization methods allowing a better control over macromolecular structure have been thoroughly investigated. For example, advanced chain-growth methods such as living anionic polymerizations and controlled radical polymerizations have opened up numerous opportunities for controlling the microstructure and architecture of synthetic (co)polymers. Yet, although more accurate than conventional polymerization approaches, these methods still lead to non-uniform samples. The next step in polymer chemistry is therefore the synthesis of uniform polymers with fully-controlled primary structures, as found in biology. Yet, classical methods such as chain growth and step-growth polymerizations are not valid options to synthesize such “high-precision polymers” for the simple reasons that are discussed above. The only way to do so is probably to borrow synthesis tools from other disciplines such as biology, biochemistry and organic synthesis. For example, solid-phase iterative chemistry, which was originally developed for peptide synthesis, is a tool of choice for preparing uniform synthetic polymers. In this lecture, I will highlight recent results obtained in my laboratory using such multistep growth strategies. In particular, I will discuss in details the synthesis of information-containing macromolecules; an emerging class of synthetic polymers that show promise for applications in data storage, anti-counterfeiting and traceability technologies.

Schematic classification of the different tools used for the preparation of synthetic (co)polymers.
We will discuss the preparation of [FeFe] hydrogenase mimetic metallopolymers via atom transfer radical polymerization to enhance the electrocatalytic activity of these materials for H₂ production. Transition metal-sulfides, both as clusters and as materials, are known to catalyze a wide variety of chemical transformations. In biology iron-sulfur clusters play key roles in electron transfer processes and redox activation of small molecules. As one important example, the butterfly [2Fe-2S] clusters in the active sites of [FeFe]-hydrogenase enzymes have been shown to reduce protons to molecular hydrogen at rates on the order of 10,000 molecules of hydrogen per enzyme per second. However, the electrocatalytic lifetime of these materials are often very short due to decomposition of the [2Fe-2S] complex under HER conditions. To alleviate this limitation, we have pursued the preparation of metallopolymers from the functional [2Fe-2S] clusters via ATRP of various vinylic comonomers to introduce well-defined (co)polymers to site isolate the complex during electrocatalysis. We will discuss in this presentation this new synthetic approach along as well as the critical role of controlled radical polymerizations and ATRP to afford next generation catalytic systems for H₂ production via water splitting. [figure1]
Atom transfer radical polymerization (ATRP) has been successfully used to synthesize various nanostructured polymers with controlled composition, topology and functionality. ATRP was carried out with ppm amounts of very active catalysts that can be externally mediated in spatiotemporal way. The resulting (co)polymers include block, graft and gradient copolymers, telechelics, densely grafted molecular brushes as well as organic/inorganic hybrids and bioconjugates with proteins and nucleic acids. Their properties and applications as specialty advanced materials in energy, environment and biomedical fields will be discussed.
Polymeric materials are important for their physical properties that lead to a wide array of products and applications. In order to understand how the chemical structure of a polymer controls the physical properties has been a major topic of the physics of soft materials. The ability to control the precise structure of a high molecular weight polymer has resulted in a lack of models systems that allow the detailed exploration of the structure function relationships. Over the past few decades, the strategies and that have led to significant advances in the synthesis of small molecules have been applied to controlled polymer synthesis. These techniques fall into the class of reactions that allow precise control of molecular weight and in many cases the stereochemistry of the polymers. We have developed a family of initiators that have found many applications in organic synthesis that also provide precise control of polymer structure. A family of brush polymers provide an excellent example of how synthetic control and modern instrumental methods allow for a precise model of the evolution of properties with structural changes.
POLY 174: Coarse-grained simulation of the dilute solution structure of bottlebrush polymers

Sarit Dutta¹, Matthew Wade¹, Dylan Walsh¹, Damien Guironnet², Simon Rogers¹, Charles E. Sing¹, cesing@illinois.edu. (1) Chemical and Biomolecular Engineering, University of Illinois, Savoy, Illinois, United States (2) Chemical and Biomolecular Engineering, UIUC, Urbana, Illinois, United States

Bottlebrush polymers have recently found use in a wide variety of materials, ranging from lubricating brushes and nanostructured coatings to elastomeric gels that exhibit structural color. They have unique properties that stem from densely-grafted side chains, which act to increase the stiffness of the chain backbone. It remains a challenge to specifically understand conformational properties of these molecules, due to the wide range of architectural parameters that can be present in a system, and thus there is a need to accurately characterize and model these molecules. To address this challenge, we will use coarse-grained computer simulations to gain insight into the conformational properties of dilute bottlebrush polymers. Our simulations are a combination of Brownian Dynamics and Monte Carlo, with parameterization inspired by the bottlebrush chemistry and in close collaboration with experimental synthesis and characterization. We compare against a series of model bottlebrushes consisting of a poly(norbornene) (PNB) backbone with poly(lactic acid) (PLA) side chains; here we use both intrinsic viscosity and hydrodynamic radius as experimental observations sensitive to molecular architecture, exhibiting distinct differences with different choices of branch and backbone lengths. We show that this exhibits quantitative matching to experimental results, enabling us to characterize the overall shape of the bottlebrush via a number of metrics that can be extended to more general bottlebrush architectures.
Photonic crystals (PC) are periodic nanostructures engineered in nature to reflect different wavelengths of light for camouflage, signaling, photosynthesis, and heat control. These natural photonic crystals can be mimicked through the self-assembly of block copolymers (BCPs). The challenge of BCP self-assembly to photonic crystals is that chain entanglement often impedes the self-assembly of linear BCPs into a periodic structure of required domain size. By engineering the macromolecular architecture to reduce the BCP’s capacity for chain entanglement in order to enable self-assembly to large nanostructures, it is possible to provide an approach to polymer based visible-light reflecting PCs. For example, bottlebrush BCPs are often used to reach domain sizes large enough to reflect visible wavelengths of light and beyond. However, recently it has been shown that rigid, yet linear, BCPs can self-assemble to photonic crystals that reflect wavelengths of light across the visible light spectrum and into the near infrared depending on the molecular weight of the polymer. These rigid linear polymers have a unique dendritic architecture that promotes interesting dynamic melt and mechanical properties. These dendritic polymers possess many characteristics that are similar to those of bottlebrush polymers when compared to the responses that a non-rigid, linear polymer would produce. These responses include a rod-like conformation, a reduced capability for chain entanglement, and lower glassy moduli compared to non-rigid, linear polymers. Further, dendritic BCPs possess high free energy parameters, as well as glass transition temperatures below melt extrusion 3D printing operating conditions and are able to self-assemble into photonic crystals during the process of 3D printing. Lastly, varying the molecular weight of the BCP allows selective reflection of the PCs for wavelengths of light across the visible spectrum.
POLY 176: Aqueous self-assembly of amphiphilic cylindrical and cone-shaped (tapered) bottlebrush polymers prepared by sequential-addition of macromonomers ring-opening metathesis polymerization (SAM-ROMP)

John B. Matson, jMATSON@gmail.com. Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Due to their large size and densely grafted architecture, amphiphilic bottlebrush block copolymers exhibit unique self-assembly behavior. For example, in solution, amphiphilic bottlebrush block copolymers self-assemble to form large micelles due to their larger size compared with linear polymers (Figure 1). They also tend to form micelles with critical micelle concentrations (CMCs) significantly lower than those of comparable linear block copolymer amphiphiles. Here systematic studies of both cylindrical and tapered bottlebrush polymer self-assembly will be presented. The bottlebrush block copolymers polymers were prepared using norbornene-functionalized polystyrene and poly(acryloylmorpholine) macromonomers, accessing the tapered versions using the SAM-ROMP technique. Analysis of assemblies by small-angle neutron scattering (SANS) will be discussed, supplemented by coarse-grained molecular dynamics simulations, CMC measurements, dynamic light scattering studies, and transmission electron micrographs.
Molecular bottlebrushes have been shown to exhibit intriguing worm-to-globule shape transitions in response to external stimuli. However, such shape transitions have been restricted to dilute solutions (< 1.0 mg/g) or at interfaces, which has greatly limited the potential application of these shape-changing molecular bottlebrushes. Here we present a method to achieve worm-to-globule transitions in moderately concentrated aqueous solutions by using binary heterografted molecular bottlebrushes. These brushes are composed of a poly(ethylene oxide) (PEO) and a thermosensitive polymer as side chains, where PEO is much longer so as to shield the thermosensitive side chains to avoid intermolecular association during the lower critical solution temperature transition. A small amount of UV-crosslinkable groups was incorporated into the thermosensitive polymer, allowing the fixation of the brush shape at higher temperatures for atomic force microscopy characterization at ambient conditions. Three brush samples, BMB-5k, -2k, and -750, were synthesized by grafting a thermosensitive polymer with a degree of polymerization (DP) of 43 and a PEO with a DP of 114, 45, or 17, respectively, onto a backbone polymer via click chemistry. While BMB-2k and -750 underwent intermolecular aggregation at a concentration of 10 mg/g upon heating, BMB-5k collapsed intramolecularly from a wormlike to a spherical shape at concentrations of 10 and 25 mg/g. Even at 100 mg/g, at least 95% of brushes underwent a worm-to-globule transition.
POLY 178: Grafting linear and linear-hyperbranched block copolymers by continuous flow chemistry polymerizations

Rigoberto C. Advincula, rca41@case.edu. Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States

Polymer grafting and the use of controlled polymerization and architectures have created new composition-structure property relationships. The advent of controlled process chemistry by using flow parameters and micro-confinement or micromixing has enabled far more efficient and high yielding reactions especially in organic synthesis and the development of new pharmaceutics or drugs. The continuous flow synthesis of polymers allows for the in-situ and real-time production of materials necessary for the production of plastics, hydrogels, surfactants, proteins, etc. In this talk, we will demonstrate the possibilities for grafted linear and block copolymer polymerization and hyperbranched polymer synthesis under continuous flow chemistry conditions and their possible using in nanostructuring and nanomaterials synthesis including grafted particles. This can be done by producing better pressure, volume, and temperature control often reaching supercritical or optimized flow conditions. For example, better polydispersity, molecular weight, block copolymer and branching efficiencies have been reported in flow chemistry. We will also report our recent results in living free radical polymerization and microparticle modification methods.
POLY 179: Manipulating monomer segment distributions to tune self-assembly and macromolecular properties in ion-conducting block copolymer systems

Thomas H. Epps\textsuperscript{2,1}, thepps@udel.edu, Melody A. Morris\textsuperscript{2}, Cameron K. Shelton\textsuperscript{2}, Priyanka Ketkar\textsuperscript{2}. (1) Materials Science & Engineering, University of Delaware, Newark, Delaware, United States (2) Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware, United States

The self-assembly of block polymers (BPs) presents unique opportunities to design materials with attractive chemical and mechanical properties based on the ability of BPs to form periodic structures with nanoscale domain spacings. One area of recent progress in our group focuses on the behavior of tapered BPs (Figure 1) in which the segment distribution at the interface between blocks is synthetically varied to tune morphology, domain density profiles, thermal transitions as well as mechanical and transport properties. Two application targets for these materials are lithium-ion conducting membranes for batteries and nanostructured thin films for nanotemplates and barrier membranes. In the first target area, we found that the taper volume fraction and composition allow us to manipulate the self-assembly of salt-doped BPs in a well-defined manner that permits optimization of morphology and ion-content. Additionally, we found that the tapered interfaces influence the glass-transition behavior of the ion-conducting block leading to significant changes in lithium-ion transport (ion conductivity). In the second target area, we found the taper content alters the rate of self-assembly as well as the rate of island/hole formation (and ultimate island/hole size) upon thermal annealing. Additionally, using reflectivity techniques, we probed the domain density profiles as a function of taper composition and linked these profiles to changes in domain spacing and glass transition temperature. Overall, these studies show the versatility of tapering to provide a unique handle for simultaneously optimizing multiple materials properties.
Designing both conductive and structural components into ion transport membranes is important for improved electrolytes for lithium ion batteries and other uses. We have synthesized block copolymers by ring opening metathesis polymerization based on an oxynorbornenedicarboximide backbone structure with an oligomeric ethylene oxide sidechain in one block and a phenyl side group in the other. The homopolymer of this ion soluble block has a measured conductivity of $\sim 1 \times 10^{-4}$ S/cm at 80 °C. The morphologies of thin film samples of the copolymers have been studied using atomic force microscopy (AFM) and SAXS both neat and with added salt. The block polymers with added salt order well, especially with the use of solvent vapor annealing, and produce dominantly cylinder and lamellar morphologies. The range of block copolymer compositions with lamellar structure appears to widen with added salt. Both photo-induced force microscopy (PiFM) and viscoelastic mapping mode (AM-FM) AFM techniques have been used to establish the identity of topographic AFM domains by chemical composition and relative modulus, respectively. Ion dynamics in block copolymer thin films were also studied with time-resolved electrostatic force microscopy (trEFM) and demonstrate the measurement of ion motion in the ion conductive domains at the nanometer length scale.
Poly 181: Exploring ionic conduction mechanism in the nanoscale by self-assembled block copolymer electrolyte films

Daniel Sharon^1,2, dssharon27@gmail.com, Peter Bennington^1, Shrayesh Patel^1,3, Paul F. Nealey^4,2. (1) Institute of Molecular Engineering, The University of Chicago, Chicago, Illinois, United States (2) Material science division, Argonne National Laboratory, Lemont, Illinois, United States (3) Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois, United States (4) IME, Chicago, Illinois, United States

Block copolymer electrolytes are promising candidates for electrochemical solid-state devices such as fuel cells and batteries. Their ability to conduct ions, while retaining their structural integrity makes them a safe choice for future technologies. Nevertheless, these materials often show a lower conductivity even after accounting for the reduced volume fraction of the conducting phase. The reason for the ionic transport hindrance is still under investigation. Many researchers attribute the slowdown in ionic conduction to combination of multiple phenomena such as tortuosity of the conducting pathways, poorly connected domains, grain boundaries, and low mobility near the polymers interfaces. The common denominator for all of these phenomena is that they occur in nanoscale domains which exist in different morphologies of block copolymers. However, most block copolymer electrolytes membranes studies are done in the micron scale which might be not sensitive and accurate enough. Here, we present a new approach to this challenge wherein we can fully align the block copolymer nanostructure along the direction of the electric field produced by coplanar interdigitated electrodes, thus enabling us to divorce morphological effects from other molecular-level effects. We observe that a poorly conducting region near the interface of the two blocks might explain the lower conductivity.
Polymerized ionic liquids (PILs) are promising polymeric materials for energy applications which are ionically conductive, thermally stable and synthetically versatile. The structure-properties relationship of linear PILs and various copolymers (random, block) have been extensively studied, yet little is known about the role of architecture, such as networks, on the morphology and transport properties. We have synthesized linear and network PILs containing precise linker lengths between charges using step-growth polymerization. Two different of linker chemistries, either an 11 atom hydrocarbon chain (HC) or tetra(ethylene oxide) (EO, also an 11 atom backbone), to vary the network polarity. The anion is TFSI and the cation is ammonium in all cases. Thermal analysis by differential scanning calorimetry revealed the glass transition temperature (Tg) was -38 °C for both EO and HC linear PILs. In contrast, the Tg in network PILs was 7 and -5 °C in the HC and EO networks, respectively. Wide-angle X-ray scattering (WAXS) measurements revealed that the ionic aggregation peaks were less intense in the EO systems, consistent with a more polar chemistry providing better ion solvation. Network PILs of both HC and EO linkers had a more pronounced ionic aggregation peak intensity than their linear counterparts, indicating a role of polymer architecture on ion clustering. It was anticipated that the network would help reduce clustering due to topological constraints, but this is not the case experimentally. In addition to a more pronounced aggregation peak, the EO network showed a two order of magnitude increase in conductivity relative to the linear analogue at Tg + 10 °C. Linear and network PILs with HC linkers show identical Tg normalized conductivities. This systematic study provides a new insights on how polymer architecture and polarity can influence the aggregation and transport of ions in PILs.
Polymeric Ionic Liquids (PolyILs) has the advantage of being single ion conductors with high transference number for the mobile ion. However, the low conductivity at ambient temperature limits their practical applications. To improve conductivity, one of the strategies is to decrease the glass transition temperature (Tg) of the system. Here, we report a single-ion conducting polymer electrolyte with PDMS backbone, exhibiting low Tg and high lithium conductivity at room temperature. A regular polymer electrolyte, polymer of (methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl) imide (MPA-TFSi Li), has been synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization as a reference sample. The PDMS backboned sample was synthesized via thiol-ene chemistry between the MPA-TFSi Li and thiol functionalized PDMS. The presence of flexible PDMS backbone drops the Tg significantly (from 334K to 284K) and increases conductivity (from $4.1 \times 10^{-13}$ S/cm to $1.0 \times 10^{-11}$ S/cm) at room temperature. Copolymerization with low-Tg PEO segments further decreased Tg. By tuning the ratio of EO:Li, the highest Li conductivity of $2.9 \times 10^{-6}$ S/cm at ambient temperature was achieved. Tg value can be as low as 218K when EO:Li ratio is 18:1. Furthermore, study of the similar system with sodium ion proves that the same strategy also works for Na.
POLY 184: Effect of relative humidity on the ionic conductivity of poly(ionic liquid) networks containing variable counteranions

Kevin M. Miller¹, kmiller38@murraystate.edu, R. D. Johnson¹, Nicholas C. Bontrager¹, Samantha A. Radomski¹, Nicholas C. Bontrager¹, Samantha A. Radomski¹, (1) Department Of Chemistry, Murray State University, Murray, Kentucky, United States (2) Calloway County High School, Murray, Kentucky, United States

Poly(ionic liquid)s (PILs) continue to be a fascinating area of research in that these materials often exhibit the mechanical stability found in most macromolecular architectures while maintaining most of the attractive properties of ionic liquids (variable thermal and electrochemical stability; ionic conductivity). In this study, a series of covalently crosslinked, imidazolium-containing PIL networks were prepared using a thiol-ene photopolymerization technique. The counteranion was varied (Cl, NO₃, OM₃, OTf, ClO₄, PF₆, NTf₂) in order to observe the corresponding changes in thermal, mechanical and conductive properties of the networks. Additionally, as these anions have a variable degree of hydrophilicity, the effect of humidity on ionic conductivity was measured and analyzed in terms in ion mobility and transport. Humidity was found to have a profound effect on the conductivity and ion mobility of hydrophilic anions such as chloride and nitrate but no effect whatsoever on hydrophobic anions such as hexfluorophosphate and bis(trifluoromethanesulfonyl)imide.
POLY 185: Developing a new approach to describe ion sorption and transport in Nafion membranes

Rahul Sujanani¹, rsujanani@utexas.edu, Jovan Kamcev², Eui-Soung Jang¹, Donald R. Paul¹, Benny D. Freeman¹. (1) Mcketta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States (2) Department of Chemistry, University of California, Berkeley, Berkeley, California, United States

Ion exchange membranes (IEMs) are widely used in water purification applications, such as reverse osmosis and electrodialysis and are also applied and explored for energy generation applications, such as fuel cells or reverse electrodialysis. IEMs are composed of charged polymers that contain charged moieties bound to the polymer backbone. The presence of these charged groups has significant impact on ion and water transport through these materials and allows for selective permeation of ionic species, making them attractive for the separations required for water and energy applications. However, a detailed understanding of the impact of polymer structure and morphology on ion and water transport properties in IEMs remains largely incomplete.

We recently developed a theoretical framework, consistent with thermodynamics, to calculate, and in some cases predict, fundamental ion transport properties in charged polymers. We validated this framework via careful, systematic measurements of water and ion sorption, permeability, and ionic conductivity. We are now extending this framework to Nafion, a perfluorinated sulfonic acid polymer. Nafion has a significantly different chemical structure and morphology than the previous IEMs we have studied. Due to Nafion's exceptional ionic conductivity and robust mechanical and chemical stability, it is considered the benchmark material for fuel cells. The fundamental origins of these unique properties are often debated in the literature. Results for NaCl and MgCl₂ sorption in Nafion show that our framework describes the experimental data remarkably well. Transport measurements were also performed, showing similar behavior reported in the literature, and efforts are underway to model these properties. A key goal of these studies is to identify and elucidate the molecular features of IEMs that can be used to rationally design materials with rapid and selective ion transport.
POLY 186: Biomimetic neurons using polyelectrolytes: Experimental implications on current models

Susan Kozawa¹, susan.kozawa@case.edu, Loren Kreider⁴, Gillian Tierney¹, Anita Venkataswamy¹, Anne Y. Walker³, Gary E. Wnek². (1) Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States (2) Case Western Reserve University, Cleveland, Ohio, United States (3) Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States (4) Indiana Institute of Technology, Fort Wayne, Indiana, United States

From developing an electrolyte-based system that exhibits movement, the dynamics studies of charged ions moving through a charged system and the interactions they have on each other can be inferred. Using a polyelectrolyte based system, the overall movement of the polymer, which moves completely moves from one side to the other, is dictated by the ions and their effects. Looking into the overall experimental effects of whipping and dragging motion of the polymer through ion charges and gradients, a more fundamental look at electrostatic gradients and diffusion, and the interplay they have on the hydration size of each aspect. Understanding these driving forces of movement from a macromolecular perspective can give rise to the underlying principles that govern the movement of muscles and neurons.

40mM NaCl – PAA – 27mM CaCl₂ movement at increasing time points from a-d. The video, a time lapse of 2.53 hours, shows the ‘whipping’ movement of the gel thread. The thread end in 27mM CaCl₂ solution ‘whips’ over to the 40mM NaCl side. It is also seen that the motion initiates in the middle of the gel thread, where the solutions meet and between the air gap.
POLY 187: Platinum-acetylide polymers: An investigation of ultrafast photoinduced charge transfer

Ru He¹, chashe@ufl.edu, Silvano Valandro³, Kirk S. Schanze². (1) Department of Chemistry, University of Florida, San Antonio, Texas, United States (2) Chem Dept, University of Florida, Gainesville, Florida, United States (3) Chemistry, University of Texas at San Antonio, San Antonio, Texas, United States

Platinum-acetylide polymers upon photoexcitation undergo fast intersystem crossing resulting in triplet-excited state. Relatively high triplet energy level, large triplet yields and significant amount of phosphorescent emission make them attractive materials for organic light emitting diodes, photovoltaic cells and non-linear optical process. We are interested in exploring the triplet excited state dynamics of Pt-acetylide polymers as well as the photo-induced charge transfer between Pt-acetylide polymers and [6,6]-Phenyl-C₆₁ butyric acid methyl ester (PCBM) in blending films. In this work, we synthesized Pt-acetylide polymers (poly-PtTh and poly-PtPh) having thienyl and phenyl spacer groups, respectively. Steady state and time resolved photophysics of Pt-polymers were explored in solution as well as in thin films. Both of the polymers yielded high amounts of triplet excited state and were phosphorescent at room temperature. In order to provide direct evidence for the photo-induced charge transfer, femtosecond transient absorption experiments were carried out in solutions and thin films in presence and absence of PCBM. Pt-acetylide polymers showed a convolution of two transient absorption spectral features: (i) at early times stage, two transient absorption bands in the visible and NIR range can be attributed to the excited state absorption (ESA) of the Pt-acetylide polymers; (ii) as the delay time increased, the intensity of the ESA decreased while a new band in the visible range was founded. This band was attributed to triplet-triplet absorption. Upon the addition of PCBM, a new feature in the NIR region was observed. This new feature, a shoulder at 1050 nm, can be assigned to the PCBM radical anion generated by the charge transfer between the Pt-acetylide polymers and PCBM. Our studies of Polymers/PCBM in solution and blending films suggest that charge carriers are produced in a photo-induced electron transfer involving the triplet excited state of Pt-acetylide polymers in the picosecond time scale.
POLY 188: Assembling graphene oxide at fluid-fluid interface: A new way to architect hybrid structures for advanced application

Peiran Wei, pxw182@case.edu, Emily Pentzer. Chemistry, Case Western Reserve University, Cleveland, Ohio, United States

Fluid-fluid interfaces have widespread applications in oil recovery, mineral processes, etc. and are versatile platforms for generating advanced materials. To stabilize the interface and reduce the interfacial energy between two fluids, surfactants are indispensable. Complementary to emulsions using small molecule surfactants, particle-stabilized emulsions have outstanding stability and unique applications. To date, novel particle surfactants and different fluid-fluid systems have been used for the development of next-generation systems for advanced applications. One type of particle that has attracted attention for use as a surfactant is graphene oxide (GO), nanosheets of carbon atoms functionalized with oxygen functional groups. Of particular interest, GO nanosheets can be modified by simple chemical reactions of the oxygen-containing functionalities. Here I report a simple modification of GO particles and their assembly at fluid-fluid interfaces to access unique architectures and applications. By controlling factors that govern the assembly of GO nanosheets, hollow spheres, filled capsules, and shell-stabilized bubbles can be fabricated, and the structure-property-application relationships of these systems are studied.

Assembly of Graphene Oxide at Fluid-Fluid Interface
Polymer metal-organic cage (polyMOC) gels are polymer networks with well-defined MOC junctions formed from the multicomponent assembly of appropriate ligands (L) and metal ions (M), where the cage architecture can vary greatly depending on the bite angle of L. Cages that provide high branch functionality (such as M_{12}L_{24}) produce polyMOC gels with relatively high shear modulus as well as a large number of loop defects. These inelastic loops can be exchanged with functional free ligands at little cost to the modulus, allowing the practical application of polyMOC gels through the incorporation of endo-functionalized free ligands. As a result, this material provides a template that can be tailored to adsorb water pollutants with high specificity: since the nanoenvironment inside each MOC is easily interchangeable with different free ligands, multiple water pollutants can be adsorbed with high affinity by using polyMOC gels in combination. Our modular system uses telechelic tetra-arm poly(ethylene glycol) (PEG), end-functionalized with M_{12}L_{24}-forming bispyridine ligands. The self-assembly of this telechelic PEG with functionalized free ligand and platinum salt produces a robust gel that has been able to withstand up to 12 wash and reuse cycles. Using free ligand endo-functionalized with a fluorinated alkyl chain, we have created a polyMOC gel able to adsorb model compound perfluorooctanoic acid (PFOA) at 95% efficiency ([PFOA]_{0} = 160 \mu g/L, [gel] = 6.4 mg/mL). Preliminary results show that contents encapsulated within MOCs can be washed, regenerating the polyMOC gel for reuse.
POLY 190: Tuning mechanical properties of polymer brush surfaces to dictate wrinkle morphologies

Cassandra Reese¹, cassandra.reese@eagles.usm.edu, Wei Guo¹, Brittany Thompson¹, Christopher M. Stafford², Derek L. Patton¹. (1) Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) NIST, Gaithersburg, Maryland, United States

Surface instabilities are universal phenomena in natural and synthetic systems over a wide range of length scales. Common examples in everyday life are wrinkling in human skin, dried fruit, and imperfectly cured coatings. In recent years, researches have focuses on utilizing wrinkling to tailor material properties for applications in stretchable electronics, microlens arrays, controlled wetting surfaces, tunable surface adhesion, and anti-counterfeit technologies. However, predictable control of wrinkle wavelength remains a challenge. Recently, we reported a simple route to engineer ultrathin poly(styrene-alt-maleic anhydride) (pSMA) brush surfaces with tunable wrinkled morphologies using post-polymerization modification, where the length scale of the buckled features can be tuned using reaction time and anhydride conversion. Although, we were able to quantify swelling ratios that result in the observed wrinkled morphologies, the applied compressive strains that dictate wrinkle wavelengths have yet to be determined. Herein, we derived an expression relating applied compressive strain, cystamine-modified “skin” thickness, wrinkle wavelength, and wrinkle amplitude. We validate the derived expression using wrinkling behavior of a model system, e.g., polystyrene film mounted onto a poly(dimethylsiloxane) substrate. Next, we applied this expression to quantify the applied compressive strains that result in the wrinkled morphologies of pSMA brushes. Finally, we elucidate the relationship between the applied compressive strain and the persistence length of aligned wrinkles via AFM lithography. We demonstrate a method to align wrinkled morphologies by tuning anhydride conversion.
POLY 191: Facile synthesis of carbon flower particles from a novel polyacrylonitrile system

Shucheng Chen¹, shucheng1222@gmail.com, Zhenan Bao². (1) Chemical Engineering, Stanford University, Stanford, California, United States (2) Chemical Engr Dept MC 5025, Stanford University, Stanford, California, United States

It is of great importance to design some facile and efficient methods to synthesize carbon materials for any desirable application since carbon catalysts are of great interest for energy conversion processes and devices because of their wide tunability and much low cost. Porous polymer framework structures provide high versatility in tuning carbon structure and chemical composition. In this regard, we have studied different polymer systems that can be tailored to prepare carbon materials for targeted applications. In this talk, I will specifically talk about a novel polymer system that can be tailored to produce carbon materials for different energy and environment applications. Three-dimensional hierarchical porous carbon materials with flower-like superstructures are advantageous for energy applications due to the unique structures for enhanced mass transportation. Finding a controllable way to make porous carbons with such specific shapes has been challenging. We have discovered a tunable and simple method for one-pot synthesis of polyacrylonitrile and its copolymer nanostructured particles with various superstructures (flower, pompom, hairy leave, and petal shapes) controlled by employing various solvents or by the incorporation of different co-monomers. The correlation between polymer particle shapes and solvent properties has been identified through Hansen solubility parameters analysis. The obtained carbons from this polymer system have demonstrated advantageous properties for applications in electrocatalysts, pressure sensors, and thermo-switchable safe batteries, and etc.
POLY 192: Photopolymer design for additive manufacturing of elastomers

Philip Scott¹,³, scottpj@vt.edu, Viswanath Meenakshisundaram¹,², Maruti Hegde¹,³, Justin M. Sirrine¹,³, Nicholas A. Chartrain¹,²,⁴, Christopher Kasprzak¹,³, Keyton Feller¹,², Christopher B. Williams¹,², Timothy E. Long¹,³. (1) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia, United States (3) Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States (4) Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia, United States

Vat photopolymerization (VP), a leading additive manufacturing platform, enables the rapid fabrication of complex architectures with unprecedented precision through layer-by-layer photocrosslinking of liquid photopolymer precursors. However, the viscosity requirements of the process restrict the current library of suitable photopolymers to low molecular weight monomers and oligomers, severely limiting the mechanical and elastic performance of 3D printed objects. An array of innovative synthetic strategies in photopolymer design is imperative to overcome this obstacle and produce networks with high molecular weight between crosslinks ($M_c$) from low-viscosity precursors. A novel approach involves simultaneous thiol-ene step-growth chain extension and acrylate crosslinking to combine the processing advantages of low molecular weight systems with tunable (thermo)mechanical performance similar to high $M_c$ networks. A liquid polybutadiene oligomer/dithiol resin cures selectively under UV exposure with photoinitiator to form uniquely high-strain, elastic parts in comparison to traditional oligomeric diacrylate systems. In concert with VP, this system enables the fabrication of well-defined elastomeric architectures. In our most recent efforts, a unique approach utilizes colloidal morphology to effectively decouple molecular weight from viscosity through the sequestration of polymer chains into discrete internal domains. Upon introduction of photoreactive crosslinking chemistry, this novel system introduces a previously inaccessible range of polymer structure, molecular weight, and mechanical performance to VP photopolymers. Collectively, these strategies represent unique synthetic strategies to address the obstacles limiting the application of VP additive manufacturing for high-performance elastomers.
Polymerization-induced phase separation has shown promise in generating materials with controllable morphology and mechanical properties. In this work, we show that irradiation intensity and formulation chemistry allow direct control of phase separation in photo-cured hybrid radical/cationic systems. Our investigation reveals that irradiation intensity has a deterministic effect on the formation of phase-separated domains. By increasing the irradiation intensity in butyl acrylate (BA) and di-oxetane (DOX) photopolymerizations, the morphology changes from one with a continuous softer BA domain to one with co-continuous BA (soft) and DOX (hard) domains. At higher irradiation intensity, the domain size of each phase is decreased due to fast photopolymerization which limits significantly monomer/polymer diffusion. On the other hand, irradiation intensity has little to no effect on polymer structure and mechanical properties for systems with low concentrations of BA as no phase separation is observed. Dynamic mechanical analysis demonstrates that phase separation in systems dramatically enhances mechanical properties such as Young’s modulus and elongation at break when the irradiation intensity is increased. The extent of phase separation is controlled further by incorporating multi-functional monomers that either cross-link the soft acrylate domain or connect the hard and soft domains using a hybrid acrylate-oxetane monomer. Atomic force microscopy shows that the domain size of the harder oxetane phase reduces with increasing crosslinker concentration because of faster gelation. Phase separation is maintained for up to 3 wt% crosslinker concentration but is significantly suppressed with very small phase-separated domains at higher crosslinker concentrations. Interestingly, an approximately three-fold increase in toughness is observed with higher elongation at break due to small hard and soft domains facilitated by controlled cross-linking and photo-cure intensity. These results demonstrate the ability to control the morphology and thereby significantly enhance properties of radical/cationic systems through photopolymerization-induced phase separation by modulating irradiation intensity and cross-linker design.
POLY 194: Chalcogenide Hybrid Inorganic/organic Polymers (CHIPs): A unique class of optical polymers for IR imaging and photonics

Tristan Kleine, tkleine@email.arizona.edu, Richard S. Glass, Robert A. Norwood, Jeffrey Pyun. University of Arizona, Tucson, Arizona, United States

The use of organic polymers for infrared (IR) optical applications has been an important technological advance that has not been realized due to the high absorbance of organic moieties in critical spectral windows required for imaging and photonics. Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) have changed this paradigm by allowing, for the first time, access to solution and melt processable materials possessing both high refractive index \( (n \sim 2.0) \) and low absorption in the IR owing to a very high \( (\leq 90 \text{ wt\%}) \) loading of inorganic chalcogenide units (namely sulfur and selenium). Since the first report on this class of materials, further improvements have been realized in both the thermomechanical and optical properties of these materials. Increasing the glass transition of CHIPs from \( \sim 25 \degree C \) to over \( 100 \degree C \) was accomplished by the synthesis of new organic crosslinkers, and realizing polymers with the highest refractive index ever reported \( (n = 2.1) \) was accomplished by incorporation of elemental selenium into CHIPs; furthermore, these materials retained excellent transparency in the Mid-Wave IR for use in bulk IR optics. In addition, utilizing CHIPs materials as the high refractive index component in 1D photonic crystals allowed easy, solution processing based fabrication of highly reflective (>90%), all polymer reflective coatings at very few bi-layers (11). Lastly, an emerging area of research has focused on developing materials that enable photodefinition of regions of high and low refractive index for the purposes of facile waveguide fabrication.
Emulsion polymers are employed in a range of paint markets such as house paints which are produced at a rate of more than 700 million gallons each year in the US alone. Waterborne coatings also include smaller volume but technically challenging applications such as liquid sound damping formulations. Damping materials are used in automobiles and other applications to provide reduced noise and vibration through dissipation of structural borne energy. Liquid applied dampers, are complex, dynamic multiphase systems that are typically spray applied directly to the structure and cured at elevated temperature. These materials provide a number of advantages over traditional damping materials such as automated application and lower weight. Liquid applied dampers contain film forming polymer particles which function as both the binder of the inorganic materials in the coating as well as the source of energy dissipation. In this study, coating samples were analyzed to determine relevant performance properties and internal structure of the coatings. Vibrational damping of the materials was measured using Oberst-bar testing. Scanning Electron Microscopy of the coating formulations and final cured coatings were used to explore structure-property relationships. Emulsion polymers with different viscoelastic properties and chemical compositions were designed and used to probe vibrational performance as well as other key application properties such as cohesion and adhesion to vehicle substrates. Results indicate that the polymer composition and latex particle characteristics are large contributors to desired performance aspects of the damping layer.
POLY 196: Hydrophobic polymers for improved barrier properties in industrial coatings

Danniebelle N. Haase, dhaase@dow.com. Dow Chemical Company, New Castle, Delaware, United States

Emulsion polymers and by extension coatings for application to exterior metal and wood substrates are designed to resist harsh conditions and provide the longest possible lifespan for the substrates (Figure 1). In addition to good scratch, chemical, UV and block resistance, flexibility and toughness, hardness and durability, these resins must be good barriers to moisture. There are many approaches to prepare polymers with good barrier properties. Incorporating hydrophobic monomers into the polymer backbone is one such approach. Now described are the recent efforts aimed at preparing hydrophobic acrylic emulsion polymers with a good balance of properties, and in particular, enhanced water resistance and improved anti-corrosion resistance.
Highly stable water-in-oil emulsions are common in the production, transportation, and refining of petroleum and related products. The emulsions are stabilized by a variety of surface-active compounds found in crude oil such as natural surfactants (specifically asphaltenes), carboxylic organic acids, and fine minerals. A critical step in the processing of crude oil is to break the interfacial film formed at the oil/water interface to enable the release of water from the oil. Demulsifiers are commonly used to promote the coalescence and separation of water from the crude oil. However, demulsifiers must compete with other surface active materials found in crude oil. This presentation will describe our research efforts on breaking water-in-oil emulsions focusing on water-in-oil interfacial properties that govern emulsion stability and demulsification. Semi-automated, high throughput techniques for rapid synthesis and screening of demulsifiers were used to determine the effectiveness of various demulsifiers and to develop fundamental understanding of various demulsifiers in emulsion breaking mechanisms.
Controlled radical initiators, such as ATRP or RAFT initiators, have become commonplace for the synthesis of a variety of polymeric materials. The use of these initiators allows one to more easily control the molecular weight and/or the polydispersity of the resultant solution polymers. Attachment of controlled radical initiators to solid substrates, however, is quite difficult, involving multiple synthetic steps, and is often very substrate dependent. We have designed a simple method for attachment of RAFT agents or iniferters to membranes and other solid substrates by taking advantage of the hydrogen abstracting ability of Type II photoinitiators such as benzophenone. Irradiation of nylon membranes coated with a solution of benzophenone and a xanthate-functional compound results in H-abstraction from the membrane surface. The free radical is trapped by transfer of the xanthate ester, resulting in a xanthate-functional membrane. This reaction process can be extended to other types of thiocarbonylthio-containing agents, such as dithioesters, dithiourethanes, and trithiocarbonates. E-beam irradiation provides an alternative and simple mechanism for generating radicals on substrates, which can subsequently be trapped by an appropriate thiocarbonylthio-containing compound. The functionalized substrates can be coated with free radically polymerizable monomers, then irradiated with UV or LED sources, to provide polymer-grafted substrates. We have grafted a variety of ionic monomers out of aqueous solution to provide ion exchange membranes for protein purification applications. However, a variety of other applications can be envisioned, and the entire process is potentially amenable to roll-to-roll manufacturing operations.
POLY 199: Sustainable plastics: Using polymer stabilizers to yield recyclable polyolefins

Katrina M. Knauer, katrina.knauer@basf.com, Roswell E. King. Plastic Additives, BASF Corporation, Tarrytown, New York, United States

Plastic packaging is essential for the preservation of food and prevention of food waste. Besides these beneficial properties, food packaging, often as a single use item, causes rising concern for the environment due to its high production volume, and problems related to irresponsible waste management (littering). Reduction, reuse, and recycling support the aims of the circular economy. These tools also have the potential to decrease the environmental impact of food packaging. Yet recycling remains a challenge since the polyolefins used in food packaging will begin to yellow and degrade after multiple heat processing cycles. In this work, we focus on developing stabilization chemistry with the goal of improving the recyclability of polyolefins. However, with the growing regulation of chemicals in plastics, it is of importance to also consider the concentration of additives, as well as their potential transformation products. Therefore, we aim to create chemistry that can more efficiently and effectively stabilize the polymer through several processing cycles.
POLY 200: Tailored EPDM architecture for automotive extruded profiles

Juan Tuberquia, juan.c.tuberquia@gmail.com, Colin Li Pi Shan, Sharon Wu, Greg Li, Lena Nguyen. The Dow Chemical Company, Lake Jackson, Texas, United States

EPDM is the material of choice for automotive extruded profiles because of its excellent weathering and heat resistance, as well as its ability to accept large amounts of fillers and process oil. Extruded profiles provide insulation from water, vibration, and aerodynamic noises to maximize comfort at the interior of the car and their design has become increasingly complex as a response to light weighting trends, and improved aesthetics in the automotive industry. Improved performance with a competitive advantage requires polymer molecular architectures that facilitate mixing, provide shape retention, and enable both rapid extrusion and faster curing to maximize productivity.

Although Ziegler Natta (ZN) EPDM polymers have been traditionally used in this application, this paper discusses how EPDM produced with Advanced Molecular Catalysts tailor the molecular design and microstructure of the polymer to impart these properties in the context of a more sustainable process technology. In contrast to ZN EPDM polymers that sometimes exhibit high elasticity and very broad molecular weight distributions (MWD), Advanced Molecular Catalysts have enabled the access to new polymer architectures at a constant Mooney viscosity with minor changes in the MWD. Such distinct Mooney-molecular weight (MW) relationship versus the general understanding has profound implications because it implies that MWD, MW, and elasticity can, for practical purposes, be individually tailored.
Poly(2-alkyl-2-oxazoline)s are very attractive materials for various applications in biological applications as well as in engine oil technologies. By simply tuning the length of the alkyl group, it is possible to obtain the right solubility behavior in aqueous solutions or in engine oils. In this talk, I will be discussing the synthesis of functional oxazolines and their direct applications in gene delivery and lectin binding properties as well as their effect when used as engine oil additives.
New thermo- and pH-responsive polymers were synthesized by the cationic ring-opening polymerization of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, or 2-carboxyethyl-2-oxazoline, initiated by the random copolymers of chloromethylstyrene and N-isopropylacrylamide using the “grafting from” method [1,2]. The polymers were characterized by NMR, and GPC and the conformational transition of graft copolymers was determined by the NMR, turbidity and DSC measurements. The transition temperature of the graft copolymers could be fine-tuned through the composition of the macroinitiator and the graft copolymer. An increasing quantity of the hydrophobic comonomer chloromethylstyrene in the macroinitiator lowered its LCST, while in the graft copolymer an increasing content of the hydrophilic segment of poly(2-methyl-2-oxazoline), poly(2-ethyl-2-oxazoline) or poly(2-carboxyethyl-2-oxazoline) raised the transition temperature. In case of 2-carboxyethyl-2-oxazoline were obtained pH sensitive graft copolymers and stable micelle-like aggregates were formed by increase of temperature in a specific pH range of 4.5 to 5.5. The micelles were successfully cross-linked by electron-beam irradiation yielding stable core-shell type nanogels of about 100 nm diameter with reversible thermo- and pH-dependent swelling behaviour addressed independently within the core and shell structure. The reversible bi-sensitivity of core-crosslinked nanogels was verified by dynamic light scattering and atomic force microscopy measurements demonstrated the predicted core-shell structures of the aggregates.

Figure. DLS measurements of nanogels below and above the phase transition temperature of the core against pH.
POLY 203: Sequence-selective dynamic covalent assembly of information-bearing oligopeptoids

Timothy F. Scott, tfscott@umich.edu, Samuel C. Leguizamon. 3074 H.H. Dow Building, University of Michigan, Ann Arbor, Michigan, United States

Nucleic acids represent a particularly versatile class of materials for producing nanostructures as, through careful consideration of their residue sequence, they can be designed to self-assemble via the hybridization of complementary strands into complex, molecular ladder-based structures with nanometer precision. Unfortunately, the versatility of nucleic acids as nanoconstruction media is tempered by the thermal and mechanical instability of the assembled structures, attributable to the weakness of the hydrogen bonds that hold the strands together. To address the instability of self-assembled molecular ladders bearing hydrogen bond-based rungs, we describe the sequence-selective assembly of peptoid oligomers bearing amine and aldehyde pendant groups as a dynamic covalent reaction pair. Here, scandium triflate, a Lewis acidic rare-earth metal triflate, was employed as a multi-role reagent to effect the in situ deprotection of ethylene acetal-protected aldehyde groups, to affect the equilibrium of the amine/aldehyde condensation reaction, and to catalyze imine rearrangement reactions. Thus, by controlling the reaction equilibrium with high initial loadings of Sc(OTf)₃ to deprotect and separate complementary strands, then reducing the Sc(III) concentration via extraction and annealing at raised temperature, the sequence-selective assembly of these oligomers was achieved. This selective assembly was demonstrated by employing mass-tagged precursor oligomers bearing spacer residues of varying lengths, enabling characterization of the generated structures by mass spectrometry.
POLY 204: Designing amphiphilic peptoids for bio-inspired synthesis of hybrid materials

Chun-Long Chen, chunlong.chen@pnnl.gov. Physical Science Division, Pacific Northwest National Laboratory, Richland, Washington, United States

Inspired by peptide- and protein-controlled formation of hierarchically-structured biominerals (e.g. bones and teeth) in nature, many biomimetic approaches have been developed for the preparation of nanostructured inorganic-organic hybrid materials. These approaches are attractive because they generate complex, functional nanomaterials under mild aqueous synthetic conditions. The unique integration of bio- and inorganic nanomaterials has demonstrated superior performance. Despite the advances in developing biomimetic approaches, the rules of designing sequence-defined molecules that lead to the predictable synthesis of inorganic nanomaterials are unknown. Herein we report the design of sequence-defined peptoids for controlled synthesis of well-defined plasmonic nanomaterials. By engineering peptoid sequences and investigating resulting particle formation mechanisms, we developed a rule of thumb for designing peptoids that predictively enabled the morphological evolution from spherical to nanocoral-shaped metallic nanoparticles. We demonstrate that the individual nanocoral-shaped gold particles exhibit a plasmonic enhancement as high as $10^5$ fold. This research significantly advances our ultimate vision of predictive bio-inspired hybrid materials synthesis using sequence-defined synthetic molecules that mimic proteins and peptides.
Surface functionalization by grafting poly(2-alkyl-2-oxazoline)s (PAOXAs) has enabled to tune the interfacial physicochemical properties of a variety of (bio)materials and prevent or modulate unspecific biological contamination. Latest advances in the designing of PAOXA-based surface modifiers have shown that a fine tuning of polymer topology can be exploited to broadly vary biopassivity, steric stabilization and tribological properties on the functionalized materials. This is valid for macroscopic, inorganic surfaces, complex tissues, as well as for colloids. Simultaneously, the chemical composition of PAOXA-based coatings can be modulated as a function of the type of support, and determines the chemical stability, physical properties, and bioinertness of the obtained surfaces.

In this contribution, an overview of some of the most advanced surface-functionalization strategies involving PAOXAs will be given, posing particular attention on how a chemical and topological tuning of molecularly designed adsorbates can be exploited to fabricate polymer interfaces featuring a wide range of properties and functionalities. While the era of poly(ethylene glycol) (PEG) as a universal panacea for resisting non-specific protein adsorption and provide lubrication to surfaces is approaching an end, PAOXAs emerge as extremely versatile alternatives for tailoring the interfacial properties of materials.
We had earlier first demonstrated the favorable hydration and excellent "antifouling" effect of surface grafted polysarcosine peptoid brushes. Such brushes are important since they can be used to resist the fouling by adsorption of proteins and attachment of cells, which can enable a wide range of potential applications from preventing bacteria infection and opsonization of nanotherapeutics, to maintaining marine and engineering surfaces. Subsequent work showcased also the flexibility of using sequence-specific peptoids as model polymers to experimentally study the role of "zwitterionic" mixed charged systems in antifouling. Interesting, such zero net-charge polyampholytic peptoid brushes yielded very similar apparent antifouling performance as polysarcosine. We now present recent work using molecular dynamics (MD) simulations to study the molecular behavior and hydration properties zwitterionic peptoid brushes. We include in our study polysarcosine as an uncharged comparison, and show how molecular volume and hydration effects are intertwined in a zwitterionic (peptoid) polymer brush. For example, the zwitterionic design promotes an extended brush layer structure (conformation) and could actually lower the overall electrostatic potential. Some properties promoted by the balanced charges, such as chain flexibility and hydration, increase more prominently at “low” to “intermediate” grafting densities. These and other observations suggest the ability of zwitterionic peptoids to assume antifouling properties under more situations and inform the design of antifouling polymer brushes.
Post-polymerization modification reactions (PPMRs) are an indispensable tool in the design of functional polymer structures, playing a key role in the design of next generation materials, such as polymer-drug conjugates and stimuli responsive materials. Within this work we explore the modification of poly(2-oxazoline)s bearing pendant ester groups. More specifically, the transesterification and amidation of these pendant esters are studied, as well as the kinetics of the respective reactions with a broad range of functional alcohols and amines. Here trends could be distinguished between different substrates, where the reaction rate was influenced by nucleophilicity, steric hindrance and the presence of moieties enabling hydrogen bonding. Hence, the present method allows for a broad range of functionalisation opportunities, which are briefly discussed.
Schizophyllan (SPG) is a member of the beta-1,3-glucan family and known to exist as a triple helix in neutral conditions and as a single chain in alkaline solutions. When the alkaline solution of SPG is neutralized, the single chain retrieves its original triple helix. When a certain homo DNA such as poly(dA) with an enough chain length (ca., bp > 20) is mixed in this neutralization reaction, a novel complex is formed between SPG and DNA. There are several b-1,3-glucan receptors expressed by immunocytes and they also bind to the DNA/SPG complex, indicating that this complex can provide immunocyte-specific delivery of the bound DNAs. This paper reviews our recent studies to apply the complex to cure immunological disorders and to use cancer immunotherapy.
POLY 209: Guanylurea-functionalized conjugated polymers for efficient gene knockdown in normal human bronchial epithelium cells

Md. Salauddin Ahmed¹, Rajib Dutta², Prakash Manandhar¹, Hoshang Unwalla², Joong Ho Moon¹, jmoon@fiu.edu. (1) Chemistry and Biochemistry, Florida International University, Miami, Florida, United States (2) Immunology and Nanomedicine, Florida International Univ, Miami, Florida, United States

In human airway epithelium possessing additional extracellular barriers such as mucus layers, transfection using conventional lipid-based or positively charged carriers is extremely limited. In the mucus layer, dense mucin fibers and negatively charged proteoglycans provide the adhesive and viscous protective layer that often trap and remove positively charged carriers, resulting in poor delivery of payloads to the underlying epithelial cells. Because understanding on the genetic and molecular changes upon external stimuli or viral infections is pivotal to develop proper preventive or therapeutic tools by controlling the gene expressions, developing a novel delivery material that overcomes the biological barrier is highly needed. Here, we report a direct chemical modulation technique that introduces hydrophilic group at the guanidine group via guanylurea bond formation. Guanylurea side chain-containing conjugated polymers (CPs) exhibit an efficient knockdown of a target gene in well-differentiated primary normal human bronchial epithelium (NHBE) cells, while conventional lipid-based and positively charged carriers exhibit no or very poor transfection efficiency. Because the primary culture of NHBE cells reproduces the in vivo morphology and key physiologic processes to regenerate the native human bronchial epithelium, the transfection efficacy demonstrated in this report can be reasonably correlated to real in vivo environment.

Microscopic images of NHBE cells treated with guanidine-containing (left) and guanylurea-containing CP (right). (A): contrast, (B and C): fluorescent, and (D): merged image. Nucleus and CPs were imaged under the blue and green channel, respectively. Scale bar: 20 μm.
POLY 210: Poly(amino acid)-based gene delivery systems: The story starts after the synthesis

Carmen Scholz¹, cscholz@chemistry.uah.edu, David Ulkoski². (¹) Chemistry, Univ. of Alabama in Huntsville, Huntsville, Alabama, United States (²) AstraZeneca, Boston, Massachusetts, United States

Aside from containing a cationically charged polymeric vector a functioning gene delivery system must (i) condense DNA into micron size particles with preferentially positive zeta potentials, (ii) protect DNA-polplexes against DNase action, (iii) have a low cytotoxicity, (iv) maintain long-term stability in serum, (v) maintain the cells’ ability to express proteins and (vi) express the target protein in satisfactory yields.

Amino acids impart their chemical and physical properties upon the polymers they form, poly(amino acid)s, PAAs. Poly(L-Lysine), p(L-Lys), is a thoroughly investigated polymer for gene delivery applications as its positively charged terminal side chain functional groups interact with and condense DNA. Polymersomes have been identified as effective gene delivery vehicles, using p(L-Lys) for DNA condensation and their self-assembly is driven by a hydrophobic moieties such as poly(L-Leucine), p(L-Leu). Poly(ethylene glycol), PEG, used to initiate metal-free ring-opening polymerizations, ROPs, of the respective amino acid N-carboxyanhydrides, NCAs, provides the polymersomes with biocompatibility. Under the conditions used here the NCA ROPs follow a living mechanism and therefore allow for the synthesis of block copolymers. PEGylated PAA triblock copolymers were synthesized and the molecular architecture was varied so that the hydrophobic p(L-Leu) block would form either the middle block PEG-b-p(L-Leu)ₓ-b-p(L-Lys)ᵧ or the terminal block PEG-b-p(L-Lys)ᵧ-b-p(L-Leu)ₓ, moreover, diblock copolymers were synthesized, where the amino acid repeat units form a copolymer, PEG-b-p((L-Lys)ᵧ-co-(L-Leu)ₓ). The impact of the molecular architecture and chain length on the effectiveness and stability of these gene delivery systems in light of the above ascertained parameters will be discussed, showing that PAA block copolymers form the more effective polymersomes for gene delivery applications, with PEG-b-p(L-Lys)ᵧ-b-p(L-Leu)ₓ, exhibiting advantages over PEG-b-p(L-Leu)ₓ-b-p(L-Lys)ᵧ.
POLY 211: Gene expression of aspect ratio-controlled polyplexes based on the effect of multi-arm poly(ethylene glycol)

Atsushi Harada, harada@chem.osakafu-u.ac.jp, Eiji Yuba. Department of Applied Chemistry, Osaka Prefecture University, Osaka, Japan

The morphology of drug carrier on internalization mechanism has been studied in detail for several nanoparticle systems. However, the reports on the effect of the aspect ratio as an indicator of the morphology of the complexed DNA with polycations termed polyplexes is limited. We have investigated head-tail type polycation as polycation-based gene vectors. This head-tail polycation is composed of polyamidoamine (PAMAM) dendron head and poly(L-lysine) (PLL) tail, in which tertiary amines in the interior of PAMAM dendron could exhibit buffering effect for endosomal escape and PLL tail could form stable complex with pDNA. Also, the PEGylation to the periphery of PAMAM dendron head provide the PLL terminally bearing multi-arm PEG chain (maPEG-PLL). As the effect of PEGylation, DNA condensation in the polyplex was effectively inhibited due to the steric repulsion among maPEGs at the polyplex surface. Further, an increase in intrapolyplex PEG crowding effect provides the elongation of polyplex morphology from globule to nanorod or nanofiber shapes.

In this study, we evaluated in vitro performances of the polyplexes with various aspect ratios including globule, nanorod and nanofiber as a gene vector. The polyplexes with various aspect ratios were prepared by mixing pDNA with the mixtures of maPEG-PLL and PLL homopolymer, in which the crowding of maPEG part at the polyplex surface could be apparently controlled based on maPEG-PLL content. The maPEG-PLL polyplexes had most elongated morphology and the decrease in maPEG-PLL content induced a decrease in aspect ratio of polyplexes. For these polyplexes with varying aspect ratio, the reaction of pDNA with enzymes, the cellular uptake and in vitro transfection efficiency were evaluated for a function of maPEG-PLL content. As a result, the transfection efficiency showed optimal maPEG-PLL content, i.e. optimal aspect ratio of polyplexes, determined by a balance between cellular uptake and transcription efficiency.

Figure 1. Luciferase activity of HeLa cells treated with the polyplexes prepared from varying maPEG-PLL contents.
POLY 212: Enzymatic synthesis of aptamer-targeted polynucleotide drugs for cancer therapy

Lei Tang¹, Sonal Deshpande², Yungi Yang¹, Renpeng Gu², Ashutosh Chilkoti², Stefan Zauscher¹, zauscher@duke.edu. (1) Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States (2) Biomedical Engineering, Duke University, Durham, North Carolina, United States

The use of DNA as a polymeric building material transcends its function in biology and is exciting in bionanotechnology for applications ranging from biosensing, to diagnostics, and to targeted drug delivery. Our research is motivated by the complexity and low yield of syntheses of current aptamer-targeted nanoparticle drug carriers that are typically carried out by multi-step chemical conjugation of aptamer and drug to a carrier. Here, we demonstrate a highly efficient in situ enzymatic polymerization strategy that “grows” a polynucleotide drug segment and a self-assembly segment from an aptamer “initiator.” Specifically, we exploit the ability of a template-independent DNA polymerase—terminal deoxynucleotidyl transferase (TdT)—to catalyze the polymerization of 2’-deoxyribonucleoside 5’-triphosphates (dNTP, monomer) from the 3’-hydroxyl group of an oligodeoxyribonucleotide (initiator). We found that the reaction kinetics follows a “living” chain-growth polycondensation mechanism, and that like in “living” polymerizations, the molecular weight of the final product is determined by the starting molar ratio of monomer to initiator. Our synthesis approach can incorporate a wide range of unnatural dNTPs into the growing chain, such as, hydrophobic fluorescent dNTP and 5-fluoro-2’-deoxyuridine (FdUTP), a nucleotide analog of the anticancer drug 5-fluorouracil (5-FU). This “one-pot” enzymatic reaction approach offers a new, dramatically simplified and innovative route for the synthesis of nuclease-resistant, multifunctional block-copolymers which can self-assemble into micellar structures for drug delivery applications.

An aptamer initiates the TdT catalyzed enzymatic polymerization (TcEP) of FdUTP, and aids in cellular internalization. The incorporation of hydrophobic nucleotides generates amphiphilic block polynucleotides that self-assemble into aptamer-presenting, micellar nanoparticles.
POLY 213: RAFT polymerization for the synthesis of tertiary amine-based diblock copolymer nucleic acid delivery vehicles

Adam E. Smith¹, aes@olemiss.edu, Tracy A. Brooks², Annie K. McClellan¹, Taisen Hao³. (1) Department of Chemical Engineering, University of Mississippi, University, Mississippi, United States (2) Department of Pharmaceutical Sciences, Binghamton University, Binghamton, New York, United States (3) Department of BioMolecular Sciences, University of Mississippi, University, Mississippi, United States

The synthesis and characterization of a family of pH-responsive, diblock copolymers designed to effectively deliver nucleic acids is reported. The stabilizing A block is comprised of an oligo(ethylene glycol) methyl ether methacrylate to impart water solubility. The cationic blocks of varying degrees of polymerization are derived from three pH-responsive, tertiary amine-containing methacrylates capable of complexing negatively charged nucleic acids. The cytotoxicity studies utilizing human embryonic kidney cells (HEK-293) and MCF-7 breast cancer cells indicate no decrease of cell viability with the diblock copolymers, with the exception of the two highest DPs of the cationic blocks with ethyl-substitutes tertiary amine. Gene knockdown experiments indicate high siRNA delivery and MYC gene knockdown in MCF-7 breast cancer cells for eight of the nine studied block copolymers. The results of the current study enable further development of the pH-responsive copolymer family for promising nucleic acid delivery vehicles applicable for clinical use.

Gene knockdown experiments indicate high siRNA delivery and MYC gene knockdown in MCF-7 breast cancer cells for eight of the nine studied pH-responsive block copolymers.
POLY 214: Cationic star-shaped glycopolymer brushes for targeted gene delivery

Renjie Liu¹, r.liu@qmul.ac.uk, Anna K. Blakney², Yilmaz Gokhan⁴, Paul F McKay², Robin J Shattock², Remzi Becer³. (1) School of Engineering and Materials Science, Queen Mary, University of London, Shanghai, China (2) Department of Medicine, Division of Infectious Diseases, Imperial College, London, United Kingdom (3) School of Engineering and Materials Science, Queen Mary University of London, London, United Kingdom (4) University of Nottingham, School of Pharmacy, London, United Kingdom

The unique recognition and complexation behavior of β-cyclodextrin and adamantane in aqueous solutions allow the creation of an ideal copolymer system that has both nucleic acid complexation and lectin targeting properties. Firstly, PDMAEMA with different chain length was initiated from β-cyclodextrin core to yield seven-arm star-shape polymers. In parallel, adamantane acrylate was copolymerized with pentafluorostyrene and dimethylacrylamide to afford a water-soluble copolymer, followed by a click reaction of para-fluorine with glucose units to obtain glycopolymers. Then the CD-adamantane complex formation of these two copolymers was monitored via 2D NOESY NMR and DLS. Finally, in vitro plasmid DNA delivery assays were conducted to investigate the gene delivery efficiency and specific targeting properties through the lectin-carbohydrate interaction. Results showed the successful complex formation in aqueous system and enhanced gene delivery efficiency of utilizing this system.

Figure 1. Schematic representation of polymer-pDNA complex formation process.
POLY 215: Polypelex interaction strength impacts potency during cancer immunotherapy

**Shannon J. Tsai**, sjtsai@umd.edu, James Andorko¹, Xiangbin Zeng¹, Joshua Gammon¹, Christopher Jewell¹-³. (1) Fischell Department of Bioengineering, University of Maryland, College Park, Maryland, United States (2) United States Department of Veteran Affairs, Baltimore, Maryland, United States (3) Robert E. Fischell Institute for Biomedical Devices, College Park, Maryland, United States

To overcome the immunosuppressive microenvironment of tumors, toll-like receptor agonists (TLRas) have emerged as a novel class of adjuvants that may enhance anti-tumor T cell responses. Many experimental cancer vaccines are exploring CpG, a DNA motif that agonizes toll-like receptor 9 (TLR9). Because TLR9 is located intracellularly, CpG must be internalized to trigger immune responses. Here, we electrostatically assembled rapidly degradable cationic poly(β-amino esters) (PBAEs) with anionic CpG (Fig. 1a). These polypelexes improve delivery of CpG to activate stronger immune responses. Polypelexes formed over a range of PBAE:CpG ratios displayed increasingly positive charge and stronger binding as PBAE:CpG ratio increased (Fig. 1b). Surprisingly, although higher PBAE:CpG ratios exhibited improved CpG uptake (Fig. 1c), lower ratios—which condensed CpG more weakly—activated tumor specific T cells more effectively (Fig 1d). In mechanistic studies, reduced T cell proliferation correlated with reduced TLR9 signaling, suggesting that decreased polypelex interaction strength improves CpG accessibility to TLRs (Fig. 1e). In line with these results, during a mouse melanoma model, polypelexes with lower binding affinities improved survival compared to polypelexes exhibiting stronger CpG interactions (Fig. 1f). Thus, physiochemical properties, particularly the interplay between charge, uptake, and affinity, play an important role in determining the nature and efficacy of the immune response generated and remain a key consideration in engineering effective immunotherapies.

a) Polypelex assembly  b) Reduction in fluorescent intensity indicates displacement of fluorescent signal by PBAE and stronger interaction strength  c) Polypelexes improve CpG uptake and d) increase T cell proliferation  e) TLR9 activity decreases in treatments exhibiting higher N:P ratio  f) Intratumoral injection promotes survival in a mouse melanoma model
POLY 216: Encapsulation and ultrasound-triggered release of G-quadruplex DNA in hydrogel microcapsules

Aaron Alford\textsuperscript{1}, aaaron@uab.edu, Nirzari Gupta\textsuperscript{4}, Veronika A. Kozlovskaya\textsuperscript{2}, David E. Graves\textsuperscript{5}, Eugenia P. Kharlampieva\textsuperscript{3}. (1) University of Alabama at Birmingham, Birmingham, Alabama, United States (2) Chemistry Department, University of Alabama at Birmingham, Alabama, United States (3) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States (4) The University of Alabama at Birmingham, Birmingham, Alabama, United States (5) Dept Chem, University of Alabama at Birmingham, Birmingham, Alabama, United States

Nucleic acid therapeutics have the potential to be the most effective disease treatment strategy due to their intrinsic precision and selectivity for coding highly specific biological processes. Recently, the delivery of therapeutic nucleic acids to modify gene expression has emerged as a promising way to treat a range of inherited or acquired diseases. The G-quadruplex, a stacked series of G-tetrads in guanine-rich DNA, is a unique DNA structure that can be found within promoter regions of oncogenes as well as in the telomeric regions of the chromosome. The G-quadruplex is nuclease resistant and plays a role in transcriptional regulation. As chromosomes with damaged or shortened telomeres have been shown to cause miscoding that may result in cancerous cells, delivery of G-quadruplex DNA is being investigated as a component of gene-mediated anticancer treatment. However, freely administered nucleic acids of any type are quickly destroyed or rendered inert by a host of defense mechanisms in the body. To combat this, a versatile method to encapsulate the DNA and protect it from degradation until reaching the desired location is required. We show that the G-quadruplex sequence can be encapsulated within two-component hydrogel microcapsules of poly(methacrylic acid)/poly(N-vinylpyrrolidone) (PMAA/PVPON) obtained via multilayer assembly of polymers onto sacrificial calcium carbonate microparticles, crosslinking with cystamine, and template dissolution under physiologically safe conditions. We demonstrate that the PMAA/PVPON capsules can release the nucleic acid payload on demand in response to safe $<14 \text{ W/cm}^2$ ultrasound irradiation as well as in response to enzymatic degradation of the capsule shell by intracellular concentrations of reduced glutathione. The encapsulation and controlled release of G-quadruplex oligonucleotides herein can be applied to new therapeutic strategies and may provide a promising methodology for the design of effective carriers for DNA vaccines and medicines for a wide range of immunotherapies, cancer therapy and/or tissue regeneration therapies in the future.
The development of novel degradable biomaterials is largely restricted by the paucity of well-defined functional degradable polymers with which to access materials with useful properties. As such, one focus of our research is to investigate methodologies that can be used to access new materials that are able to be specifically tailored to a range of applications. To this end, we are interested in designing and synthesizing materials in which many of the starting materials are derived from sustainable resources using novel catalyst systems and applying metal-free ‘click’ chemistries.

Our synthetic approaches allow for the development of materials with properties that are hard to obtain by other methods. We are focussed on understanding and controlling the properties of our materials on all length scales. From the development of new materials with precisely tailored macroscopic mechanical and degradative properties as well as biological interactions, to the 3-dimensional control of structure at the micron-scale as well as the controlled nanoscale assembly to provide novel materials, hydrogels, scaffolds and nanoparticles for tissue engineering, regenerative medicine and drug/gene delivery applications.

This presentation will focus on recent work that has been directed towards the synthesis and study of novel degradable polymeric materials that are derived from sustainable resources and have significant potential for in vivo applications.
Redox-active catalysts are described whose chemoselectivity for ring-opening polymerization reactions can be altered with the choice of metal precursor and oxidation state of the catalyst. Control over polymer composition, sequence, and architecture can be achieved through judicious choice of monomers and with in situ application of redox equivalents. Replacing chemical redox reagents with electrochemical potential provides access to redox-switching that is more ammenable to automation and that is also suitable for surface initiated polymerization reactions. Aspects of catalyst design, polymerization mechanism, and materials applications of the resulting polymers will be discussed.

Redox-switchable polymerization catalysis to control macromolecular composition, sequence, and architecture.
A research progression from 2D-motifs to 3D-metallocages leading to the one-step assembly of fractal-based, metallosupramacromolecular materials will be presented. The specific control over shape, size, and transformations of these assemblies is challenging due to its inherent dynamic nature. Introduction of tailored multiplanar, directed polyterpyridine vertices in conjugation with a series of different metal ions generated metallosupramolecular cages with tunable conformations responding to specific stimuli, such as: concentration, temperature, and counter ions. Extending the fractal designs to a new family of hybrid metalloendrimers with a cuboctahedron core has been realized, opening a door to new precise unimacromolecular micelles. Moreover, secondary hierarchial self-assembly of these discrete macromolecules will be discussed. Utilizing precision-tuned monomers, a series of supramacromolecules with a rigid triangular framework can be assembled into shape-complementary, highly ordered nanostructures, which open avenues to smart designer materials.
POLY 220: C–H functionalization of polyolefins

Frank A. Leibfarth, FrankL@email.unc.edu, Jill Williamson, Christina Na, Erik J. Alexanian. Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States

Polyolefins are high-volume, low-cost engineering thermoplastics with high tensile strength, low density, attractive chemical resistance, and excellent processability. Currently, polyolefins constitute nearly 60% of world polymer production. For their ubiquity, however, these hydrocarbons do not interface with other materials, drastically limiting their ability to form composites, coatings, adhesives, or to be used in high-performance engineering applications. Imparting functionality onto these materials without comprising the desirable properties of the parent material would uncover new and unusual properties not typically associated with polyolefins. There is a considerable unmet need to develop chemistry that transforms these abundantly available commodity polymers into functional materials without resorting to de novo synthesis.

Developing methods to transform polyolefins into the functional materials of the future will require polymer chemists to rethink their approach to post-polymerization modification, seeing C–H bonds as potential points of diversification rather than unreactive functionality. To address this challenge, our approach to polyolefin C–H functionalization takes advantage of the high parent N–H bond dissociation energies of amidyl radicals to create custom reagents for the mild and selective addition of thiocarbonyl groups to commercial polyolefins. The versatile chemistry of these thiocarbonyl groups enable the rapid diversification of polymer function through simple chemical manipulations, thus generating a wealth of new materials from a universal synthetic platform. Initial work has developed both photochemical and thermal approaches to modify commercial polyolefins without polymer degradation. The presentation will focus on our current work, including comprehensive reagent design and optimization efforts, including probing radical identity and lifetime in situ, to make this process viable for functionalization within a reactive extruder.
POLY 221: Compression-activated fluorescence in polymeric networks

Christopher Kabb¹, Christopher O'Bryan², Cameron Morley², Thomas E. Angelini², Brent S. Sumerlin¹, sumerlin@chem.ufl.edu. (1) Department of Chemistry, University of Florida, Gainesville, Florida, United States (2) Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida, United States

We have prepared hydrogel networks crosslinked by mechanoresponsive anthracene-maleimide adducts. When the networks are subjected to compressive forces, cycloreversion of the adduct occurs, liberating fluorescent anthracene groups. As expected, the extent of cycloreversion is strongly dependent on the applied pressure; higher fluorescence intensities are measured with larger pressures. Furthermore, networks that are more densely crosslinked exhibit mechanochemical responses at lower pressures. Finally, the “off-on” response was demonstrated as an “invisible ink” by stamping Anth-Mal-containing networks.
Injectable biopolymer hydrogels have gained increasing attention for clinical translation as engineered biomedical scaffolds to promote cardiac function and prevent negative left ventricular (LV) remodeling post-MI. However, the majority of hydrogels tested are not candidates for minimally invasive catheter delivery because of excess material viscosity, rapid gelation times, and concerns regarding hemocompatibility and potential for embolism. As a result, clinical translation of most injectable biomaterials for the heart has been hindered. Solutions are needed for this broad class of promising biomaterial.

Here, we describe novel progelator materials formulated in some cases as sterically constrained cyclic peptides to prevent self-assembly and provide a free flowing solution for low resistance injection. Importantly through our design, we provide the first demonstration of self-assembling peptides (SAPs), and related polymer-peptide conjugate scaffolds, amenable to cardiac catheter injection. Ultimate linearization by MI-associated enzymes induces rapid self-assembly into rehealable hydrogels. The versatility of our platform is shown through the functionalization of two different SAP sequences, which exhibit disparate self-assembly mechanisms, and yet form progelators with identical responsiveness. Hemocompatibility analyses and in vivo application in a rat ischemia repurification model provide evidence that our simple synthetic modifications do not induce toxicity nor alter the capacity to self-assemble within a biological environment. Finally, we demonstrate that labeling of our progelators with a small molecule dye (rhodamine) does not interfere with self-assembly. Thus we envision that a chemically complex hydrogel can be generated in vivo through simple mixture of different progelators, each bearing a small molecule drug, tag, or reactive moiety. The work presented sets the stage for structurally dynamic biomaterials for therapeutic hydrogel delivery to the heart for the prevention of negative LV remodeling.
Future progress in soft robotics, wearable electronics, and personalized medicine requires synthesis of soft materials that are capable of mimicking mechanical properties of biological tissue. These materials have a broad range of the mechanical properties which is reflected in their complex response to the external deformation. In particular, biological tissues are strain adaptive with a strong nonlinear dependence of the deformation on the applied stress. A variety of polymeric systems (i.e. networks and gels) has been developed in an attempt to replicate mechanical properties of tissues. However, the applications of these materials are limited since the mapping of the mechanical properties requires simultaneous variation of multiple parameters such as solvent fraction, crosslinking scheme, and chemical compositions. We develop a computationally driven approach for design of soft materials with solvent free network architecture. This approach is based on the theoretical and computational studies of the mechanical properties of networks made of graft polymers such as combs and bottlebrushes. In particular, it is demonstrated that the graft polymers in a melt behave as ideal chains with effective Kuhn length. This model of graft polymers is applied to model mechanical properties of networks of graft polymers and to correlate network’s mechanical response with architectural and chemical structure of the network strands. This approach is verified by replicating elastic materials with mechanical properties of jellyfish, lung, and arterial tissue in PDMS networks of combs and bottlebrushes. This technique lays the foundation for a computationally driven materials design that will enable encoding of a broad range of mechanical properties of soft materials in solvent free elastomers.

Figure 1: Mimicking gels’ mechanics. (a) Protocol for replicating mechanical properties through architectural mapping. (b) True stress-elongation curves: experimental data of the assorted gels (dots), fitting theoretical model (dashed lines), and experimentally measured PDMS replicas programmed with \([n_{sc}, n_g, n_x]\) parameters generated by theoretical model (solid line).
POLY 224: Exploring the power of PISA

Rachel K. OReilly, r.oreilly@bham.ac.uk. School of Chemistry, University of Birmingham, Birmingham, United Kingdom

We have been interested in exploring polymerisation induced self-assembly (PISA) for the preparation of polymeric nanoparticles of tunable size, functionality and morphology. We have reported methods to predict monomers capable of undergoing PISA, explored new polymerisation methods for PISA and also explored the utilisation of PISA to create biohybrid nanoparticles.
POLY 225: Predicting 3D printability of functional polymers: balancing rheology with reactivity

Timothy E. Long¹, telong@vt.edu, Gayan Adikari Appuhamillage¹, Justin M. Sirrine¹, Maruti Hegde¹, Jana Herzberger¹, Daniel A. Rau², Xi Chen¹, Clay B. Arrington¹, Mark F. Cashman¹, Philip Scott¹, Emily Wilts¹, Viswanath Meenakshisundaram², Nicholas A. Chartrain², Christopher B. Williams². (¹) Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (²) Department of Mechanical Engineering and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

All-aromatic polyimides demonstrate excellent thermomechanical properties for high temperature applications. 3D printing of pyromellitic dianhydride, 4,4'-oxydianiline (PMDA-ODA) using mask-projection stereolithography (SLA) involves precursor polymers containing acrylate groups, enabling light-induced, chemical crosslinking for spatial control in the gel state. Thermal treatment of the printed parts form PMDA-ODA polyimide with isotropic shrinkage. Alternatively, we will describe UV-curable polyamic acid (PAA) salts via vat photopolymerization (VP) and direct ink write (DIW) methods. Tuning the rheology enabled the minimization of shrinkage and warping. Our stereolithographic research also involves simultaneous thiol-ene step-growth chain extension, acrylate crosslinking during 3D printing to overcome VP challenges. Liquid polybutadiene oligomer/dithiol resin cures selectively forming high-strain, elastic parts. Photorheology elucidated curing as a function of resin composition and UV intensity. This work expands additive manufacturing (AM) by a solvent-free resin with a processable oligomer and elastic properties of a higher molecular weight polymer. This lecture will also highlight our most recent efforts with a facile two-step synthesis to afford PEG-based supramolecular polymers using a low molecular weight PEG end-functionalized with quadruple hydrogen bonding cytosine derivative, ureido-cytosine, 3D printed via extrusion-based AM. Rheology revealed a temperature dependent viscosity due to hydrogen bonds dissociation, association enabling tuning viscosity. We have also focused on the synthesis, characterization of poly(lactide-co-glycolide) (PLGA)-based photoactive precursors to 3D print tissue scaffolds via SLA. Ring-opening polymerization of lactide and glycolide yields a PLGA-diol, then functionalized to PLGA-diacrylate. Presence of photo-initiator yields a crosslinked biodegradable material.
In this presentation, two methods involving synthetic, water-soluble polymers for the stabilization of enzymes, and most generally proteins, will be discussed. On the one hand, end-functional polymers obtained by RAFT polymerization are assessed as alternative to PEGylation in a biotechnological/pharmaceutical context (Figure A). Straightforward conjugation experiments are followed by careful chromatographic purification leading to the isolation of semi-discrete protein-polymer species. The latter enable a more precise evaluation of the effect of conjugation on the stabilization of proteins, which is studied in various conditions to produce relevant phase diagrams. On the other hand, we investigate the coating of enzymes with a thin layer of hydrogel (Figure B). Particularly, we present a simplified protocol for single-protein encapsulation that maintains the nanoscopic character of the protein, an important feature for bionanotechnology, yet with a full coverage of the enzyme surface. This leads to enhanced resistance of the biocatalysts towards organic solvents or pH variations. Through an extensive study with a range of proteins with various functions and sizes, we postulate the universality of the method. The intrinsic reactivity of the hydrogel coating is further exploited for labeling and surface immobilization.
POLY 227: Practical synthesis of complex glycopolymers using water-soluble amino-oxy functional scaffolds

Antonio Laezza1, a.laezza@warwick.ac.uk, Sarah-Jane Richards2, Matthew I. Gibson3. (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) The University of Warwick, Coventry, United Kingdom (3) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom

Glycopolymers are an exciting class of synthetic macromolecules which can display increased affinity towards carbohydrate-binding proteins (especially lectins). This is due to the cluster glycoside effect, which results in a non-linear increase in affinity as the valency increases. These multivalent glycan interactions are involved in a range of biological processes such as cell-cell and cell-pathogens communications, and hence their application as decoys in anti-adhesive therapy or to modulate signaling is of huge interest.

Most previous studies on glycopolymers involve relatively simple monosaccharides, which do not enable reproductions of the complex 3-D presentation found in native glycans and hence do not have high selectivity. Furthermore, most binding studies are against model plant lectins, and use simple aggregation assays.

To address the above, we will present a practical method to obtain water-soluble amino-oxy functional polymers which can be directly reacted with reducing glycans enabling aqueous post-polymerization modification. This strategy is useful as it allows the use of both larger glycans and those bearing sulphated and other residues which are crucial for affinity in some cases. The route involves a two-step modification of poly (N-hydroxyethyl acrylamide) (PHEA) obtained from RAFT polymerization then subsequent glycan capture. We will present both the synthesis and the utility of this to study their interactions to human and pathogenic carbohydrate binding proteins using colourimetric assays and biolayer interferometry.
Polypeptides with brush-like architecture are emerging as ideal candidates for nanomedicine due to their unique physiochemical properties as well as excellent biological functions. To date, polypeptide brushes have been achieved by various living polymerization methods such as ring-opening metathesis polymerization (ROMP) and reversible deactivation radical polymerization (RDRP). However, several issues including cytotoxicity stemming from residual metal catalysts and peptide degradation at high polymerization temperature still remain. In this contribution, we present a benign and metal-free approach towards polypeptide brushes by photoinduced reversible-deactivation radical polymerization (photoRDRP), giving rise to a library of functional polypeptides with well-defined architecture (i.e., statistic and block), predetermined molecular weights, and low polydispersity. Two general classes of functional polypeptides including enzyme-responsive polypeptides and pro-apoptotic polypeptide brushes were accessed via photoRDRP, indicating its versatility in polypeptide synthesis. In the case of enzyme-responsive polypeptides (with pendent GPLGLAGG sequence), self-assembled spherical micellar nanoparticles exhibited shape-transformability through morphological metamorphosis into worm-like micelles upon enzyme-triggered cleavage of coronal peptide side chains. Moreover, pro-apoptotic KLA based polypeptides containing pendent (KLAKLAK)₂ side chains exhibited not only enhanced cell-penetrating activity but also increased cytotoxicity to cancer cells in comparison with free KLA peptide. Importantly, in vitro cell study showed that packing density of KLA side chains plays a crucial role in dictating the cytotoxicity of polypeptides. Those results clearly indicate the robustness of photoRDRP method in engineering the structure and properties of polypeptides, highlighting its immense potential in nanotechnology and biomedical applications.
Atom transfer radical polymerization (ATRP) has been successfully used to covalently attach polymer chains to various biomolecules such as proteins, enzymes and nucleic acids. Recently ATRP was also employed to conjugate polymers to surfaces of exosomes to enhance their stability and function. Properties of the resulting bioconjugates will be presented.
In 2014, we reported a photoinduced living/controlled radical polymerization technique, named photoinduced electron/energy transfer - reversible addition fragmentation chain transfer polymerization able to polymerize a large range of monomers, including methacrylates, acrylates and acrylamides, in water and biological media as well as organic solvents. This polymerization technique employs low concentrations of a photocatalyst (typically around 1-100 ppm to monomers) and enables low energy visible LED light to afford well-defined polymers with narrow polydispersities \((M_w/M_n < 1.3)\). In this talk, different parameters and catalysts, including photocatalyst concentrations and solvent effects, were thoroughly investigated. In addition, successful polymerizations in biological media have been reported with good control of the molecular weights and molecular weight distributions \((M_w/M_n < 1.4)\). Finally, polymer bioconjugates were demonstrated.
Glycodendrimers are a versatile class of biopolymers with diverse biological applications. In our lab, we are focused on the development of glycodendrimers as anti-viral agents, with our current focus on HIV-1. In nature, many cell-surface proteins are presented in multiple copies, or multivalently. Glycodendrimers are also multivalent in structure, which can lead to stronger binding to a target protein than one would expect from a one to one interaction. HIV-1 presents its proteins, gp41/gp120 on the viral surface as a heterotrimeric complex, with gp41 membrane bound and gp120 electrostatically associated with gp41. Our glycodendrimers are designed as multivalent inhibitors of gp120 binding to the host cell. The objective our work is to design and synthesize diverse glycodendrimer structures to serve as potential anti-HIV agents.

This presentation will focus on the development of our glycodendrimers as anti-HIV agents, beginning with our early inhibitors that incorporated the commercially available dendrimer core, poly(amidoamine), or PAMAM. Building on what we learned in this initial set of compounds, we developed a green synthetic pathway whereby water is used as a solvent when possible, microwave-assisted reactions are utilized, and protecting group chemistry on the sugars has been eliminated through the use of chemoselective conjugation chemistry. This strategy allows us to create large glycodendrimers in an efficient, high yielding manner. Once synthesized, our glycodendrimers are evaluated for anti-HIV activity through the use of two separate biological assays. The results of these assays will also be discussed.
Polymer-conjugation has been widely explored to improve the pharmacokinetics of therapeutic proteins, exemplified by PEGylation. Key benefits include extended circulation times, reduced immunogenicity and enzymatic resistance. In this talk I will discuss two new and unique examples of bioconjugation: i) Recombinant antifreeze proteins to nanomaterials; and ii) Synthetic polymers to the surface of living cells.

i) Antifreeze proteins (AFPs) from polar fish are potent modulators of ice growth and could have a broad range of biotechnological applications, from cryopreservation to aerospace if they can be incorporated into materials. We have developed fusion proteins of AFPs to enable chemo-selective ligation of these onto the surface of polymer-coated gold nanoparticles. In particular the use of the SNAP-tag ligation will be shown for covalent immobilisation, which enables retention of ice recrystallisation inhibition activity as well as retaining the ability of the proteins to bind specific ice crystal faces.

ii) The conjugation of polymers to proteins has been widely explored, but less so to living cells. We have exploited glycan metabolic labelling to enable the introduction of azido groups into sialic acid residues on living cell surfaces, for ‘click’ conjugation of synthetic polymers. This method is shown to be straightforward, not affect cell viability and can be used to bring additional functionality to the cell surface, bypassing the need for genetic techniques.
The complexity of polymer-protein interactions makes rational design of the best polymer architecture for any given biointerface extremely challenging, and the high throughput synthesis and screening of polymers has emerged as an attractive alternative. Here, we have adapted a porphyrin catalysed photoinduced electron/energy transfer - reversible addition-fragmentation chain transfer (PET-RAFT) polymerisation to enable high throughput synthesis of complex polymer architectures in dimethyl sulfoxide (DMSO) on low volume well plates in the presence of air. The polymerisation system shows remarkable oxygen tolerance, and excellent control of functional 3- and 4-arm star polymers. We then apply this methodology to investigate the effect of polymer structure on protein binding, in this case to the lectin concanavalin A (ConA). Recently, we have incorporated this technology into a highly automated liquid handling platform that allows us to reliably produce large libraries of diverse polymers in a high throughput manner. With this simple yet powerful technique, we are now discovering very well-defined polymer architectures capable of protein-like features. We anticipate that such an approach could be applied to screen the structure – activity relationships for any number of polymer-protein interactions.
Redox flow batteries (RFBs) are one of the most promising technologies for grid-scale energy storage from discontinuous power sources, such as wind and solar. The importance of storing energy from these discontinuous power sources has resulted in a need for continued development and understanding of redox couples and their supporting electrolyte counterparts, as well as improving separator membranes for RFB operation while reducing system cost. Current RFB systems employ separator membranes from the perfluorosulfonic acid (PFSA) family (e.g. Nafion, Aquivion, and 3M PFSA), which exhibit environmental specific material properties, such as electrolyte-concentration-dependent ion conductivity and solvent uptake. While the structure/property relationships of PFSAs are well-known and studied when exposed to either water-vapor or liquid-water environments, they are not for PFSA membranes in concentrated electrolyte.

In this work, we discuss our progress in linking the physical structure of PFSA membranes, in different electrolytes, to the transport of ions in PFSA membranes, using existing knowledge in water environments as the framework for our understanding. Sulfuric and hydrochloric acids represent the majority of supporting electrolytes used in RFB applications and are the primary focus of this study. Small angle X-ray scattering was used to probe the polymer structure when immersed in different electrolytes consisting of pure supporting electrolyte or with redox active species (e.g. Fe$^{3+}$). Ionic conductivity and Fe$^{3+}$ permeability was measured under similar conditions and correlations developed to explore the PFSA structure/function relationship and how it is impacted by water activity as well as the presence of other ions.

The effect of increasing supporting electrolyte concentration on the membrane conductivity and Fe$^{3+}$ permeability (i.e. selectivity) where the dashed blue line represents a constanty selectivity of 97%.
POLY 235: Interplay of electrostatic interactions, nanoparticle dispersion, and ion transport in ionomer nanocomposites for vanadium redox flow batteries

Allison B. Jansto¹, allison.jansto@gmail.com, Apoorv Balwani¹, Tyler Martin², Ronald L. Jones², Eric M. Davis¹. (1) Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina, United States (2) NIST, Gaithersburg, Maryland, United States

Ionomer nanocomposites have emerged as a promising replacement to traditional polymer electrolyte membranes for technologies like vanadium redox flow batteries as they curtail undesired vanadium ion crossover while maintaining high proton conductivity. However, studies have shown that the nanoparticles exist in both the hydrophobic and hydrophilic domains of Nafion, indicating that simple steric hindrance, as previously hypothesized, may not adequately describe the mechanism for reduced vanadium ion crossover. In this study, nanoparticle surface chemistry, along with nanoparticle loading and diameter, were systematically altered to tune nanoparticle dispersion within the ionomer (also known as the nanoparticle ‘dispersion state’). The impact of the nanoparticle dispersion state on vanadium ion crossover and proton transport were measured via ultraviolet-visible and electrochemical impedance spectroscopies, respectively. Additionally, electron imaging was used to determine the impact of these interactions on the nanoparticle dispersion state. Results indicate that the silica nanoparticle surface chemistry plays a vital role in controlling both nanoparticle dispersion and ion transport through the nanocomposite membranes. Specifically, silica nanoparticle aggregation reduced vanadium ion crossover as compared to well-dispersed particles with the same end functionality. Additionally, the overall nanoparticle surface charge is a key factor in controlling vanadium ion permeation through these composite membranes.
A series of sulfonated poly(biphenyl alkylene)s have been synthesized in order to evaluate them as candidates for alkaline redox flow battery cation exchange membranes. Free standing films were cast from solution and used for electrochemical impedance spectroscopy (EIS), GPC, NMR, FTIR and reagent permeability measurements. Ionic conductivity was measured as a function of electrolyte composition and was found to correlate with the water uptake of these materials. The ionic conductivity of these membranes as measured by EIS was higher or comparable to those measured for perfluorinated films, such as Nafion 112. Notably the permeability of redox-active reagents across these films was at least one order of magnitude lower than the values measured for Nafion 112. NMR, GPC, and FTIR studies indicate that the polymers remain stable after exposure to strongly alkaline aqueous environments. Thermally crosslinkable or hydrophobic aromatic moieties were introduced into the polymer backbone to study the effect of polymer chain packing on molecule cross-over, ion transport and water uptake. The effect of polymer composition on the membrane properties and electrochemical cell performance will be discussed.
POLY 237: New ion transport membranes for large-scale energy storage

Michael A. Hickner, mhickner@mac.com. The Pennsylvania State University, State College, Pennsylvania, United States

New polymer membranes are needed to advance energy storage and conversion technologies for distributed and grid-scale applications. We have recently demonstrated new ion-conducting polymer membranes that have achieved excellent performance and long-lifetime stability in vanadium redox flow batteries, a leading technology candidate for deployment in renewable power networks and grid-scale energy storage systems with sizes ranging from 10s to 100s of megawatts. By tuning the nanoscale self-assembly of the ionic domains in the polymers, we are able to increase the cycle life of the device by impeding vanadium ion transport through the membrane while facilitating high conductivity in the electrolyte to maintain the battery current density. For instance, by decreasing the vanadium permeability of the membrane by a factor of two, we have been able to double the lifetime of the device, which provides significant life-cycle cost savings. We have also demonstrated membranes with nearly zero vanadium permeability that show 100% coulombic efficiency in flow battery charge-discharge cycling tests. Currently, we are working on demonstrating these membranes over 100s of charge-discharge cycles. This talk will detail the structure-property relationships of these types of membranes and point out routes to further improvements in membranes for large-scale batteries.
Incorporation of silica nanoparticles (SiNPs) into perfluorosulfonated ionomers (such as Nafion) has gained popularity as a means of reducing vanadium ion crossover as compared to traditional proton exchange membranes (PEMs) for vanadium redox flow batteries. However, the impact of these nanoparticles on the structural dynamics and transport kinetics of the composite PEMs remains elusive. Therefore, elucidating such structure–property relationships can provide vital insights regarding the mechanism of crossover reduction in these composite materials. In our study, time-resolved Fourier transform infrared-attenuated total reflectance (tFTIR-ATR) spectroscopy was employed to characterize the ionomer swelling kinetics and water transport in a series of nanocomposite membranes with varying nanoparticle concentration and surface chemistry (both anionic- and cationic-functionalized surfaces). Water transport through these membranes was found to be strongly coupled to the viscoelastic response of the composite membrane. Specifically, anomalous, multi-stage viscoelastic relaxation and water diffusion was observed. We conjecture that this multi-stage behavior is caused by structural reorganization of the ionomer during hydration. In addition to tFTIR-ATR spectroscopy measurements, neutron spin echo (NSE) spectroscopy and dielectric relaxation spectroscopy (DRS) were employed to characterize the impact of SiNP surface chemistry on local chain dynamics in Nafion fluorocarbon network. While DRS provides a measure of motion of polar side-chains, NSE allows us to evaluate changes to segmental dynamics at the length scale of the ionomer backbone spacing. Thus, these combinatorial spectroscopic techniques helped to resolve the implicit interactions between SiNPs and Nafion by probing local network dynamics that span across multiple time and length scales. Interestingly, changes in bulk polymer dynamics, as measured by NSE, were found to be analogous to swelling dynamics measurements from tFTIR-ATR spectroscopy, providing unique insight into the impact of SiNPs (and interfacial interactions) on water transport in these ionomer nanocomposites.
POLY 239: Fluorocarbon-based ionomers with single- and multi-acid side chains at nanothin interfaces: What matters

Seefat Farzin\textsuperscript{1}, Tyler Johnson\textsuperscript{1}, Charles Nguyen\textsuperscript{2}, Joseph Turner\textsuperscript{2}, Shudipto K. Dishari\textsuperscript{1}, sdishari2@unl.edu. (1) Department of Chemical Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, United States (2) Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, United States

Technological advancement of energy conversion and storage device is critical to achieve energy sustainability. A major barrier, negatively impacting efficiency of energy conversion devices like proton exchange membrane fuel cells (PEMFCs), is poor ion conductivity at ionomer-catalyst interfaces on electrodes. Exploring the routes to ion conduction limitations in nanothin ionomer films can be the key to design more efficient ionomer-catalyst interfaces and improve the oxygen reaction efficiency in PEMFCs. This work explored the local hydration and proton conduction environment within three of the most promising fluorocarbon based fuel cell ionomers, 3M PFIA, 3M PFSA and Nafion, using fluorescent photoacid probe. 3M PFIA has two different acid groups per side chain, (i) highly acidic bis(sulfonyl)imide (-SO\textsubscript{2}-NH-SO\textsubscript{2}-) and (ii) perfluorosulfonic acid (-CF\textsubscript{2}-SO\textsubscript{3}H) group; while 3M PFSA and Nafion both have single perfluoro sulfonic acid group per side chain with slight differences in side chain structure. We found that proton conductivity did not necessarily scale with water uptake in all sub-micron thick films of all three ionomers. Interestingly, the ionic domain size, measured independently using steady state fluorescence and small angle X-ray scattering (SAXS), followed the same trend as proton conductivity: 3M PFIA > 3M PFSA > Nafion. Moreover, the close match in ionic domain size obtained from two independent techniques indicates that fluorescence is a very powerful and reliable technique that can tell us accurately what is happening inside the ionic domains. We also performed spatial mapping using contact resonance atomic force microscopy (CR-AFM) and developed a model utilizing CR-AFM data to quantitatively obtain viscoelastic properties of ionomer ultrathin films. The spatial correlations of mechanical behavior with proton conduction properties helped a great deal to better understand the ionomer-catalyst interfaces.

Working principle of photoacid probe 8-hydroxypyrene-1,3,6, trisulfonic acid sodium salts (HPTS) (top); the deprotonation ratio (I\textsubscript{d}/I\textsubscript{p}) of HPTS in ionomer films at different RH and film thickness (bottom).
Alkaline fuel cells (AFCs) that employ solid-state anion exchange membranes (AEMs) as the electrolyte separator are of great interest as they produce high power densities at low operating temperatures (< 200 °C) and enable the use of non-platinum electrodes (e.g., nickel), significantly reducing cost relative to proton exchange membrane fuel cells. Several challenges limiting the wide scale use of membrane-based AFCs is the alkaline chemical stability and ion transport of polymers used as AEMs. Recent results from our laboratory have demonstrated excellent alkaline chemical stability of AEMs containing styrene-based saturated N-heterocyclic cationic chemistry (e.g., covalently attached cations = methylpyrrolidinium, methylpiperidinium). In this work, the ion transport in a variety of highly chemically stable homopolymers, diblock copolymers, and multiblock polymers synthesized in our laboratory will be discussed. Specifically, a fundamental study of ion transport relative to cation type, polymer morphology, water content will be presented in relation to AFC performance.
Alkaline exchange membranes (AEM) fuel cells are an attractive cost-saving alternative to traditional proton exchange membrane (PEM) fuel cells. In recent years, anion conducting polymer membranes have reached levels of ionic conductivity and chemical stability that rival that of Nafion, the current state of the art in PEM technology. However, these two important qualities have not been achieved before in the same AEM material until now.

In this study, a series of tetrablock copolymers containing an all-hydrocarbon backbone and tethered quaternary ammonium groups were synthesized based on vinyl addition polymerization of norbornene. Several variations of block copolymer AEMs with different ion exchange capacities (IEC) were made by adjusting the ratio of hydrophilic to hydrophobic blocks. Correlations were found between the ionic conductivity and mechanical properties to the polymer structure, channel size, and degree of phase separation. Furthermore, it was found that light crosslinking of the membranes allows for high IEC materials to be used while maintaining acceptable water uptake. The crosslinked AEMs have demonstrated record-high hydroxide conductivities (198 mS/cm) for a chemically stable polymer. The chemical degradation at 80°C in 1 M KOH was <1% degradation in 1,200 hours. The AEMs were also used to construct MEAs for alkaline fuel cells with peak power densities of over 700 mW/cm².

Synthesis of poly(norbornene) block copolymer
POLY 242: Effect of phosphonated triazine monomer additive in disulfonated poly(arylene ether sulfone) composite membranes for proton exchange membrane fuel cells

Tiffany N. Thompson, tiffyt_17@yahoo.com. Life & Physical Sciences, Fisk University, Madison, Tennessee, United States

Polymer electrolyte membrane fuel cells (PEMFC) are equipped with a proton exchange membrane (PEM) that convert chemical to electrical energy through an oxidation potential. Inadequate membrane performance at temperatures above 180 °C, low relative humidity or high sulfonation levels limit widespread PEM commercialization. Since polyfunctional acid materials exhibit proton conduction at high temperature and low relative humidity, this work aimed to synthesize and characterize 2,4,6-triphosphonic acid-1,3,5-triazine (TPAT) to implement as an additive in poly(arylene ether sulfone) (PAES) copolymers for applications in PEMFCs. Reaction of 1,3,5-triazine and triethyl phosphite followed by acid hydrolysis yielded the TPAT monomer, confirmed via $^{31}$P, $^1$H and $^{13}$C NMR. TPAT in various wt% amounts was added to acidified disulfonated biphenol-based PAES copolymers to produce BPSH-35/TPAT membranes exhibiting non-linear thermal, water performance, and proton conductivity properties. The 1% TPAT membrane showed the highest proton conductivity under 90% relative humidity and hydrated state at 0.015 S/cm and 0.032 S/cm respectively. ATR-FTIR analysis confirmed that membranes with 3 and 5 wt% TPAT exhibited hydrogen bonding that restricted proton conduction.

![Chemical Structure](image)
The need to operate proton exchange membrane fuel cells under hot and dry conditions has driven the synthesis of new ionomer materials based on perfluorinated chemistry. Shorter side chain versions of Nafion®, such as 3M and Aquivion® PFSAs, as well as the alternative side-chain chemistries like 3M’s imide-containing PFSAs, have drawn attention during past decades. These membranes could lead to enhanced fuel cell performance under harsh conditions; however, the underlying origins of which are not completely understood. In order to tackle this problem, we conducted a systematic mass transport study under controlled relative humidity and elevated temperatures on these membranes to assess their behavior under dry-hot conditions. The effects of side chain chemistry and length, equivalent weight (EW), and temperature on membranes’ water sorption and conductivity are examined and the relationships between water content, proton conductivity, and proton mobility were investigated. In addition, the impact of temperature on the membrane nanostructure was investigated through small-angle X-ray scattering (SAXS) in dry and hydrated conditions. Membranes’ structural features and mass transport properties are correlated to establish the role of side-chain chemistry and EW in structure-transport relationship of these ionomers.
Polymer brush functionalization has become a powerful approach to tailor interfaces, often creating properties and behaviors that are inaccessible using analogous bulk materials. Their unique nature stems from versatility in polymer chain length, spacing, conformation, and chemical design. Brush-modified surfaces have led to great advances in surface and interface engineering, with their most well-known applications in the biomedical field, antifouling, functional nanomaterials and nanofabrication, wettability, colloidal stabilization, and other advanced technologies. As brush-modified technologies become more prevalent, accessible characterization of these interfaces and their response to changing experimental conditions remains a challenge.

Herein, we demonstrate the utility of silicon photonic microring resonators as a platform for the in-situ characterization of polymer brush surfaces. Microring surfaces were modified using surface-initiated atom transfer radical polymerization, enabling the construction of well-defined polymer brushes of hydrophilic, hydrophobic, and stimuli-responsive natures. Diffusion and partitioning of small molecules into the brushes were observed in real-time and conformation changes were quantified by measuring and fitting shifts in the resonance wavelength. In particular, this platform allows not only determination of solvent compatibilities based on small molecule partitioning depth, but also determination of partition and diffusion coefficients for small molecules in various polymer brushes. Additionally, polymer brush pKa can be extracted as a function of brush length and solvent conditions. Thus, we demonstrate that our technique allows for accessible characterization of diverse polymer layers in the presence of complex analyte-solvent interactions.
Since the first discovery in 1969, polyenynes received much attention due to their intriguing optoelectronic properties that made them useful materials for molecular sensors. Although there have been extensive studies for the synthesis of various polyenynes, only a handful of polyenyne motifs were reported to date. Furthermore, most of the synthetic routes to polyenynes relied on topochemical synthesis in solid state, limiting their versatility in applications due to poor solubility. More recently, syntheses of soluble polyenynes were realized by step-growth mechanism, but the preparation of conjugated polyenynes with high molecular weights in a controlled manner remained impossible.

To overcome these limitations, we developed a new cascade polymerization method by combining two different organic reactions; olefin metathesis and metallotropic 1,3-shift. By rationally designing stable multialkyne monomers, a series of metathesis and metallotropy reactions proceeded by Grubbs catalyst in a sequence-specific manner to afford conjugated polymers containing unique polyenyne motifs in their backbone. For example, tetradeca-1,6,8,13-tetrayne moieties underwent a cascade transformation of ring-closing/metallotropic 1,3-shift/ring-closing reactions to efficiently generate a conjugated polyenyne backbone with a Z-E-Z alkene sequence and one triple bond. In addition to this tetrayne monomers, other two classes of monomers, pentaynes and hexaynes, underwent remarkably complex cascade reactions (up to 5 independent transformations for one repeat unit) at high levels of selectivity to afford unprecedented conjugated polyenyne structures. This new polymerization, which we call cascade metathesis and metallotropy (M&M) polymerization, is the first example of making polyenynes by chain-growth mechanism, which enabled the precise control over molecular weights with narrow dispersities. Furthermore, living M&M polymerization realized the synthesis of block copolymers consisting of fully conjugated polyenyne backbones, highlighting its versatility.
Ring-opening metathesis polymerization (ROMP) of cyclopentene has captured the interest of polymer chemist since the 1950s. While the field of ROMP has blossomed over the recent years and provided chemist a new tool to synthesize precision materials, the use of low strain cyclopentene has been overlooked due to challenges associated with it. Recently, our group has advantageously used the low ring stain to allow for total control on the polymerization of cyclopentene and derivatives. This methodology has allowed access to structurally complex materials, such a graft polymers, that were previously unobtainable in a controlled manner. Insight into this journey and new ways to use cyclopentenes low ring strain advantageously will be discussed.
POLY 247: Macromolecular engineering through metal-free ring-opening metathesis polymerization

Pengtao Lu, pl24@uw.edu, Andrew J. Boydston. Chemistry, University of Washington, Seattle, Washington, United States

Since the discovery of metal-catalyzed olefin metathesis, traditional metal-based ring-opening metathesis polymerization (ROMP) has already evolved to a ubiquitous technique for making functional polymeric materials both in academia and in industry. However, it is significantly challenging to remove residual metal after the end of polymerization and the presence of even trace amount of metal contamination dramatically limit the application of ROMP polymer as components in both pharmaceutical and microelectronics industry. Toward preparation of “greener” polymers without residual metal contamination, metal-free ring-opening metathesis polymerization (MF-ROMP) has emerged as an alternative to metal-mediated ROMP. Unlike traditional ROMP procedure, MF-ROMP is triggered by oxidation of vinyl ether initiators through excited organic photoredox catalysts. Since vinyl ether moieties could be easily installed on various substrates, we envision that MF-ROMP, aside from its inherent metal-free merits, can also provide opportunities to develop expedient synthetic approaches toward engineering macromolecular architectures, which is crucial in shaping both physical and chemical properties of resulted polymers. Herein, we describe our recent efforts in preparing polymers with distinct chain topology and chemical functionality by integration of MF-ROMP with organocatalytic ring-opening polymerization (o-ROP). Furthermore, by choosing select reagents and solvent, we are now able to access those completely metal-free polymers in “one-pot” procedure.
Shape, size and composition are nature’s most fundamental design features, enabling highly complex functionalities. Despite recent advances, the independent control of shape, size and chemistry of macromolecules remains a synthetic challenge. We report a scalable methodology to produce large well-defined macromolecules with programmable shape, size and chemistry. Specifically, bottlebrush polymers (branched polymers with high branch density all originating from a linear backbone) are synthesized with variable brush length along the backbone. This enables the construction of any axisymmetric shape including: cone, sphere, hourglass, football, and bowtie shapes.

The synthesis is enabled by the combination of reactor engineering principles and controlled polymerizations. One controlled polymerization synthesizes the arms of the bottlebrush (ring opening polymerization or anionic polymerization) and the other polymerizes the backbone of the bottlebrush (ring opening metathesis polymerization). Theoretical derivations, in conjunction with a numerical model, are used to aid in the design and characterization of the shaped macromolecules. We have further characterized the materials through atomic force microscopy (AFM) as well as rheology. Rheological data is further correlated back to Brownian dynamics simulations. This methodology provides a unique opportunity to study the impact of macromolecules shapes.
POLY 249: Postpolymerization modification strategy to solid state block polyelectrolytes

David J. Goldfeld1, djgoldfeld@gmail.com, Eric Silver1, Madalyn R. Radlauer1, Marc A. Hillmyer2. (1) Chemistry, University of Minnesota, Minneapolis, Minnesota, United States (2) University of Minnesota, Minneapolis, Minnesota, United States

Charged polymer membranes are a promising material for the desalination of aqueous systems in a process that can be used for the purification of drinking water as well as the desalination of fermentation broths and road runoff. Previously, work with charged membranes for water desalination has suffered from ill-defined morphologies and a lack of mechanical integrity. Many of the membranes also require harsh conditions for functionalization and are often processed in a charged state, which brings an added level of difficulty. We have developed new block polymer systems that are easily processable in a neutral state using a controlled radical polymerization approach with substituted styrenic monomers. After casting solid thin films, we transform the polymers to charged species using mild conditions with readily available reagents. Preliminary work used reversible addition-fragmentation chain transfer (RAFT) polymerization to grow the block polymers in a controlled manner, which then self-assemble into a variety of thin film morphologies. Subsequent functionalization is performed in a single step in the solid state to yield both positive and negative charged domains while maintaining the initial morphology. By incorporating the charged groups into a composite membrane, we aim to create high efficiency water desalination membranes.

Charged membrane fabricated through postpolymerization modification of a neutral ABC triblock polymer synthesized through RAFT polymerization.
Atom transfer radical polymerization (ATRP), one of the most commonly used controlled radical polymerization techniques, enables facile synthesis of precision polymers using commercially available starting materials. More recently, the application of external stimuli to control ATRP has been investigated. For example, photoredox catalyzed variants of ATRP have been explored using Ru- and Ir-containing photocatalysts (PCs), enabling the synthesis of well-defined polymers under mild conditions using visible light to drive the reaction. While the development of photoredox catalyzed ATRP was a major advance, researchers sought to replace the transition metal-containing PCs used for these reactions with organic PCs to avoid issues with metal contamination of the polymer product and to provide more sustainable catalyst alternatives. This motivation led to the development of organocatalyzed ATRP (O-ATRP).

Similar to traditional ATRP, the O-ATRP catalyst is responsible for controlling the polymerization through mediation of a reversible-deactivation equilibrium. Thus, design of improved O-ATRP catalysts is key for pushing the current bounds of this polymerization method. However, few organic PCs which can access excited states with sufficient reduction potentials to reduce typical ATRP initiators or the alkyl halide chain end of dormant polymer chains are well-studied. As such, a major challenge for the improvement of O-ATRP methods has been the identification and understanding of new organic PC families that can access strongly reducing excited states. To this end, the work disclosed herein is on the development of N-aryl phenoxazines as strongly reducing PCs for O-ATRP. Through the synthesis and characterization of phenoxazine derivatives bearing different N-aryl and/or core substituents, structure property relationships for altering the photophysical and redox properties of this class of molecules has been established. Moreover, the application of these PCs for the O-ATRP of methyl methacrylate was used to determine the effects of PC properties on catalytic performance.
Cellulose nanocrystals (CNC) are a naturally abundant, renewable macromolecules that typically follow the behavior of rod-like polymers. Their outstanding combination of mechanical strength, potential for liquid crystalline self-assembly, high specific surface area, and tailorable surface chemistry make them of interest for numerous aerospace applications including high strength composites. For example, adding low levels of CNC to polymers can be used to tailor composite surface energy and increase mechanical strength. Similarly, adding low levels of polymers to CNC dispersions can be used to reduce the brittleness typically associated with thick films comprised of rigid colloidal materials. However, some of the most interesting applications are based on pure CNC films produced by exploiting the liquid crystalline self-assembly of sulfonated CNC. In a recent series of work, we have shown the individual and combined impacts of material and processing parameters on the optical properties of CNC films. These results highlight the potential for CNC films to be used in photonic filters, security applications, UV barrier protection, and reflective polarizers that reduce the energy consumption of displays through light recycling. In related work, we have fabricated functional microelectromechanical systems (MEMS) from CNC that can achieve the small feature sizes and mechanical properties associated with traditional silicon MEMS. A key advantage of CNC MEMS is that their production does not require the multimillion dollar infrastructure typically associated with silicon fabrication. Therefore, they can enable local agile production of both mechanical sensors and biomedical sensors in response to emerging needs and threats. This talk will provide key findings from recently published work and highlight CNCs' potential in a range of applications.

The initial dispersion microstructure and film processing conditions control the size of regions with uniform reflectance color as well as the presence of biomimetic photonic band gaps such as those exhibited by some beetles.
POLY 252: Substitution of formaldehyde in phenolic networks for ablative composites

Sylvain Caillol, sylvain.caillol@enscm.fr. Institut Charles Gerhardt, Montpellier, France

Phenolic resins are industrially used in a wide range of applications from commodity and construction materials to high-technology aerospace industry. They are mainly produced from the reaction between phenolic compounds and formaldehyde. Nevertheless, formaldehyde is a highly volatile and hazardous compound, classified as a Carcinogenic, Mutagenic and Reprotoxic chemical (CMR). Vanillin is a bio-based and non-toxic aromatic aldehyde compound obtained from the abundant lignin resources. Also, its aromaticity is very interesting for the synthesis of phenolic resins with high thermal stability. However, because of the relatively low reactivity of its aldehyde function toward phenolic compounds, it has never been used to synthesize phenolic resins.

We developed innovative functionalization reactions and designed new bio-based aromatic aldehyde compounds from vanillin. Those innovative compounds present improved reactivity toward phenolic compounds compared to vanillin. Moreover, they have target structures to synthesize highly cross-linked phenolic resins with high aromatic densities. We have obtained phenolic resins from substituted vanillin, thus without the use of any aldehyde compound classified as CMR. The analytical tests of the cured resins confirmed that those bio-based resins exhibit high levels of performance with high thermal stability and high rigidity properties for aerospace applications.
POLY 253: Synthesis of biorenewable polyphenols from cardanol: Precursors to high-performance materials

Jake Muldoon, jakemuldoon90@gmail.com, Michael Garrison, Benjamin G. Harvey. Chemistry, US Navy, Ridgecrest, California, United States

Renewable phenolic compounds are intriguing substrates for the generation of high performance thermosetting materials. The unique functionality of bio-based phenols often allows for enhanced material properties, and efficient, high throughput synthetic techniques for synthesizing monomers. Cardanol, a low cost component of cashew nut shell oil, is a phenolic compound with a 15-carbon unsaturated chain in the position meta to the hydroxyl group. Recent work has shown that polythiols are effective for cross-linking the side-chain alkenes of cardanol while concomitantly catalyzing the cure of thermosetting groups attached to the aromatic ring. This novel synergistic approach allows for a significant reduction in the cure temperature, while enhancing the rate and degree of cross-linking. In addition to novel dual cure strategies, this presentation will describe the synthesis, characterization, and cure chemistry of various cardanol-based thermosetting monomers and polymers.

![Chemical Structures and Reactions](image-url)
POLY 254: Sustainable polymers in society: Demos of renewable polymers manufacture in the lab for HS students from a chemical/environmental engineering summer camp

Lucian A. Lucia¹,³,⁴, lalucia@ncsu.edu, Richard A. Venditti², Hasan Jameel², Medwick Byrd², Lokendra Pal⁵, Jennifer Piercy², Joel Pawlak², Shana McAlexander². (1) Departments of Forest Biomaterials and Chemistry, North Carolina State University, Raleigh, North Carolina, United States (2) Forest Biomaterials Dept, North Carolina State University, Raleigh, North Carolina, United States (3) Chemistry, North Carolina State University, Raleigh, North Carolina, United States (4) State Key Laboratory of Bio-based Materials and Green Papermaking, Qilu University of Technology/Shandong Academy of Sciences, Jinan City, Shandong, China (5) Forest Biomaterials- 3205 Biltmore Hall, North Carolina State University, Raleigh, North Carolina, United States

The Department of Forest Biomaterials in the College of Natural Resources at NC State University have held an engineering summer camp for local high school students to entice and awaken interest in the STEM fields. As part of that camp, we provide a primer on polymers and the possibility of introducing renewable polymers (e.g., bioplastics, hydrogels) in response to the environmental burdens associated with petroleum-based plastics. This short discussion will review the purpose of our camp, introduce and detail the two polymer-based labs, and provide a summary of the overall response from the students to the camp. We are currently writing a J. Chem. Ed. that will feature more information on the experiments, results from a survey, and comments from the students.
POLY 255: Combining thiol-ene and acetal chemistries to synthesize degradable, environmentally friendly networks

Benjamin M. Alameda¹, Nicholas Pierini², ngpierini@gmail.com, Derek L. Patton³. (1) School of Polymer Science and Engineering, University of Southern Mississippi, San Luis Obispo, California, United States (2) California Polytechnic State University, Santa Maria, California, United States (3) Campus Box #10076, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Millions of tons of plastics end up in landfills, oceans and the environment. It is a serious environmental problem and will continue to worsen as only a small fraction of the total plastics produced are recycled. For instance, only 14% of plastic packaging is recycled each year. Thiol-ene chemistries offers a scalable and efficient platform to make UV curable thermosets. Incorporating hydrolysable acetal crosslinks into these thermosets enables full degradation into aqueous solutions with tunable degradation rates defined by acetal stability. For our materials, we synthesized a library of acetal-based monomers with varying stabilities and polymerized them with multifunctional thiols by UV photopolymerization. Mass loss vs. time was measured gravimetrically for each thermoset composition by removing degradation samples at specific time points and measuring their dry mass after lyophilization. Degradation was also monitored by time-lapse optical microscopy to observe the visual degradation differences between samples. Mechanical properties and glass transition temperatures for all materials were measured using dynamic mechanical analysis, while thermal degradation temperatures were found using thermogravimetric analysis.
POLY 256: Crosslinked biodegradable thermoset polymer films based on sodium alginate

Kevin D. Barz¹, kevin.barz@mines.sdsmt.edu, Tsvetanka Filipova². (1) Chemistry and applied biological sciences department, South Dakota School of Mines and Technology, Rapid City, South Dakota, United States (2) Chemistry, South Dakota School of Mines and Technology, Rapid City, South Dakota, United States

The environmental problems associated with the usage and disposal of petroleum-based polymers for short-term applications has increased in recent years due to bioaccumulation and degradation of these traditional materials. To reduce this problem both the removal of traditional plastics from the environment and the implementation of systems to prevent plastic accumulation must be achieved. To this end, the purpose of the present study is to explore the possibility of producing a functional thermoset biopolymer film that not only is similar in material properties but also does not accumulate in the environment. To produce these thermoset biopolymer films a mixture of sodium alginate (ALG), polyvinyl alcohol (PVA), glycerol (GLY), and citric acid (CA) is formulated. A low-cost glycerol is used to enforce the flexibility of the films, and citric acid is used as a cross-linking agent which helps to reduce the water vapor permeability of the films. The crosslinking reaction parameters (different ratios, curing time, cross-linking content) were studied by comparing the characteristics of the films, such as glass transition temperature (Tg) values and Fourier transform infrared (FTIR) spectral data, as well as the impact of the crosslinking reaction on surface morphology and thermal stability.

SEM Image of surface morphology for glycerin: sodium alginate : citric acid thermoset biopolymer film
Zwitterionic phosphorylcholine-based polymers have emerged as an intriguing materials platform due to enhanced stability and compatibility in biological settings. Poly(2-(methacryloyloxy) ethyl phosphorylcholine) (PMPC), containing anionic phosphate and quaternary amine moieties in a single repeat unit, serves as a model example in various design strategies of nanocarriers and bioconjugates. Engineering PMPC into oppositely-charged AB diblock polyelectrolytes results in associative phase separation to form zwitterionic polyelectrolyte complex (Z-PEC) micelles. However, subtle differences between the complexation behavior of Z-PECs and systems bearing uncharged, neutral blocks (e.g. polyethylene oxide) remain unclear, complicating the interplay of overarching physical and ionic contributions to PEC formation and behavior. To alleviate this uncertainty, we rapidly synthesized a series of well-defined, PMPC-based diblock copolymers via aqueous reversible addition chain-transfer (RAFT) polymerization using a parallel synthesizer. This method of accelerated synthesis allowed us to directly compare libraries of PMPC systems with an assortment of charged building blocks. Product purity, composition, and molecular weight were characterized through proton nuclear magnetic resonance spectroscopy and size exclusion chromatography. Resulting polymers were studied to determine the effects of molecular weight, constituent monomer, and ionic strength on (1) the self-assembly of micelles in water and (2) the size and stability of complex-core micelles over time with multi-angle light scattering. Ongoing study of these parameters on the quality of Z-PEC hybrids will enable more precise and tailorable complex materials for relevant biotechnologies such as the encapsulation and delivery of nucleic acids, peptides, proteins, and other biomolecules.
In order to use complex coacervates in applications such as drug delivery, competition-cooperation effects between water, salts and polyelectrolytes need to be further investigated. This study investigates how the water content of coacervates with strong and weak polyanions changes with salts of varying strengths according to the Hofmeister series. This study focuses on the weak and strong polyelectrolyte systems of poly(allylamine hydrochloride)/poly(acrylic acid) (PAH/PAA), poly(allylamine hydrochloride)/poly(methylacrylic acid) (PAH/PMAA), and poly(allylamine hydrochloride)/poly(sodium 4-styrenesulfonate) (PAH/SPS).

Thermogravimetric Analysis (TGA) and mass measurements were used to quantify the water content of the coacervates. The water content decreases with the increasing solubility influence (as you go down the Hofmeister series) of salt anions in the PAH/PAA and PAH/PMAA system with mixed results for the PAH/SPS systems as it has a strong polyanion. Titration curves were obtained to identify the polyelectrolytes’ pKa values in order to identify the degree of ionization. These pKa values were relatively close to literature values. Dynamic Light Scattering was used to determine particle size and uniformity. Overall, the PAH/SPS system has a larger average particle that is less uniform than the PAH/PAA system. The PAH/SPS system becomes smaller and less uniform when KBr is present. This decrease in size may further indicate the greater amount of intrinsic interactions of the polyelectrolytes when KBr is present. We will use Neutron Activation Analysis to determine the identity and amount of salt ions in each coacervate system.

Overall, it was found that water acts as a plasticizer while salt ions screen charges and increase water-polylelectrolyte interaction. Overall, this allows for greater intrinsic interactions because of the increased chain mobility and screening of repulsive chain charges on each polyelectrolyte.
Herein we report the synthesis and characterization of a diblock polypeptide composed of poly(ethylene oxide-b-lysine), where the lysine block has been modified with an electron withdrawing group. The ε-amine of the lysine is modified utilizing a monomer modification approach prior to polymerization. We hypothesize that modifying the lysine monomer with an electron withdrawing group will tune the pKa of the resultant poly(lysine) block from pH 9 to a more biorelevant region (pH ~ 6-7). Incorporation into a diblock copolymer will imbue the system with enhanced functionality and pH responsiveness, where conformation changes in the lysine secondary structure may result in overall assembly morphology transitions. These copolymer systems can be utilized in areas such as drug delivery, whereby modified pH-responsive blocks can be incorporated into delivery vehicles where cargo can be spontaneously released upon pH driven morphology transitions.
POLY 260: Assessing warping issues with 3D printed ceramic models using SLA 3D printers

Leslie Rodriguez, kwleslie3@ufl.edu, Nancy Ruzycki. University of Florida, Gainesville, Florida, United States

Additive manufacturing or three-dimensional (3D) printing is a type of method used in manufacturing where you create materials using a layer by layer method. For this experiment, an Autodesk stereolithography apparatus (SLA) 3D printer, which creates layers by curing a liquid photopolymer with a UV light, was used. The advantages of using 3D printing as a manufacturing technique is that it is one of the fastest techniques with little waste, and low cost per object. It also has the ability to create complex shaped objects of all sizes. SLA printers have high accuracy and resolution for very small 3D objects. This results in research being done on 3D printing biocompatible materials for application such as, bone implants, tissue engineering, and dental application because those applications require high resolution and their designs require microscopic accuracy. Ceramic-polymer composites are used in the biomedical industry, but they are one of the most challenging materials to print owing to the polymer controlling crosslinking and ceramic fill controlling strength of the material and there is very little literature on optimization on this type of system. SLA 3D printers use a polymer resin that is mixed with a ceramic powder filler in order to print ceramics and then firing is required to get the desired outcome. Some problems that are encountered with ceramic 3D printing, is lack of adhesion to the build head, warping caused by not enough exposure time or gravity weighing down sides of the material, and shrinkage. Many of these issues are related to the ceramic filler interfering with the crosslinking process of the polymer. In this experiment, porcelain ceramic made of crystalline silica mixed with acrylates crosslinking monomers is studied with a focus on optimizing crosslinking parameters to reduce warping. Printing parameters include exposure time, layer thickness, wait time, and slide velocity, all factors that affect the quality of the print that effect warping of the material. This research determines optimized parameters to reduce warping in 3D printed ceramics.
The rapid prototyping capability of 3D printing has revolutionized manufacturing giving manufacturers the ability to design, produce and test models in a fraction of the time compared to traditional manufacturing methods. A myriad of printers are available commercially and have enabled rapid prototype designs. These new applications are in large part due to their new widespread availability and simplicity. Although 3D printing is so disruptive and innovative, there remain some shortcomings regarding material development. Most commercial printers can print many different materials, but only if the build material comes in a standard form. Therefore, these printers do not allow for rapidly prototyping thermoplastic material and developing new 3D-printable materials. To enable direct printing of powders we developed a 3D printer capable of printing thermoplastic powder materials through a process of powder melt extrusion (PME). This prototype was found to be capable of printing a variety of powders ranging from commercially available to experimentally developed thermoplastic polymers. With respect to the commercially available polymers such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and high impact polystyrene (HIPS), PME was able to achieve prints of similar print quality to that of a fused filament extrusion printer. Comparative thermal and mechanical analyses were conducted using prints from the PME printer and a commercial fused filament fabrication (FFF) printer to determine if the resulting print properties greatly differed from each other. Results indicated that while 3D printing using PME rather than FFF caused minor differences in the thermal or viscoelastic properties of the printed parts, the bulk tensile properties of the prints are where the differences between PME and FFE were further exemplified. The addition of PME enables the direct 3D printing of powders and will further expand the current landscape of manufacturing.
Three-dimensional (3D) printing has offered a manufacturing technique for complex shapes that promises accurate replication and reduction of wasted material. Stereolithography (SLA) printers have drawn attention for their accuracy and ease of use. However, there are several interchangeable parameters and materials available for these printers, including polymer, ceramic and glass filled photopolymer blends. Ceramic resins work by combining ceramic powders with monomer crosslinkers so that UV light activates photo-initiated monomers for crosslinking in order to bind ceramic powder filling. The ceramic filling is held in a polymer matrix until firing and polymer burn off. The research frontier of ceramic SLA printing is relatively new, therefore literature has not yet fully developed. Printing of ceramic resin is more challenging than standard resins since ceramic prints require firing. The process requires temperatures to be elevated and maintained at the polymer burn-off temperature and then raised to the firing temperature for the ceramic material. After this process, prints acquire unwanted shrinkage. The objective of this investigation is to establish a relationship between print parameters and shrinkage in order to minimize shrinkage and quantify an expected shrink range to anticipate possible shrinkage before firing in order to optimize the printing process. The ceramic used is Porcelite, a crystalline silica resin by Tethon. A complex model of known dimensions will be used for prints to measure results effectively using volume displacement as well as physical measures of samples. Layer thickness and exposure time will be changed individually in order to assess their impact post-firing. Data collected through this investigation will help those interested in 3D ceramic SLA printing to understand the impact print parameters have on ceramic prints post-firing.
Surface instabilities in polymer thin films have received increasing attention due to the ability to generate well-defined and complex topological features. The formation of highly ordered surface wrinkles represents one class of instability-drive phenomena, and examples are readily available in nature, such as wrinkling in skin or dried fruit. Following nature’s lead, strain-induced wrinkling of polymer films has emerged as a powerful technique to design materials for various applications in advanced adhesion, antifouling, and flexible electronics. Herein, we demonstrate a simple route to design ultrathin polymer brush surfaces with tunable wrinkled morphologies using post-polymerization modification (PPM) techniques, where the length scale of the buckling features can be tuned using PPM time. The PPM reaction occurs under poor solvent conditions, which collapses the brush and partially crosslinks the brush at the near-surface region. This PPM reaction occurs in a front-like process, forming a diamine-modified “skin” thickness ($h_1$) and an unmodified “substrate thickness” ($h_2$). The swelling behavior of the polymer brushes and PPM kinetics can be investigated using in-situ ellipsometry, and the through-thickness brush composition is determined by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). These techniques allow us to determine the parameters that influence the buckling behavior. Additionally, the wrinkle orientation can be controlled by AFM lithography techniques.
Smart materials are designed materials that have properties that can undergo controlled change by external stimuli and these materials are increasingly being used as sensors and actuators for robotics and artificial intelligence systems. In this study, polymeric bilayers acted as smart materials that could bend, curl, and twist after applying and releasing a mechanical strain. The polymeric bilayers were created using polyolefin thermoplastic elastomers (TPEs). Ethylene octene copolymer TPEs (POEs) with different degrees of crystallization were compression molded separately then adhered to one another through compression molding. The samples were then cut into strips of varying length to width (L/W) ratios and uniaxially strained. After release of the strain the strips either bent, curled, twisted, or showed a combination of 2 responses depending on the elastic recovery difference between the 2 layers and the applied strain. This study showed that easily processable TPEs can be used as actuators for mechanical strain applications and the deformations can be reversed through heat application at low temperature for a very short period of time.
Toward an understanding of dielectric breakdown through incorporating defects into polyetherimides

Jeffrey Lockwood, jeffrey.lockwood@uconn.edu. Chemistry, University of Connecticut, Plantsville, Connecticut, United States

Electric cars, the electro propulsion of ships, and electromagnetic railguns are examples of new electrochemical devices that are being introduced to the contemporary industry. High energy density storage systems are needed to function these devices, demanding the advancement of capacitors that are capable of storing large amounts of energy over long time periods. This project aims to discover the cause of dielectric breakdown, which would lend suggestions of how to increase the energy density of a capacitor to make it better able to power an electrochemical device. Polymers represent an intriguing class of dielectric materials for use in capacitors because of their easier processing techniques, and increased mechanical integrity, compared to their inorganic counterparts. Further, the Navy would like materials that undergo ‘graceful’ failure.

ULTEM 1000 polyetherimide was chosen to study because of its high glass transition temperature, making it stable at the high temperatures associated with these capacitors. ULTEM 1000 derivatives were synthesized through step-polymerization combining 4,4-Bisphenol A Dianhydride, m-Phenylenediamine, and differing end cap molecules that incorporate specific free volume defects at the ends of the polymer chains. Causes of dielectric breakdown are not currently understood, but it is known that free volume defects decrease dielectric constant suggesting that these modifications will also affect dielectric breakdown. t-Butylaniline, Tri-t-butylaniline, and 1-aminoadamantane were chosen as end caps because of their bulky substituents allowing for free volume variation in the polymer film. Polymer molecular weight was controlled using these endcap reagents, and higher molecular weights resulted in fewer endcaps and hence lower free volume.

Polymers were synthesized with molecular weights of ca. 40kDa as determined by gel permeation chromatography and nuclear magnetic resonance spectroscopy. Polymer samples were then subjected to dielectric testing, where their Weibull DC breakdown was compared to commercial ULTEM 1000 produced by SABIC company.
POLY 266: Oral multiparticulates as a platform approach for pediatric drug development

Matt Santangelo, Matthew.Santangelo@pfizer.com, Jeremy A. Bartlett. Drug Product Design, Pfizer Inc., Groton, Connecticut, United States

Pediatric formulation development presents unique challenges, such as designing formulations that are acceptable in terms of swallowability and palatability. Historically, a majority of pediatric formulations are oral solutions or suspensions. Oral liquids are an excellent option for pediatric administration as they offer simple, flexible dosing for children who may be unable to swallow tablets or capsules. However, masking unpleasant drug taste in these formulations can be challenging. Taste of medication, if unacceptable, could lead to patient compliance issues and is therefore a critical attribute to consider in the design of acceptable dosage forms. The pharmaceutical industry has been shifting toward the use of flexible oral solid dosage forms to address the needs of pediatric patients.

This presentation summarizes the development of a coated multiparticulate intended for pediatric administration. The multiparticulate formulation consists of an immediate release (IR) melt-spray-congeal (MSC) core which is barrier coated to improve taste attributes. Two broad coating approaches are explored, pH independent and pH dependent (reverse enteric) systems. These formulations will be studied in a taste and pharmacokinetic (PK) study to select the most suitable one to progress to commercialization. The finished dosage form could be a sprinkle capsule or bulk multiparticulate product for administration through a novel dosing device.

Figure 1: Uncoated MSC core; Barrier coated MSC core; Sprinkle capsule finished drug product (Left to right).
Softgels formulations provide the flexibility to incorporate a wide spectrum of functional excipients that can be included in the fill or in the shell. The fill formulations can be a solution, simple suspension or more complex lipid-based formulations. Excipients ranging from simple oil or polyethylene glycol to more creative self-emulsifying drug delivery systems with the addition of hydrophilic or lipid-based surfactants, or a hydrophilic cosolvent are being utilized. Polysaccharide-based capsules have been developed in recent years that are compatible with higher processing temperatures and pH, extending the range of ingredients that can be formulated allowing more concentrated film to be created and higher melting fats to be encapsulated.

Examples for recent innovation: Nintedanib (Ofev®) is a lipid suspension of the active substance in medium chain triglycerides, hard fat and lecithin. Selection of the lipophilic excipients mix was generally based on technical and functional formulation requirements and active substance stability. Calcifediol (Rayaldee®) is an extended-release 30 mcg capsules that utilize Softgels innovation to deliver controlled release as well as low dose of vitamin D. The product formulation uses non-gelatin carrageenan shell to encapsulate high melting fat in order to achieve the extended release properties. Other inventions include the use of a mixture of long-chain mono-, di-, and triglycerides with polyethylene oxide followed by annealing process to achieve not only the control release properties but also to form an abuse-deterrent Softgels. Another invention is the formulation of chewable Softgels for targeted buccal delivery.
POLY 268: Progress in the development of high-solids, quick-set pharmaceutical tablet coatings

Thomas H. Kalantar, kalantar@alum.mit.edu, Mladen Ladika, Hui Shao, Stacey Dean, Keith Harris, Paul Sheskey, Karen Coppens, Karen Balwinski, Debora Holbrook. The Dow Chemical Company, Midland, Michigan, United States

Pharmaceutical tablet coatings are commonly based on hydroxypropyl methyl cellulose, poly (vinyl alcohol), and acrylic polymers. Currently available tablet coating technology includes spraying of a dilute polymer solution over the tablets, and a time-consuming drying process. Amphoteric latex coating materials contain weak acid and strong base stabilizing moieties on the latex surfaces, and exist as a low-viscosity dispersions at high solids at mildly acidic pH. An increase in pH deprotonates the carboxylic acid group and leads to its ionic linkage with the quaternary ammonium groups also present. This ionic coacervation mechanism enables the coating to set quickly. This study focuses on the evaluation of amphoteric polyacrylate latex-based film forming materials for tablet coatings. A series of amphoteric latexes was prepared from monomers already used in the synthesis of FDA-approved polyacrylate polymers. Polymer composition was systematically varied in order to understand the effects on polymer film formation temperature, setting efficiency as a function of pH, and film properties such as tack, puncture, gloss, optical clarity, water permeability, etc. Latex films made from these suspensions showed equal or superior performance compared with commercially-used cellulosic and poly (vinyl alcohol) tablet coatings. Several requirements for tablet coatings have been achieved, including high solids (~40 wt %); good optical properties (clarity > 90%, transmission > 93%, and haze < 6%); no tackiness, and low permeability (water vapor permeability < 2 x 10^{-7} g / Pa s m).
Poly 269: Intracellular Delivery of Biomolecules via Freeze Concentration Using Polyampholyte Nanocarriers

Kazuaki Matsumura, mkazuaki@jaist.ac.jp, Sana Ahmed. School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan

Penetration of biomolecules into cells is of great importance in biotechnology such as in genetic modification, bio-imaging, delivery system etc. A numerous strategy has been used for effective penetration of nano-sized particles such as electroporation, sonication. However, these methods show highly cell damage. In order to develop low toxic and efficient process, we developed a new method called “freeze concentration” process. Freeze concentration is described as a physical phenomenon wherein at extreme low temperature; the water is transformed into ice-crystals leads to eject the solute molecules, which increases its concentration. We previously showed the effective use of freeze concentration process in effective protein delivery system.1), 2) Among the nanosize particles, liposomes are one of the most popular particles in biomedical application. However, liposomes exhibited instability that can limit its use. Therefore, conjugation of polymers in liposomes is highly attracted for retaining its stability for delivery system. The characterization of liposome was determined by DLS analysis. The sizes were in the range of 200-300 nm in diameter. The protein encapsulating efficiency in liposomes was determined by Bradford assay, the encapsulation efficiency of protein in polyampholyte-modified liposome was greater rather than bare liposome. An effective adsorption onto the cell membrane and internalization into cytosol of protein/liposome complex by facile freeze thawing method were confirmed by comparing with unfrozen cells (Fig.1). A new polyampholyte modified liposome was developed which has high efficacy in facilitating the endosomal escape to the cytoplasm of the cells with low toxicity. This evidences strongly prove that freeze concentration based strategy can be widely used not in cancer immunotherapy but also in gene therapy.

Fig.1. Internalization of FITC labeled polyampholytes (green) and Rh-PE labeled liposomes (Red) into L929 cells during non-freezing and freezing conditions. Scale bar- 20µm
POLY 270: Blood-brain barrier crossing nanoparticle for the delivery of antiretrovirals for targeting HIV-infected brain reservoirs

Nagesh Kolishetti¹, polynag@gmail.com, Mohammad Zahid Kamran², Anuj Shah², Bapurao Surnar², Madhavan Nair³, Shanta Dhar². (¹) Department of Immunology and Nano-Medicine, Florida International University, Miami, Florida, United States (²) Biochemistry and Molecular Biology, University of Miami Miller School of Medicine, Miami, Florida, United States

Over the last few decades, nano-formulations have shown significant promise in medicine for therapy and diagnosis of various diseases. Nano-formulations can be derived from lipids, polymers, inorganic materials, dendrimers, drug conjugates, or viral based particles. All these nanomaterials have played increased role in the development of nanomedicine because of their unique abilities and properties which assist in improved pharmacokinetics and biodistribution compared to the free drug. However, only liposomal and polymeric based nanocarriers found their usage in the clinic. In this presentation, I will discuss about polymeric nano-formulations derived from FDA approved poly(lactic co-glycolic) acid (PLGA), and polyethylene glycol (PEG) functionalized with a terminal triphenylphosphonium (TPP) cation for delivering various antiretrovirals and neuroprotectants to the brain.
POLY 271: Development of a novel 3D printed, drug-eluting, biodegradable ring for treatment of eosinophilic esophagitis

Alka Prasher¹, alkap@email.unc.edu, Roopali Shrivastava¹, Denali Dahl¹, Preetika Sharma², Soumya R. Benhabbour¹,². (1) Joint Department of Biomedical Engineering, UNC Chapel Hill & NC State University, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States (2) Division of Pharmcoengineering and Molecular Pharmaceutics, Eshelman School of Pharmacy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States

Background: Eosinophilic esophagitis (EoE) is an emerging chronic allergic disease characterized by eosinophilic infiltration of the esophageal mucosa. The most common symptoms of EoE include heartburn, feeding intolerance, dysphagia, and food impaction. EoE represents a major healthcare burden as the estimated prevalence is at least 1 in 2000 Americans, and EoE associated healthcare costs are about $1.4 billion per year. Because there are no FDA approved treatments for EoE, patients are prescribed asthma preparations such as fluticasone in an inhaler. This rudimentary approach leads to poor outcomes and low compliance. To address these limitations, we report the development of an esophageal-specific drug delivery platform, a drug-eluting 3D printed biodegradable ring, for a local and sustained release of fluticasone in the esophagus.

Methods: In this work, we have designed and fabricated biocompatible and biodegradable fluticasone loaded rings using a top-down, Digital Light Processing (DLP) Gizmo 3D printer (Figure 1). 3D printed rings were fabricated by dissolving fluticasone into polycaprolactone-dimethacrylate (PCL-DMA) resin formulations at 1.4% w/w (fluticasone:resin) at a target dose of 1-2mg/day

Results: In vitro drug release studies of fluticasone loaded rings showed that fluticasone elutes at zero order release kinetics, and the addition of diluent to PCL-DMA slowed down the drug release (50% in 18 weeks) compared to the higher crosslinked 100% PCL-DMA (50% in 9 weeks). In vivo pharmacokinetic studies of fluticasone-loaded rings were carried out in a pig model. A new LC-MS/MS method was successfully developed to quantify fluticasone in pig plasma (LLOQ 10 pg/mL) and esophageal tissue (LLOQ 100 pg/g).

Conclusions: We have developed an innovative technology for EoE, which is in need of new treatment options and drug delivery systems. This foundational work can serve as a platform for the treatment of other esophageal diseases including esophageal cancer.

Figure 1 Prototyping steps for EoE ring fabrication using top down 3D printing technology. A) CAD file, B) 3D printing, C) 3D printed EoE ring
POLY 272: High-capacity matrix excipients for controlled drug release: surpassing the state-of-the-art

Victor R de la Rosa¹, victor.retamerodelarosa@ugent.be, Aseel Samaro², Valerie Van Hoorne², Ali Tigrine¹, Martin Purino³, Maarten Vergaelen¹, Bryn Monnery¹, Chris Vervaet², Richard Hoogenboom³. (1) Organic and Macromolecular Chemistry, Ghent University, Gent East Flanders, Belgium (2) Laboratory of Pharmaceutical Technology, Ghent University, Ghent, Belgium (3) Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

Sustained release drug products offer many advantages in comparison to conventional immediate release formulations by maintaining the desired drug plasma concentration within the therapeutic range over a longer time period. This results in improved effectiveness, less side-effects, greater compliance and lower costs.

The development of sustained release matrix formulations is especially challenging for highly dosed and highly soluble active pharmaceutical ingredients (APIs) as the drug release is often too fast and/or shows a burst release. Several polymers are currently used for formulation of sustained release tablets. However, no commercially available polymers can ensure sustained drug release of highly soluble APIs with a drug load higher than 40% (w/w).

In contrast to the currently available matrix formers, poly(2-oxazoline)s can sustain the release of slightly to freely soluble APIs with a drug load up to 70% (w/w). This is illustrated in the shown figure, comparing the dissolution profile of formulations consisting of metoprolol tartrate (MPT), a freely soluble API, and suitable commercial polymers with that of poly(2-sec-butyl-2-oxazoline) (PsecBuOx), a newly developed amphiphilic polymer for formulation.

All formulations were processed on the same injection molding equipment. Compared to the formulation based on PsecBuOx, the drug release rate from the other formulations was similar or faster. However, it should be noted that the poly(2-oxazoline) based formulation included more than twice the drug load (i.e. 70% w/w MPT vs. 30% w/w MPT). These examples highlight the unique release sustaining capacity of poly(2-oxazoline)s for highly dosed, highly soluble APIs in comparison to polymers that are among the best currently available release sustaining polymers.

In the present contribution, the synthesis of several high molar mass (> 50 kDa) amphiphilic poly(2-oxazoline)s will be shown, followed by the dissolution kinetics of different APIs in formulations prepared via different routes, from direct compression to hot melt extrusion and injection molding. The ability to stir the dissolution profile by modulating the polymer hydrophilicity will also be displayed.
Flavopiridol is a small molecule drug that has been tested for the treatment of acute myeloid leukemia, atheroma, arthritis, and inflammation. Flavopiridol is most often delivered in its soluble form, or more recently encapsulated in poly(lactic-co-glycolic acid) (PLGA) microparticles produced via emulsion. Standard emulsion method produces polydispersed microparticles with a wide size range, leading to difficulties in fine tuning the release kinetics and maintaining reproducibility. Existing emulsion methods also required the use of toxic solvents, such as dichloromethane (DCM), that are biologically incompatible and environmentally undesirable. In this presentation, a new synthetic approach based on microfluidics is used to produce flavopiridol loaded PLGA microparticles. In this system, the biocompatible solvent dimethyl carbonate (DMC) replaces DCM. PLGA microparticles with predefined diameter and flavopiridol load were produced, and the physical properties and drug release kinetics were determined in vitro, showing similar release profiles as conventional methods. The results demonstrate uniformity within, < 3%. The particle morphology and intraparticular structure have been characterized using time-dependent SEM to allow size and structure measurements as well as degradation monitoring. The drug release kinetics was measured and compared similarly with the conventional method of production of PLGA microspheres. The advantages of using green solvent as well as in vivo applications will also be discussed in this presentation.

SEM images of flavopiridol loaded PLGA microparticles during in vitro release to reveal the structural and morphological evolution.
A. (t = 0 hours), B. (t = 65 hours), C. (t = 108 hours)
Scale bar = 10.0 μm
3D printing has enabled bench-top fabrication of customized bioengineered constructs with intricate architectures. Various approaches are being explored to enable optimum integration of such constructs into the physiological environment including addition of bioactive fillers. Previously, we established a library of multifunctional polyesters with “peptide-like” pendant functional groups. Based on this platform, we synthesized a low modulus polyester (SC5050) for extrusion-based 3D printing at room temperature without the presence of solvents, initiators, and monomers. In this work, we incorporated a corticosteroid drug, dexamethasone (Dex), in the SC5050 polyester and examined the effect of Dex incorporation on 3D printing, rheology, drug release, and degradation of the polymer. Dex-SC5050 interactions were characterized by plotting thermodynamic binary phase diagrams based on the Flory-Huggins theory. The effect of Dex composition on the 3D printability of the SC5050 polyester was examined by rheological characterization and by image analysis of each layer of the 3D printed scaffolds. The drug release and the degradation of the polymer from the 3D printed scaffolds was used to analyze the effect of Dex composition on the performance of the 3D printed scaffolds. We found that Dex was insoluble in SC5050 polyester at relevant 3D printing temperatures and the insoluble drug particles physically reinforced the polymer, increased the viscosity and the shear modulus of the base polymer. In addition, the reinforcing effect improved the shape fidelity of the printed filaments and the overall quality of the 3D printed scaffolds. Furthermore, the Dex particles demonstrated a two-phase release, with an initial burst release and a slower sustained release of drug under in-vitro conditions.
POLY 275: Active loading and triggered release of charged molecules with porous nanocapsules

Weiyu Zhang, weiyu.zhang@uconn.edu, Sergey Shmakov. Chemistry, UCONN, Storrs, Connecticut, United States

Loading drugs into delivery vehicles, or containers, is a critical step that determines the ability to preserve expensive materials, prevent premature release, and employ drugs with low stability. One can differentiate active loading, or loading against concentration gradient, vs. passive diffusion of cargo molecules into the containers. In this work, we achieved active loading of organic molecules into porous nanocapsules by using electrostatic attraction between oppositely charged molecules. For example, by using entrapped positively charged polyelectrolyte, we were able to take in 99% of negatively charged molecules from the solution. Changing the charge on the polyelectrolyte reversed the interactions with cargo molecules and served as a trigger for release. By adjusting the pH of the environment, PAMAM dendrimers entrapped in the nanocapsules get protonated or deprotonated, which makes it possible to catch the target molecules through the pores of capsules or release them when interaction disappears at a different pH. Compared to passive loading, pH-mediated active loading achieves high intracapsule concentration and cause minimal waste of cargo molecules.
Macromolecular prodrugs have the potential to increase the therapeutic window of small molecule drugs, but their limited synthetic modularity and scalability have hindered widespread clinical translation. We have developed an efficient, convergent synthesis of highly branched macromolecular prodrugs that enables the rapid incorporation of a wide range of therapeutic agents including small molecule and biologic drugs. The modularity of our approach allows for precise tuning of unmodified drug release mechanism and rate, which directly translates to improved therapeutic windows in vivo. In addition, this system is readily scalable, generating macromolecular prodrugs with identical characteristics from the 10 mg to the 1 kg scale. This talk will introduce our approach to macromolecular prodrug synthesis, and will discuss preclinical scaling, safety, and efficacy studies in the context of liver fibrosis and cancer. Lastly, efforts to merge nitroxide-based magnetic resonance imaging with controlled release of therapeutics for image-guided drug delivery will be presented.
Commercial polysaccharide-based materials represent a multi-billion-dollar industry, but these sustainable feedstocks could be used more broadly if they exhibited a more diverse set of properties. Based primarily on cellulose, its derivatives, and other forms of poly(α/β-glucose) such as starch, polysaccharide materials are strong and have good oxygen barrier properties, but they are generally difficult to process, brittle, have low tear strength, and lack toughness. Such polymer property deficits can be addressed through polymer blending, combining polymers that each have drawbacks to obtain materials with properties unattainable from either polymer alone. Here the synthesis of novel polysaccharide block copolymers will be discussed, as will their use as compatibilizers to enable blending of polysaccharides with other commercial polymers. Novel synthetic methods for cellulose functionalization combined with modern polymer chemistry enable the synthesis of these well-defined copolymers.
Surface-initiated polymerization (SIP) techniques are powerful tools for the preparation of thin, surface tethered polymer films. Surface grafted polymer films produced via SIP are often colloquially referred to as polymer brushes. SIPs are characterized by a number of unique features, which include the ability to (i) prepare polymer brushes with precise control over chemical composition and film thickness; (ii) generate polymer films that present very high surface concentrations of functional groups; (iii) conformally coat both simple, planar substrates as well as complex, 3D structured or porous substrates and (iv) tune the conformation of the surface grafted polymer chains by engineering the average distance between neighboring anchoring points. This presentation will highlight recent work from our laboratory that illustrates the use of SIP to generate thin polymer films with sensory or responsive properties as well as results from recent work, which shows that the stretched conformation of these surface grafted polymer chains also has an impact of their chemical reactivity, potentially opening avenues towards novel mechanically responsive surfaces.
Polymeric materials and their assemblies have made a tremendous impact on a multitude of biomedical applications. For example, nucleic acid delivery vehicles have promise to promote selective genome editing/gene therapies. Also, the development of polymer excipients can improve the solubility and bioavailability of small molecule drugs. To accommodate such diverse function, the chemistry and engineering parameters should be readily tunable for activity in each specific application while remaining biologically benign. Indeed, the properties of polymers containing functional monomers can be tuned based on chemistry, sequence, composition, and molecular weight to yield diverse function and properties while remaining biologically benign. Here, the synthetic design and characterization of tailored block and statistical polymers that contain hydrophilic, cationic, and hydrophobic domains will be presented that serve as attractive shape and size-regulated vehicles for the delivery of drugs, DNA, RNA, and Cas9 protein. Specific arrangement and length of the blocks offer tuning of self-assembled morphologies such as micelles and core-shell complexes that control the solution and biological properties and efficacy. Complexation of these structures with biomolecules in a hierarchical manner has been studied in detail and their application in the improvement of pharmaceutical bioavailability and as novel vehicles for genome editing applications will be presented.
Efficient and orthogonal click chemistry is developed which allows for the coupling of functional copolymers to give well-defined block copolymers with controlled architectures at high molecular weights.
The role of branching in non-linear polyolefins is critical in the tailoring of solution and bulk properties such as those found in a new generation of thermoplastic elastomers based on polyethylene copolymers. With responsibility for mass reference materials, NIST sees a clear need for more advanced polymer structures beyond the traditional linear chains for the characterization of branch distributions, both in length of the branches and their distribution along the chain. To meet this demand, we are preparing near perfect short chain branched polymers and characterizing their intrinsic viscosity among other fundamental properties for potential use as standard reference materials, as well as to understand the very role that these branches play in tailoring other properties such as crystallization and phase separation. Coupled with a new modeling tool, ZENO, we are also learning more about the solvation effects of branching.
This talk discusses the viscoelastic behavior of oligomeric sulfonated polystyrene (SPS) ionomers using the framework of the Reversible Gelation (RG) model (Chen, Q.; Huang, C.; Weiss, R. A.; Colby R. H., Macromolecules 2015, 48, 1221−1230). Percolation theory predicts that a gel point for an ionomer occurs when $p = p_c = 1/(N-1)$, where $p$ is the mole fraction of the for a precursor chain having $N$ monomers. That concentration corresponds to an average of one ionic species per chain. Below $p_c$, no percolated network is formed. The application of the RG model to the viscoelastic behavior of ionomer melts predicts the plateau behavior and that the delayed relaxation behavior is governed by the association lifetime $\tau_s$. For $p$ close to $p_c$, the effective breakup ideas of Rubinstein and Semenov appear to control the terminal relaxation and the model is consistent with the experimental result that $\tau_s$ increases with increasing Coulomb energy of the ion-pair. The RG model also predicts the experimental observation of strain hardening and shear thickening of the ionomers near the gel point (note that studies of most ionomers are normally conducted far above the gel point, so these properties are not usually observed) and the substantial increase of the melt viscosity between 90% and 100% neutralization (which explains an unresolved 35 year old experimental observation). In addition, with the aid of a linear mixing rule for the ionic dissociation frequency of a blend of two SPS ionomers, the RG model predicts the terminal relaxation time of the mixture.

Master curves of storage and loss moduli at $T_r \approx T_g + 45^\circ C$ for randomly sulfonated polystyrene ($M = 4000$ Da) with $p = 0.065$. The solid lines represent terminal behavior: $G' \propto \omega^2$ and $G'' \propto \omega$. The red lines indicate $\nu kT$. 
As a celebration of the naming of Matthew L. Becker as the recipient of the 2019 Carl S. Marvel Award for Creative Polymer Chemistry, this presentation will detail several innovative research advances that Matt has led from his time as a Ph.D. student through his exceptional rise as an internationally-leading polymer chemist and materials scientist. Matt has made significant contributions to a great breadth of important polymer advances, with an overall general theme of developing novel chemical and engineering methods by which to functionalize polymer materials with biologically-active ligands and then also devising biological assays by which to confirm biological outcomes (cell adhesion, cell migration, tissue growth, bone repair etc.). Key examples will highlight his strategies to incorporate bio-functional components within polymer materials, and how his work has inspired projects in my laboratory involving the development of functional nanoparticle systems for biomedical applications. An emphasis will be placed on recent accomplishments toward the transformation of glucose and other carbohydrates into nanomedical devices for the treatment of osteosarcoma lung metastases and recurrent urinary tract infections.
POLY 284: New resorbable materials and inks are needed if additive manufacturing will really change medicine

Matthew Becker, becker@uakron.edu. University of Akron, Akron, Ohio, United States

The evolution of resorbable materials is not keeping pace with the technology advances in additive manufacturing. Efficient, reproducible, and precise methodologies for fabricating patient specific scaffolds using three-dimensional (3D) printing techniques are evolving rapidly. Fusion deposition modelling (FDM), and photochemical printing have each been used widely for a number of applications. However, each has significant limitations, including translationally relevant materials that can be used with each printing system. Necessarily, new and promising materials must surface as alternatives to previously studied polyesters. We are developing two material platforms, amino acid-based poly(ester urea)s and functional poly(propylene fumarate), which can be printed using FDM and photo crosslinking methods, respectively. This presentation will describe the use of several translationally relevant chemistries and post-printing functionalization strategies that are impacting the practice of medicine and how physicians are planning for future therapies that were not possible previously.
POLY 285: Grafting through method for implanting of lysozyme enzyme in molecular brush for improved biocatalytic activity and thermal stability

**Xue Wang**, xue.wang25@uga.edu, Nataraja S. Yadavalli, Amine M. Laradji, Sergiy Minko. The University of Georgia, Bishop, Georgia, United States

We report a "grafting through" conjugation strategy to improve lysozyme catalytic activity and thermal stability by the synthesis of a synthetic polymer–enzyme hybrid. The lysozyme was first conjugated with glycidyl methacrylate via ring-opening reaction between epoxy groups and lysine residues of the enzyme to synthesize the enzyme macromonomer. The conjugation was followed by free radical copolymerization of the macromonomer with poly(ethylene glycol) methyl ether acrylate (PEGMEA) ($M_n = 5000$ g/mol) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) ($M_n = 500$ g/mol). We demonstrated that implanting of a single lysozyme molecule in the molecular brush polymer chain resulted a significant improvement of the thermal stability up to 90 °C and 9-time extended half-life for this synthetic enzyme structure. The improved enzyme performance is explained by the crowding effect provided by molecular brush architecture of the synthetic hybrid.
Using orthogonal grafting-from strategies to access well-defined 2-polymer, 1-protein bioconjugates

Kevin Burridge², burridkm@miamioh.edu, Madison M. Kearns², Thaisesha Wright¹, Dominik Konkolewicz², Richard C. Page². (1) Chemistry and Biochemistry, Miami University, Cincinnati, Ohio, United States (2) Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

Using a mutant of ubiquitin with a C-terminal cysteine residue and a poly-histidine tag with TEV recognition sequence, novel ABC triblock copolymers were constructed with protein as the “B” block. The N-terminus and lysine residues were modified by the activated ester of an ATRP initiator (EBIB). Then, grafting-from was performed using photo-ICAR-ATRP, with 50ppm copper catalyst and 1% photoinitiator loading, and monomer at 2wt%, under blue light. Then, the cysteine at the C-terminus was targeted by Thiol-Michael reaction of the -SH group with a maleimide-functionalized chain transfer agent (PAETC). Grafting-from was performed using photo-RAFT, with 5wt% monomer and 0.66% photoinitiator at low (1mg/ml) protein concentration. Sequence analysis confirms selective targeting of the N-terminus. Circular dichroism was performed to assess protein stabilization afforded by these modifications. Proteins with two, unique, directly and covalently attached polymers present another step towards multifunctional bioconjugates.
POLY 287: Molecular sieving on the surface of nano-armored protein

Bibifatima Kaupbayeva¹, bkaupbay@andrew.cmu.edu, Hironobu Murata², Amber Lucas¹, Krzysztof Matyjaszewski³, Jonathan S. Minden¹, Alan J. Russell⁴. (1) Department of Biological Sciences, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Center for Polymer-Based Protein Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (3) Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (4) Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Many advances in medicine, nanotechnology and biotechnology can be linked to the development of robust methods for producing well-defined protein-polymer conjugates. There are currently fourteen FDA approved PEGylated proteins, contributing to a market that exceeds $15 billion annually. Therapeutic protein lifetimes in vivo are extended by a molecular sieving effect created by surface attached polymers. Yet, even after thirty years of research, permeation rates of molecules through polymer-surrounded protein surfaces have been largely unexplored. Until now, there have not been ways to detect the permeation rates of biomacromolecules through polymer layers to the protein surface. Herein we describe an approach that quantifies the rate of binding of molecules through a layer of polymer chains to the binding site of avidin protein.

We have grown polymers from the surface of avidin using atom transfer radical polymerization (ATRP) and determine how polymer length and grafting density influence the binding kinetics of ligands of different shapes and sizes. Moreover, we show that protein shielding with polymers can be greatly improved when using appropriately designed ATRP initiators. We created a unique double-headed initiator capable of supporting the growth of two polymer chains from one initiation point and allowing synthesis of conjugates with high polymer grafting densities.

We conclude that the rate of ligand binding is strongly dependent on the density of polymer grafting and the size of the substrate, but, interestingly, far less dependent on the length of the polymer. This study unveils a deeper understanding of the relationship between polymer characteristics and binding kinetics, discovering important steps in rational design of protein-polymer-conjugates.
Genetic code expansion uses synthetic biology concepts to expand translation allowing for site-specific incorporation of non-canonical amino acids into proteins. The addition of a wide array of chemical functionalities into proteins provides unprecedented molecular control over proteins and therefore advances the capabilities of chemical biology and biomaterials. Here the advances in genetic code expansion will be discussed focusing on our development of orthogonal chemistries for to efficiently engineer proteins into biomaterials.
POLY 289: Oxygen tolerant polymerisation for the design of biomaterials

Robert Chapman, r.chapman@unsw.edu.au. School of Chemistry, UNSW Sydney, Kensington, New South Wales, Australia

While controlled radical polymerisation (CRP) techniques have enabled the preparation of complex and well-defined macromolecules, the need to remove oxygen in these reactions limits minimum reaction volumes, concentrations, and reaction setup, and makes the synthesis of large polymer libraries extremely laborious.

To circumvent these problems we have recently developed several methods for conducting controlled radical polymerisations in the presence of oxygen,[1] through the use of an enzyme,[1-3] photo-dye,[4] or photo-catalyst,[5-6] (Fig. 1). With such systems, CRPs can be conducted in low volume in microtiter plates (<40 µL), without any degassing, across a range of monomer families and molecular weights. Block extensions can be performed in a single well without any purification by simple addition of the subsequent monomer, and complex star polymers can be prepared either via polymerisation from multi-arm RAFT agents or via an arm first approach. In the case of our ZnTPP system, conversion can even be monitored spectroscopically during polymerisation.[6] We have been applying these techniques to enable the use of polymerisation as an amplification mechanism in biosensing,[7] and in the design of biomaterials through high throughput synthesis and screening of structure-activity relationships.[6]

Figure 1. Oxygen tolerant controlled radical polymerisation mechanisms based on a) enzyme degassing, b) Eosin-Y and c) ZnTPP and d) their use in structure-activity relationship screening
Silk fibroin is nowadays often used in optical devices and in pharmaceutical science. Along with its remarkable optical properties, the natural material also offers various possibilities to chemically modify its structure. To stabilize silk fibroin, e.g. in thin films or at an interface with organic materials, a hetero-bifunctional linker is needed. We herein report the synthesis of a benzophenone-based linker, which bonds to tyrosine residues in silk fibroin. It crosslinks the protein and binds it to other materials by using the principle of C,H-insertion chemistry (Figure A-C). The resulting protein-based materials are explored as optical materials and as bio-inspired surface coatings.
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 292: Polypept(o)ide-based cylindrical polymerbrushes as multifunctional nanocarriers

Christine Seidl¹,², seidlchristine@hotmail.com, Meike Schinnerer²,³, Matthias Barz¹,². (1) Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany (2) Collaborative Research Center 1066, Mainz, Germany (3) BioNTech AG, Mainz, Germany

Driven by the use of nanoparticles as carrier systems for antigens, costimulants and targeting structures the focus of cancer immunotherapy has nowadays shifted towards the activation of the endogenous immune system. It has been shown that nanocarrier uptake and activation efficiency of the immune system tremendously depend on the morphology and surface modification of the nanocarrier, besides the already known differences between various bioactive compounds. To fully exploit the potential of tailored nanocarrier structures, it is crucial to understand these systems and their structure-property relationships. By fabricating rod-like nanoparticles with well-defined aspect ratios and morphologies in combination with different biological components, correlations to uptake and activation could be obtained.

Here, we report a study on the effect of aspect ratios of the nanocarrier and number of biological components on cell uptake and activation of dendritic cells (DC). The nanocarrier is composed of azido-modified graft copolymers polylysine-g-polysarcosine (pLys-g-pSar), where Ovalbumin as model antigen, aDEC205 as antibody and CpG as adjuvant are conjugated on the surface. The high blood circulation time (BCT) of these peptobrushes mainly result from the rod-like morphology and the shielding surface of the nanocarrier. Zebrafish embryos and mouse models were used to investigate the BCT of these nanocarriers. Detailed information on morphology were obtained by atomic force microscopy (AFM) and dynamic light scattering (DLS). Distribution of cell uptake was primarily driven by number of antibodies, which was evaluated by various in vitro experiments. By varying the aspect ratios and the number of antibodies the best options of morphology and biological modification for these system combinations could be identified and characterized.

Our study demonstrates that the detailed information on structure related properties and on amount of antibody per nanocarrier are the critical parameters for long BCT and desired cell uptake, both crucial for designing multifunctional drug delivery platforms.

Synthetic strategy towards a versatile nanocarrier platform. Starting from a polylysine backbone a cylindrical polymerbrush (PB) is synthesized. Bioconjugation is achieved by an alkyne-azide click reaction.
The modification of enzymes with polymers holds tremendous promise as an approach to tune the molecular interactions of enzymes in diverse solvent environments. Here, we demonstrate the use of polymer modification to specifically modulate the thermoresponsive interactions of enzymes with non-native solvents. To demonstrate this approach, Bacillus subtilis lipase A (LipA) was modified with random copolymers of poly(acryloylmorpholine-ran-N-isopropyl acrylamide) (PAN). Modification of LipA with PAN permitted the reversible phase separation of LipA-PAN from 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) in a temperature dependent manner. By varying the compositions of the copolymer, the temperature dependence of this phase separation could be quantitatively controlled between 16-76 °C. Above the temperature of the phase transition, the enzyme was soluble in the ionic liquid (IL), resulting in enhanced transesterification activity (i.e., a 21-fold increase over unmodified LipA), whereas below the temperature of the phase transition, the enzyme could be readily separated and recycled. Remarkably, when recycled via sequential dissolution and precipitation as many as 10 times, the enzyme did not lose any activity. Using this approach, we also showed that the enzyme could be extracted into buffer as well as reversibly shuttled between buffer and the IL in response to changes in temperature. This approach ultimately permits the advantages of homogeneous and heterogeneous biocatalysis in non-native solvents to be exploited and may be readily extended to other enzymes, solvents, and external stimuli. Such an approach may further find application in other fields, including bioseparations, self-assembly, and drug delivery.
POLY 294: Enhancing CO₂/N₂ selectivity of addition-type polynorbornenes

Brian K. Long¹, long@utk.edu, Christopher Maroon¹, Jacob Townsend¹, Kevin R. Gmernicki¹, Daniel J. Harrigan², Benjamin J. Sundell², John A. Lawrence², Shannon M. Mahurin³, Konstantinos D. Vogiatzis⁴. (1) Dept of Chemistry, University of Tennessee, Knoxville, Tennessee, United States (2) Boston Research Center, Aramco, Somerville, Massachusetts, United States (3) MS 6201, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (4) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

Gas separation membranes as targeted for a variety of applications including the separation of light-hydrocarbons, natural gas purification, and the separation of harmful greenhouse gases such as carbon dioxide (CO₂). In this presentation, we will describe how the CO₂/N₂ gas separation performance of alkoxyxilysubstituted vinyl-added polynorbornenes (VAPNBs) can be enhanced through monomer design. More specifically, we will show that homopolymers and copolymers containing the monomeric unit, 5-tris(2-methoxyethoxy)silyl-2-norbornene, can be readily synthesized and cast into dense polymer membranes. We will demonstrate that as the molar ratio of 5-tris(2-methoxyethoxy)silyl-2-norbornene to 5-triethoxysilyl-2-norbornene units is increased, CO₂/N₂ selectivity increases substantially with minimal decreases in CO₂ permeability. This trend in gas separation performance essentially ignores the traditional permeability/selectivity "tradeoff", and yields membranes whose performance reaches the 2008 Upper Bound for CO₂/N₂ separations. Though it was initially hypothesized that the incorporation of these 5-tris(2-methoxyethoxy)silyl-2-norbornene units would maximize CO₂ solubility, pure gas sorption studies have shown that substantial decreases in N₂ solubility are responsible for the improved CO₂/N₂ selectivity. This is supported by fractional free volume estimations, wide-angle x-ray diffraction, computational modelling, and in-depth mixed-gas permeation tests.
POLY 295: Tailored CO₂-philic polymers for high flux CO₂ separation

Tao Hong², Peng-Fei Cao¹, Bingrui Li², Sheng Zhao², Alexei P. Sokolov¹,², Tomonori Saito¹, saitot@ornl.gov. (1) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

Most of the world’s energy is presently derived from the burning of fossil fuels, which releases vast quantities of carbon dioxide (CO₂) into the environment and results in undesirable climate change. Practical and cost-efficient methods of CO₂ separation and capture would thus solve one of the most challenging problems today. This presentation summarizes our effort on the development of novel polymer membranes functionalized with CO₂-philic groups for high flux CO₂ separation. Our strategy focuses on tuning solubility selectivity in polymers with high diffusivity for achieving high permeability membranes combined with good selectivity. Various synthetic techniques including ROMP, thiol-ene click reaction, and post functionalization were used and the careful design permits to prepare well-defined novel highly permeable polymers containing CO₂-philic groups. This study demonstrated the addition of CO₂-philic groups significantly increased the solubility selectivity of CO₂ over N₂. The membrane performance is also highly dependent on the balance of gas/functional group interaction, packing, and polymer dynamics. Tuning the balance of the interaction and dynamics by controlled degree of crosslinking and functionality especially utilizing thiol-ene chemistry, enables to achieve the CO₂ separation performance over the Robeson upper bound, e.g. CO₂ permeability 6800 Barrer and CO₂/N₂ selectivity 19, or CO₂ permeability 930 Barrer and CO₂/N₂ selectivity 38. The structure-property relationships for CO₂ uptake, CO₂ and N₂ permeability, and CO₂/N₂ selectivity will be discussed.
Glassy polymers are often utilized for the separation of mixtures of gases because of their high selectivity. The sorption behavior of gases in glassy polymers is commonly described mathematically with the dual-mode sorption model, however the physical interpretation of the dual-mode sorption model remains disputed. Furthermore, the dual-mode model uses membrane properties measured at steady state, and so its utility for describing permeation under non-steady state conditions is unknown. This work reports a combined experimental-theory-multiscale modeling investigation of the transport of two gases, CO₂ and N₂, through the glassy polymer poly(dimethyl phenylene oxide) (PPO) to better understand the relationship of glassy polymer structure and dynamics with gas transport for both steady and non-steady state conditions. The non-steady-state permeation behavior is investigated by measuring a transient pressure rise downstream as gas is transported through the polymer membrane. A multiscale model, consisting of physically-based coupled reaction-diffusion kinetics, is developed and incorporates system properties at multiple length and time scales. We find that the multiscale model can reproduce time-dependent experimental data at steady and non-steady state equally well using either a single reaction-diffusion transport mode, or an implementation of the dual-mode model. A key element of the model is a proper description of the gas concentration increase within the membrane as the external gas pressure rises, which is not instantaneous for this polymer. Because the multiscale model is physically based, it is predictive and so is used to explore the plasticization behavior of PPO during permeation by CO₂.
In recent years superglassy polymers exhibiting intrinsic microporosity established a new perspective for a number of applications, especially for gas separation membranes as these polymers combine extremely high permeabilities with attractive selectivities. The essential factor governing the structure formation in the solid film or layer is either a contorted rigid backbone (polymers of intrinsic microporosity - PIMs) or extremely bulky side groups (polynorbornenes and polytricyclononenes).

For a deeper understanding of both types of such high-performance polymers for gas separation membranes and their further development broadband dielectric spectroscopy (BDS) can provide a substantial contribution. BDS addresses molecular relaxations characterizing the dynamics of the solid polymer as a major factor determining the gas transport properties but also the physical aging behavior which is an essential issue for such polymers.

BDS is applied on PIMs where fluctuations of molecular dipoles connected to the backbone can be directly monitored. Furthermore, also polynorbornenes were investigated which carry no dipole moment in their repeat unit - the high resolution of modern equipment allows for the detailed analysis also for very small dielectric losses originating from partially oxidized moieties or marginal catalyst residues.

Additionally, from interfacial polarization phenomena, such as Maxwell-Wagner-Sillars (MWS) polarization due to blocking of charge carriers at internal interfacial boundaries on a mesoscopic length scale, valuable information on the intrinsic microporosity and its changes induced by physical aging can be obtained.

Finally, also conductivity can be characterized in detail in such polymeric systems revealing contributions of interactions of aromatic moieties (π-π-stacking) or the drift motion of charge carriers. These features also determine the structure formation in the solid state.

Figure 1. 3D-representation of dielectric loss vs. temperature and frequency.
POLY 298: Toward role of two-dimensional nanomaterials for polymeric membrane materials

Ho Bum Park, badtzhb@hanyang.ac.kr. Department of Energy Engineering, Hanyang University, Seoul, Korea (the Republic of)

Nanomaterials have tremendous potential in a wide variety of membrane applications. Within the vast range of nanomaterials, there are many cases of dense and porous membranes with exceptional strength and tailored surface properties, which can be extremely light or thin. Particularly, two-dimensional nanomaterials of atomic thickness have emerged as high-performance separation membranes with high permeability and selectivity. Currently, graphene-based membrane materials (e.g., nanoporous graphene, graphene oxide (GO), and graphene- or GO-embedded polymers) hold great promise for membrane-based gas separations. For the last decade, significant advances have been made on the development of graphene-based membranes for gas separation via both a large number of theoretical studies and some proof-of-concept experiments. Theoretically, graphene-based membranes can afford remarkably high gas permeance and selectivity with notable mass-transport properties that may be not possible with state-of-the-art commercial polymeric, inorganic, and ceramic membranes. Prompted by these theoretical calculations, as well as the unique physical-chemical properties of graphene, many experimental approaches have been extensively explored to make these membranes a reality for practical processes. In this paper, the latest achievements on both theoretical and experimental studies of graphene-based membranes, as well as other two-dimensional materials are discussed in relation to gas separation and water purification applications.
Membrane technology has emerged as a potentially economically viable alternative for CO₂ captures from fossil fuel-fired powers, enabled by advanced membrane materials with high CO₂ permeability and high CO₂/N₂ selectivity. Current leading membrane materials usually contain poly(ethylene oxide) (PEO) because the ether oxygen in PEO interacts favorably with CO₂, resulting in high CO₂/N₂ selectivity. Herein we prepare a series of highly branched amorphous polymers containing poly(1,3-dioxolane), which has an O:C ratio of 0.67, higher than 0.5 in PEO. The length of the poly(1,3-dioxolane)-based branches are tuned to yield amorphous nature, and mobile ethoxyl chain end groups are introduced to provide high free volume and gas diffusivity. These ether oxygen-rich polymers exhibit more superior CO₂/N₂ separation properties than the PEO-based materials at practical conditions for flue gas processing, and above the Robeson’s upper bound. This work demonstrates that harnessing the interactions between polymers and CO₂ may provide unprecedented opportunities in designing gas separation membranes with robust performance under practical conditions.
POLY 300: Photocurable polyethylene glycol containing thiol-ene membranes for efficient separation of CO2 from light gases

Sergei Nazarenko¹, sergei.nazarenko@usm.edu, Vivek Vasagar¹, Jacob M. Schekman¹, Majeda Khraisheh², Mariam A. AlMa’adeed², Mohamed K. Hassan³. (1) Polymer Science and Engineering, Univ of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Chemical Engineering, Qatar University, Doha, Qatar (3) Center for Advanced Materials, Qatar University, Doha, Qatar

Polyethylene glycol (PEG) based membranes have been studied and commercially employed for separation of CO2 from the light gases such as N2, CH4, and H2. In addition to its high critical temperature, CO2 can weakly interact with polar PEG moieties and these two factors result in far greater solubility and permeability of this 'acidic' gas as compared to other light gases. Thiol-ene based chemistry, because of its simplicity, versatility, low cost, and intrinsic resistance to oxygen enabled development of PEG containing, UV-curable gas separation membranes with exceptional combination of superior gas transport characteristics and mechanical properties, inherent resistance to oxygen, and tunable selectivity. This innovative technology displays a strong potential for a transformational change in the area of CO2 removal from light gases. Current presentation focuses on two fundamental aspects of CO2 separation with PEG containing thiol-ene network membranes, namely: (a) if there is the minimum amount of PEG which has to be incorporated to achieve the maximum CO2 gas solubility/selectivity effect (importantly, all prior studies employed maximum possible PEG content)? (b) if CO2 selectivity depends on the way PEG units are incorporated, i.e. directly built in into the network backbone or tethered as chain ends? To elucidate these questions several PEG containing thiol-ene network membrane designs have been proposed, implemented and studied.

CO2/N2 permeability selectivity versus PEG wt%. Colored symbols represent data obtained in this study for PEG containing thiol-ene networks Half-filled symbols are reported literature values for different PEG containing membranes
Effective separation of propylene/propane is necessary due to propylene is a feedstock for a variety of chemicals. The process that meets the purity requirement is cryogenic distillation, which is an energy-intensive process and consumes enormous cost and space. Thus, membrane/distillation hybrid process with high selective membranes has been suggested. Considerable research has been done in glassy polyimides for the membrane material, which has superior thermal, physical and chemical stability, but poor processability due to hard backbone structure. Various attempts have been made to overcome the deficiencies, including the introduction of flexible segments into the polymer backbone. In this study, we demonstrate highly selective membranes by introducing bulky ethyl substituents into the polyimide. The ethyl groups, which are placed ortho to the imide nitrogen, hinder the chain packing and increase chain stiffness and the distance between polymer chains. As the diffusion length increased, the diffusion selectivity of propylene/propane was increased. These polyimides were synthesized from various aromatic dianhydrides and 4,4’-methylenebis(2,6-diethylaniline) (MDEA), and its gas transport properties were investigated. The highest $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity was about 14.5 and $\text{C}_3\text{H}_6$ permeability about 7 Barrer of 6FDA-MDEA among the three synthesized polyimides. BTDA-MDEA and OPDA-MDEA showed $\text{C}_3\text{H}_6$ permeability about 1.8 and 2.2 respectively, and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity 11.9 and 9.1 at 35 °C. Synthesized polyimide membranes increase the feasibility of more economic propylene separation process than conventional polyimide materials.
POLY 302: Anti-plasticization of polyimide membrane for olefin/paraffin separation using 2D nanofillers

Junhyeok Lee, navigate@hanyang.ac.kr, Farhad Moghadam. Energy Engineering, Hanyang University, Seoul, Korea (the Republic of)

Light olefin gases are the main source of polymeric compounds, so they must be separated from other impurities such as paraffin counterparts to become high-quality feed materials. Membrane olefin/paraffin separation technology is one promising method, but several issues exist. Plasticization is one of the most serious issues of polymeric olefin/paraffin gas separation, as well as other condensable gas separation, deteriorating their selectivity throughout the operation. There are several solutions attempted to minimize it such as blending materials and crosslinking to inhibit polymer chain mobility, however, they generally require sacrifice of permeation performance or tractability. Zeolitic imidazolate framework (ZIF) is a representative membrane additive, so called nanofiller, to build mixed matrix membrane (MMM) due to its simple synthesis procedure and extremely high light olefin/paraffin gas selectivity owing to molecular sieving property. Here, we demonstrated two-dimensional nanofillers to increase interaction between gas permeants and fillers, while minimizing permeability reduction behavior (induced by planar morphology) using porous substrates. Zeolitic imidazolate framework (ZIF) particles were properly grown on porous graphene oxide (PGO) surfaces comprising 2D nanostructure, and incorporated into 6FDA-DAM polyimide matrix as nanofillers with several concentrations. As a result, the 2D-mixed matrix membrane (2D-MMM) performed higher selectivity under propylene/propane mixed gas condition compared to conventional MMM. This implies that these porous 2D nanocomposites can prevent plasticization more effectively than MMM with 0D nanofillers, as well as increasing separation performances.

An SEM image of ZIF/PGO composite nanofiller showing 2D morphology
POLY 303: Structural and optoelectronic landscape of semiconductor:ferroelectric blends

Aditi Khirbat\textsuperscript{1}, akhirbat3@gatech.edu, Ilaria Bargigia\textsuperscript{2}, Artem Levitski\textsuperscript{4}, Mark Losego\textsuperscript{1}, Carlos Silva\textsuperscript{2}, Gitti L. Frey\textsuperscript{4}, Lee J. Richter\textsuperscript{3}, Natalie Stingelin\textsuperscript{1}. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (3) NIST, Gaithersburg, Maryland, United States (4) Israel Inst of Technology, Technion City Haifa, Israel

The high dielectric constant and versatile ferroelectric properties of poly(vinylidene fluoride) (PVDF) and its copolymers, poly[[vinylidene fluoride-co-trifluoro ethylene] [P(VDF–TrFE)] and poly[[vinylidene fluoride–co–trifluoro ethylene–co–chlorotrifluoro ethylene]] [P(VDF–TrFE–CTFE)], are widely exploited in sensors, tissue engineering, energy storage, and beyond. However, their use in fields such as micro−/optoelectronics is limited due to their insulating properties. Contrarily, organic semiconductors, which are prevalent in electronic applications, are in many instances, limited in efficiency owing to their low dielectric constants. Blending of these low−k:high−k polymers by solution processing, has the potential to combine these rare set of functionalities (i.e. ferroelectricity and semiconductivity), provided that we can gain control of the microstructure and phase morphology of such blends and, hence, their resulting macroscopic characteristics. Here, work is presented on model systems based on the quintessential semiconducting polymer poly(3−hexylthiophene) (P3HT) and the high efficiency organic solar cell material poly[[5,6−difluoro−2,1,3−benzothiadiazol−4,7−diyl]−alt−(3,3''''−di(2−octyldodecyl)−2,2',5',2'',5'',2'''−quaterthiophen−5,5'''−diyl)] (PffBT4T−2OD), blended with PVDF/copolymers. We will discuss how the blend’s structural features including degree of crystallinity/vitrification, texture, domain size, intermixing vs. phase separation can be manipulated via the blend composition, molecular weight, as well as kinetic and thermodynamic processes. A correlation between structure, dielectrics and semiconducting features (including charge dynamics) is presented, that helps to deliver a detailed picture of the optoelectronic landscape of polymer semiconductors in such high−k surroundings. Furthermore, insights on the overall physico−chemical properties of such systems will be discussed for designing new material systems that satisfy not only existing needs but also open up new applications with the benefit of not having to design all requirements into one material.
POLY 304: Synthesis and strategic design of solution-processable diketopyrrolopyrrole copolymer semiconductors for enhanced performance in n-channel organic field effect transistors

Carolyn Buckley, carolynbuckley376@gmail.com, Elsa Reichmanis. Georgia Institute of Technology, Atlanta, Georgia, United States

The development of semiconducting conjugated polymers for organic thin film transistors (OTFTs) has been the focus of intense research efforts for their key role in plastic electronics, as well as a vision of solution processability leading to reduced costs in device fabrication relative to their inorganic counterparts. The pursuit of high-performance n-channel (electron transporting) polymer semiconductors vital to the development of robust and low-cost organic integrated circuits has faced significant challenges; mainly for poor ambient operational stability and OTFT device performance lagging far behind that of p-channel organic semiconductors (OSCs). A conjugated n-channel copolymer has been fabricated using an all-acceptor (AA) unipolar approach, poly(2-(2-decyltetradecyl)-6-(5-(5'-methyl-[2,2'-bithiaol]-5-yl)-3-(5-methylpyridin-2-yl)-5-(tricosan-11-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (PDBPyBTz). The pyridines flanking the diketopyrrolopyrrole moiety were strategically chosen to lower the energy levels and impart planarity to the monomer, both of which aid in achieving stable n-channel performance. We observed promising unipolar charge transport in OFET devices fabricated from these materials, and excellent solution processability for ease of fabrication. In incorporating PDBPyBTz into a bottom-gate-bottom-contact OFET, unipolar electron transport was observed with an average FET mobility of 1.07 (±0.018) cm²V⁻¹s⁻¹. In addition to developing a high-performance n-channel polymer, this study allowed for an investigation of structure-property relationships crucial to the design of such materials in high demand for sustainable technologies including organic photovoltaics and other solution-processed organic electronic devices.
POLY 305: Ester-functionalized, wide band-gap conducting polythiophene for organic field effect transistors

Ruwan Gunawardhana¹, kxg141730@utdallas.edu, Chandima Bulumulla¹, Prabhath L. Gamage², Michael C. Biewer³, Mihaela C. Stefan⁴. (1) The University of Texas at Dallas, Richardson, Texas, United States (2) Chemistry & Biochemistry, University of Texas at Dallas, Dallas, Texas, United States (3) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States (4) Dept Chem UT Dallas, Richardson, Texas, United States

Most organic polymers used for high performance organic field effect transistors (OFETs) exhibit a drop in charge carrier mobilities over time. A unique way to solve the air instability is by introducing ester functionality on to the thiophene backbone which lowers the HOMO level of the polymer. Herein, polymers based on ester functionalized bithiophene with 1,2-di(thiophen-2-yl)ethane for OFETs are reported. The synthesized polymers are characterized and its photophysical properties and electrochemical properties are studied. Thin film transistors (TFTs) are fabricated from the polymer with bottom-gate/bottom-contact (BGBC) architecture to evaluate OFETs parameters. The crystallinity of thin films is investigated by grazing incidence X-ray diffraction (GIXRD). The morphology of the thin films is investigated by the tapping mode atomic force microscopy (TMAFM) and transmission electron microscopy (TEM).
Conducting polymer based wearable electronics has seen a tremendous growth in the recent years. Conducting polymers such as poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is known to be a conductor of both ionic and electric current. This work deals with three different applications of printed conducting polymer on textiles. The first study, includes fabrication of a prototype fabric antenna through the replacement of the components of the commercial antenna; which includes a ground plane and a dielectric layer; with PEDOT:PSS printed fabric and uncoated fabric. The return loss of the fabric antenna was recorded to be ca. -50 dB which was at par with the signal obtained from copper antenna. The entire fabric assembly was shown to have a resonant frequency at 2.35 GHz which is the characteristic frequency for Bluetooth communications. Finally, it has also been demonstrated that the fabric antenna transmits signal to a copper antenna placed approximately 2 cm with an efficiency of 25%. In the second study, application of PEDOT:PSS wires was demonstrated by recording electrocardiogram (ECG) signal using screen printed PEDOT:PSS wires with Ag/AgCl electrodes resulting in a signal comparable to Ag/AgCl connected with copper wires. Electrocardiogram signal was then recorded with screen printed PEDOT:PSS electrodes in dry skin condition without the use of hydrogel or adhesive around the electrode. PEDOT:PSS wires were then combined with PEDOT:PSS electrodes and ECG signal was recorded at rest. A prototype shirt was also developed with PEDOT:PSS electrodes for measuring ECG signal under exercise. The signal was recorded in dry skin conditions which showed an increase in amplitude because of transpiration of water vapor from the skin. The third application comprises of a simple organic circuit comprising of PEDOT:PSS resistors and PEDOT:PSS wires printed on a nonwoven textile and has been shown to obey Kirchoff's Law. The applications of the prototypes could be extended beyond healthcare into military and gaming industry.
Lithium-ion battery electrolyte materials with minimal concentration polarization and efficient lithium-ion transport are required to enable devices with longer lifetimes and higher energy densities. Self-doped polymer electrolytes provide one strategy to achieve these objectives but suffer from lower ionic conductivity than their salt-doped counterparts; additionally, most self-doped polymers have minimal mechanical integrity. In this work, we designed a nanostructured block polymer electrolyte, which consisted of a homogenous block with high modulus (to promote mechanical robustness) and a heterogeneous block composed of self-doped and ion-conducting monomer segments. The ratio of the self-doped and ion-conducting monomer segments determined the effective self-doping ratios ([EO]:[Li]). The BPs were synthesized by sequential atom transfer radical polymerization (ATRP) and activators regenerated by electron transfer (ARGET) ATRP, which allowed the use of a low concentration of copper catalyst for more facile removal of the catalyst post-polymerization. Due to the chemistries of the BPs, all polymers were nanostructured regardless of self-doping ratio as determined by small-angle X-ray scattering. The overall conductivity was measured by alternating current impedance spectroscopy, and the lithium-ion conductivity was found by combining the overall conductivity with direct current polarization methods. These conductivities were related to the self-doping ratio of the electrolyte, and BPs with higher self-doping ratios had higher lithium-ion conductivities. Overall, this effort elucidated design parameters necessary to enhance self-doped lithium-ion battery electrolyte materials.
POLY 308: Combined computational and experimental study on the effects of side-chain architecture of polythiophene derivatives on structure and ionic conduction

Jonathan Onorato¹, Jonorato@uw.edu, Ban Dong², Christian Nowak³, Joseph Strzalka⁶, Fernando Escobedo⁵, Christine K. Luscombe¹, Paul F. Nealey⁴, Shrayesh Patel². (1) Materials Science and Engineering, University of Washington, Seattle, Washington, United States (2) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States (3) Smith School of Chemical and Biomedical Engineering, Cornell University, Ithaca, New York, United States (4) IME, Chicago, Illinois, United States (5) Olin Hall 377, Cornell University, Ithaca, New York, United States (6) X-ray Science Division, Argonne National Lab, Chicago, Illinois, United States

While mixed conduction polymer materials demonstrate a wide range of potential applications, understanding of the connection between morphology, structure and ion transport in these materials is quite limited. Herein we present a computationally driven study of two polythiophene derivatives with oligoethylene glycol side chains, investigating the effects of morphology and monomer structure on ionic conduction. Two repeat unit structures were synthesized, one with an oxygen atom directly conjugated to the polythiophene backbone (P3EGT), and one with a methylene spacer between the initial oxygen atom and the polythiophene backbone (P3MEGT). Using molecular dynamics (MD) simulations, we demonstrate that amorphous P3MEGT has a higher ionic conduction than P3EGT, whereas P3EGT has the higher crystalline conduction. The lower crystalline conduction in P3MEGT is due to ion caging, a feature not present in P3EGT. To investigate their structural evolution with Li⁺ introduction, the polymers were blended with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and studied using grazing incidence wide angle X-ray scattering. From this, it was determined that introduction of LiTFSI results in both a reduction in crystallinity and expansion of the side-chain stacking direction. Further, it is shown that LiTFSI is present in both the crystalline and amorphous regions at low loadings, though the crystalline region saturates at high loadings. The ionic conduction was measured using electrochemical impedance spectroscopy, determining that ionic conduction occurs predominantly in the amorphous domains for both polymers. Further, the measurements show that P3MEGT has a higher ionic conduction for all conditions, a result consistent with MD simulations. By using MD simulations to augment our experimental results we have deepened our understanding of the effect of monomer structure on ionic conductivity of conjugated polymers.
High theoretical specific energy density (2600Wh/kg) and high specific capacity (1675mA/g) along with natural abundance and low toxicity of sulfur have been attracting significant attention for development of an alternative battery system to replace traditional lithium ion batteries which suffer from safety and capacity/energy density limitations. However, challenges such as polysulfide dissolution and shuttling prevent mass commercialization of sulfur cathode batteries. Here we show a practical yet comprehensive approach for development of high performance lithium sulfur batteries. Aramid nanofiber (ANF) [1] based composite separators not only prevent dendrite formation [2] but also confine polysulfides on the cathode side (Figure). These composite membranes consist diverse and opposing properties including high mechanical properties, high ionic conductivity and high thermal/chemical stability. Therefore they provide a safe and long cycle life as well as high performance lithium sulfur batteries. Fabrication of such safe, affordable, flexible and high energy density battery is quite crucial in powering next generation electronics including but not limited to portable, wearable and implantable devices.
POLY 310: Flexible polyimide aerogels with aliphatic links in the backbone structure for conformal antenna application

Haiquan Guo\textsuperscript{1,2}, haiquan.guo@yahoo.com, Mary Ann Meador\textsuperscript{2}, David Tresp\textsuperscript{2}, Bushara Dosa\textsuperscript{2}, Linda McCorkle\textsuperscript{1,2}. (1) Ohio Aerospace Institute, Avon, Ohio, United States (2) NASA Glenn Research Center, Cleveland, Ohio, United States

Polyimide aerogels can be potentially used as light-weight, high performance antenna substrate due to their low dielectric constant, low density, and higher modulus. Conformal antennas require the substrate to be flexible in order to follow the curved surface of the wing or fuselage where it is mounted. In this study, flexible polyimide aerogels were fabricated by using aliphatic diamines with twelve methylene groups to replace from 25 to 75\% of the typical aromatic diamine in the backbone structure of 1,3,5-triaminophenoxybenzene (TAB) cross-linked polyimide aerogels. The effect of the polyimide backbone structure on the properties of the aerogel, including density, shrinkage, porosity, dielectric constant, contact angle, and mechanical properties will be discussed.
System needs and challenges for commercial aviation and space exploration are constantly changing. Multifunctional materials are ideal for aerospace applications because their integration into structural components has the potential to not only improve efficiency, but it can increase payload and mission capabilities without the burden of significant additions to mass and volume. Multiconstituent materials will play an important role in enabling structures with the potential to demonstrate true multifunctionality; however, modifications to traditional polymer processing methods may be necessary. This presentation will cover multifunctional materials development efforts underway at the NASA Glenn Research Center pertaining to fabricating novel electrical insulation to advance electric aircraft propulsion, impact resistant and electrically conductive textiles for space, and hybrid reinforcement for polymer matrix composites.

Figure 1: Development of impact-resistant textiles for inflatable, deep-space habitats: (a) Kevlar fabric subjected to ballistic impact; (b) Shear thickening fluid (STF)-treated fabric made from cubic-shaped AlSiO$_2$ nanoparticles; (c) Sub-ambient temperature rheological behavior of STF suspensions made from cubic-shaped AlSiO$_2$ nanoparticles
POLY 312: Boron nitride nanotube polymer composites for aerospace applications

Michael Jakubinek², jakubinek@gmail.com, Yadienka Martinez-Rubi², Behnam Ashrafi¹, Jingwen Guan², Meysam Rahmat³, Keun Su Kim², Christopher Kingston², Benoit Simard². (1) Aerospace Research Centre, National Research Council Canada, Montreal, Quebec, Canada (2) Division of Emerging Technologies, National Research Council Canada, Ottawa, Ontario, Canada (3) Aerospace Research Centre, National Research Council Canada, Ottawa, Ontario, Canada

Polymer nanocomposites enabled by carbon nanotubes (CNTs) are a longstanding subject of interest, research and application within the aerospace composites community. CNTs have demonstrated their strong potential for to improve on strength-to-weight in a next generation of aerospace structural composites, as well as for multifunctional composites based primarily on their electrical properties (e.g., electromagnetic interference shielding, heating, sensing) where CNTs appear in an increasing number of end-use applications. Boron nitride nanotubes (BNNTs), which are structurally analogous to CNTs, offer complimentary properties and have the potential to similarly impact the development of aerospace composites. Here we describe advances in our laboratory for large-scale BNNT synthesis/manufacturing and commercialization using a high-temperature plasma method, which is a key technology for the industrialization of BNNTs required to push this new frontier in nanocomposite development. Due to their complimentary properties to CNTs, including optical transparency, electrical insulation, higher temperature stability, neutron absorption and piezoelectricity, as well as higher affinity for polymer matrices, BNNT-polymer nanocomposites offer an expanded set of composites applications when combined with CNT and graphene nanocomposites. Opportunities for BNNT-nanocomposites in aerospace applications will be addressed though several examples focussed primarily on the processing and multifunctional properties of BNNT-polymer composites prepared in our laboratory for cases including (1) BNNT-reinforced adhesives, (2) transparent coatings and (3) multiscale composites.

BNNT-polymer nanocomposites based on BNNTs dispersed in adhesive (top) and on BNNT buckypaper sheets (bottom)
Aerogels are ultra-lightweight foams with extremely small pores. The most commonly thought of aerogels based on silica suffer from fragility and poor environmental durability. Recently, polymer aerogels and silica aerogels cross-linked with polymers have demonstrated unique advantages over inorganic aerogels including higher strengths and compressive moduli, greater toughness, and the ability to be fabricated as a flexible thin film. The next evolution in this family of materials is the development of nanoparticle reinforced polymer aerogels. By combining the advantages of polymer aerogels with the properties afforded by different nanoparticles, ultra-low density multifunctional (piezoelectric, radiation absorbing, electrically conductive, anisotropic thermal conductivity, etc.) aerogel composites can be fabricated. The first challenge along this path is to functionalize nanoparticles to be compatible and/or crosslink with the polymer aerogel. Herein, we describe our first results in the pursuit of boron nitride nanotube reinforced polymer aerogel nanocomposites for low-density high-temperature stable applications.
Diacid building blocks are important chemical starting materials in polymer synthesis. Like most industrial chemicals, the main source of diacid building blocks is petroleum, making it desirable to find sustainable alternatives. To this end, current research in our group has been focused on synthesizing biomass-based cyclobutane-containing diacid (CBDA) building blocks. Sorbic acid, which can be synthesized from biorenewable triacetic acid lactone, was photodimerized to form the novel semi-rigid building block CBDA-3 (Scheme 1). A 2:1 salt of ethylenediamine and sorbic acid was first prepared in order to arrange the sorbic acid molecules in the photoreactive configuration. This salt was then exposed to UV light to achieve [2+2] photocycloaddition of the tail-end olefins of two sorbic acid molecules, forming the semi-rigid cyclobutane ring of CBDA-3. The photoreaction was performed using commercially available germicidal lamps, which represent an efficient, cost-effective, and operator-friendly UV (ECO-UV) source. Furthermore, due to CBDA-3's unique structure, this presentation will also discuss the synthesis and characterization of multiple derivative building blocks made by reacting the two unreacted olefins of CBDA-3 using a variety of chemical reagents and/or further exposure to ECO-UV lamps of different wavelengths.

The addition of carbon nanotubes (CNTs) to a polymer matrix is a known method to enhance a polymer’s properties. However, CNTs aggregate due to weak interactions with the polymer, inhibiting potential enhancement. Literature has proposed that dispersion could be greatly improved through minimal functionalization of the CNT and the addition of oxidized graphene. This research aims to examine the extent CNT and graphene can be functionalized before a significant detriment to properties is observed. Further, we aim to calculate how the physical properties of nylon 6 are affected by the addition of functionalized CNT-graphene complexes. All calculations will be completed using LAMMPS with a class 2 force field. Initial results have shown that CNT-graphene interaction energy can be greatly increased through the addition of just 2-3 sets of functional groups. This has resulted in only an ~6% loss of Young’s modulus in the carbon nanostructures.
Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) are a developing class of polymers that can be used as materials for optical devices for use in the infrared region. An ultra-high refractive index polymer poly(sulfur-random-selenium-random-1,3-diisopropenylbenzene) (poly(S-r-Se-r-DIB)) was synthesized through the inverse vulcanization process, previously discovered by Pyun et al. Poly(S-r-Se-r-DIB) possesses the highest refractive index of any known organic polymer ($n > 2.0$). Due to its ultra-high refractive index, poly(S-r-Se-r-DIB) was selected for use in a Distributed Bragg Reflector (DBR). A DBR alternates layers of high and low refractive index materials, resulting in reflection at specific wavelengths based on the design of the device. A typical DBR relies on either an incredibly high number of layers or materials possessing large differences in refractive indices, like metal oxides. While attractive materials from this standpoint, DBRs cannot be fabricated using one step solution processing techniques. We have demonstrated the utility of our ultra-high refractive index, solution processable poly(S-r-Se-r-DIB) material for this application by fabricating highly reflective (98% reflectance) DBRs at relatively few number of layers compared to conventional polymer based DBRs. Spectral tunability was also demonstrated with reflectances >90% achieved at 1000 nm, 1500 nm, and 2000 nm. With so few layers and high reflectance, the fabricated DBR is at the forefront of IR-optical devices. The ability to solution process these materials, in conjunction with their high refractive index and IR transparency, will enable improvements to various other optical devices just as they have for DBRs.
POLY 317: Synthesis and characterization of novel Polyhedral Oligomeric Silsesquioxane (POSS) benzoxazine reactive diluents

Victoria C. Torres\textsuperscript{2}, torresvc@udmercy.edu, Witold K. Fuchs\textsuperscript{1}, Jeffrey S. Wiggins\textsuperscript{3}. (1) Polymer Science and Engineering, University of Southern Mississippi, Royal Oak, Michigan, United States (2) Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, United States (3) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States

Fundamental research involving polybenzoxazines (BOX) is necessary to explore its substantial potential as a next generation composite material for aerospace and Low earth Orbit (LEO) applications. In recent years the inclusion of well-defined inorganic structures such as Polyhedral Oligomeric Silsesquioxane (POSS) in systems like polyimides has been shown to improve the mechanical properties and reduce the color of the resulting matrices. This research investigated the effects of including systematically varied ratios of POSS-functional benzoxazine monomer within a difunctional benzoxazine network. The inclusion of two select POSS moieties reduced the viscosity of benzoxazine monomers and improved the thermomechanical properties of the resulting networks. Further research will lead to a deeper understanding of how the incorporation of covalently bound inorganic particles such as POSS affects the processability, thermomechanical properties, and UV stability of resulting benzoxazine matrices.
POLY 318: Manipulation of isotropic-nematic phase transitions in aqueous liquid crystals

Jessica Stelzel, j_stelzel@yahoo.com, Graham Parkinson, Paul S. Russo. Georgia Institute of Technology, Atlanta, Georgia, United States

Liquid crystals often contain extended, rod-shaped molecules. Phase behavior is a function of both the temperature and the concentration of these “mesogens”. This work investigates the disordered-to-ordered transition between the isotropic and nematic phases. At low mesogen concentrations, an isotropic phase is observed by polarized optical microscopy. When the mesogen concentration is increased beyond some critical value, the system transitions to a nematic phase. Liquid crystals rely on the shape of various mesogens for their strength and extensibility; shape is more important than chemical composition. This work explores whether small molecules dispersed in the isotropic phase of a mesogen held below its critical concentration can be assembled into rod shaped structures, thus triggering the creation of a liquid crystal phase. One such system consists of magnetic particles and liquid crystal forming mesogens in an aqueous dispersion. Concentration, magnetic field strength, and temperature were investigated for their relationship to the phase transition. Other rod-forming systems, including thermoreversible gelators, have been tested for their ability to elicit a liquid crystal response merely by induced assembly. Further development of these rod forming systems may allow for reversible, directed control of particle alignment on the nanoscale.

Isotropic to nematic phase transition induced by a rod forming system
There is an ongoing need for new transition metal mediated reactions that yield advanced macromolecular structures with enhanced properties and performance. Here, we report a novel polymerization methodology involving the direct activation of unsaturated substrates using homogenous gold catalysis (HGC). These polymerizations, performed through the reaction of an unsaturated substrate with a dialkyne, result in polymers with novel architectures and molecular connectivities. Optimization of catalyst, ligand, solvent, and various reaction parameters provides polymerizations that afford high molecular weight products containing 1,1-alkenyl linkages under facile reaction conditions. Additionally, the functional tolerance of HGC affords the integration of diverse functionalities into the polymer backbone and provides a rapid increase in molecular complexity. Thus, through the exploration of a series of unsaturated substrates with varying steric bulk, electron density, and substitution patterns, we have demonstrated a new synthetically useful transformation to access unprecedented molecular architectures from unsaturated substrates.
Synthesis of Aspirin (acetylsalicylic acid) is a common experiment conducted in undergraduate organic chemistry labs. In an effort to reduce waste in our teaching laboratories, syntheses of the cyclic dimer and trimer of salicylic acid were undertaken using the Aspirin generated in these labs, with comparison made to commercially sourced Aspirin (Scheme 1). In the first step of this synthesis, crude poly(salicylic acid) is generated by direct condensation of acetylsalicylic acid. In the second step, the crude polymer is depolymerized under vacuum at high temperature, and cyclics are collected on the cold finger of a vacuum sublimation apparatus. It is hypothesized that cyclics generated by this method will be competent monomers for ring-opening polymerization, enabling a longer term goal of synthesizing poly(salicylic acid) with controlled molecular weight and narrow polydispersity. Characterization data for these synthetic products are presented, in addition to screening with ring-opening polymerization catalysts.

Scheme 1: Synthesis of salicylide monomers by depolymerization of crude poly(salicylic acid).
POLY 321: Copper ion encapsulation via micelles of diblock copolymers

Anna E. Ringuette, aer3@williams.edu, Christina Chen, Luke L. Cai, Nora J. Lee, Ching-Hsien Ho, Jonathan J. Lee, Sarah L. Goh, Christopher Goh. Williams College, Williamstown, Massachusetts, United States

Polymers with metal-binding units may serve as metal-transport or metal-sequestering agents, and as such play important roles in a variety of processes that include removal of metals in environmental remediation, extraction of valuable metals, metal-chelation therapies or metallo-drug delivery agents. This talk describes the use of RAFT polymerization for the synthesis of acrylamide homopolymers with side-chain amine donor moieties that include \( N\)-[2-(dimethylamino)ethyl] polyacrylamide (pDMEN), \( N\)-[2-(diethylamino)ethyl] polyacrylamide (pDEEN), and \( N\)-[2-(dibutylamino)ethyl]polyacrylamide (pDBEN), and the diblock copolymers of these polymers and polydimethylacrylamide. Studies that demonstrate the ability of these polymers to form micelles, to bind copper(II) and to release the metal when mixed with ethylenediaminetetraacetic acid (EDTA) are presented.

![Diagram showing micelle formation and metal encapsulation](image)
POLY 322: Unraveling the kinetic growth mechanism of single-chain nanoparticles with Diels-Alder chemistry

Sierra E. Gosting, sgosting@calpoly.edu, Emily Wilborn, Cecilia G. Gregory, Taylor Page, William Ramos, McKenzie Hunter, Philip J. Costanzo. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and RAFT polymerization techniques were employed to prepare star-like structures with DA linkages at a central core. Upon the application of a thermal stimulus, the retro-DA was induced and star-like structures were reduced to a linear topology. Various reaction conditions were explored and the preparation of single-chain nanoparticles was explored.[figure1]
In the last couple of decades gold nanoparticles (GNPs), are used in a variety of applications, viz. photonics, therapeutics, diagnostics, and catalysis. Reduction of toxic 4-Nitrophenol (4-NP) into non-toxic 4-Aminophenol (4-AP) has become a research hotspot in recent years, and GNPs have been explored in catalyzing this reduction process. To study the effect of the capping agent and the shape of the GNPs on catalytic efficiency, here we have used gold nanoparticles-amphiphilic block copolymers conjugates. Stimuli-responsive polymers induce stability and recyclability to the GNPs. The high dispersion of the coated polymers in the reaction medium allows the reactant molecules to access the active site of the noble metal nanoparticle easily. In this work, we have designed and synthesized poly(N-isopropyl acrylamide)-b-(styrene-r-vinyl pyridine) of three different hydrophilic (NIPA) chain length and same styrene to vinyl pyridine ratio via reversible addition-fragmentation chain transfer (RAFT) polymerization to stabilize the GNPs which have different lower critical solution temperature (LCST). To get the information about the change in catalytic efficiency due to change in the gold nanoparticle shape, we have also synthesized polymer-stabilized gold nanorod and compared the efficiency with the nanoparticle. The temperature-dependent catalytic efficiency of the polymer-coated GNPs towards 4-NP reduction was also studied. The catalytic efficiency of gold nanoparticles was found to be influenced by changing the temperature below and above LCST, length of the hydrophilic chain of the coated polymer as well as the shape of the gold nanoparticles which was attributed to the altered accessibility of the reactants to the catalyst surface. There was nearly no loss of catalytic activity on recycling the polymer-coated GNPs confirms the stability of the polymer coating on GNPs. Hence, these new catalysts could be potentially useful in industrial applications.
Multi-responsive polymeric nanocarriers are emerging as smart carriers for anticancer drugs or genes to enhance the efficacies in cancer therapy. Internal as well as external stimuli, such as temperature, pH, enzymes, reductive and magnetic field were applied to disassemble the responsive polymer carriers in drug delivery. Recent studies revealed that temperature, pH and redox state of the cancer tissues are slightly different (pH < 6.0 and T= 40−43 °C, concentration of glutathione > 10 mM) compared to that of the normal tissues (pH 7.4 and T= 37 °C, glutathione concentration in micro level). Drugs can be selectively delivered in the cancer tissues by taking advantage of the above mentioned differential parameters. For accomplishing this goal, a new copolymer having thermoresponsiveness as well as redox and pH responsiveness was conceived. A pH responsive monomer 2-(2-(3, 4 bis(hexyloxy)benzyloxy)carbonyl)ethylthio)ethyl methacrylate (HBCEEM) was synthesized and was RAFT polymerized using a chain transfer agent (CTA) having a redox responsive alkyne group at one of the terminals. Separately, another CTA with azide end was used for synthesizing thermoresponsive poly(NIPA-PEGMA) (PNP) following our previous method. Following this, CuBr click chemistry mediated 1,3-dipolar cycloaddition was performed between azide and alkyne terminals of the two polymers to form a thermo, pH, and redox triple responsive block copolymer. The block copolymer was characterized by gel permeation chromatography, NMR spectroscopy, dynamic light scattering and scanning electron microscopy. The copolymer formed self-assembled nanostructure in aqueous medium which was loaded with an anticancer drug, doxorubicin. The release of drug from this nanostructures was influenced by these three stimuli (pH, temperature, redox), with the most effective release was observed at acidic pH, at temperatures > 37 °C and in presence of higher concentration of glutathione. Thus, this copolymer can be potentially useful in delivery of anticancer drugs.
Many equilibrium systems can be obtained by several energy minimizing methods. In the energy minimizing method, researchers have following consecutive procedure; first, setting the energy equations in system; next, summing up the energy equations; and finally, finding the minimum energy point via optimization process. In present study, CuPt nanorods are located between P4VP block copolymer and aqueous solution of CTAB. This system is meaningful because it shows that nanorod plays a role as a surfantant. We used the method that consists of several interfacial energy equations and several polymer stretching energy equations which calculate the equilibrium position and axial angle of the nanorod to elucidate the morphology (nanostructure) of the nanorods. By reflecting the shape of the nanorod, we mainly used the cylindrical coordinate ellipse surface integration for simulation of the system.
The manipulation of polymer molecular weight distributions (MWDs) has recently emerged as a promising avenue toward fine-tuning polymer function from polymer processability and mechanical strength to many facets of morphological phase behavior. Thermoplastic elastomers (TPEs) are a heavily commercialized class of materials which combine many of these features to achieve the desirable elasticity with the processing ease of thermoplastics. However, a common side effect of conventional elastomers is high damping of the material, leading to undesirable heat generation and ultimately premature failure. In this regard, a long-standing challenge in this field has been to develop TPEs with increased resilience without compromising favorable properties such as tensile strength and elasticity. With this grand challenge in mind, we envisioned that deliberate modification of polymer MWDs would offer the ability to tailor the function of commercial triblock copolymer TPEs. We find that the entire composition of the molecular weight distribution function can be used as a handle to predictably govern TPE material properties.
POLY 327: Synthesis and characterize of the dual-thermo- responsive diblock copolymer

Dandan Zhao¹, amberdiary@gmail.com, Robin Rajan², Kazuaki Matsumura³. (1) Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan (2) School of Chemical and Biomedical Engineering Nanyang Technological University, Singapore, Singapore (3) School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan

[Introduction]
Block copolymers have attracted wide attention due to their specific chemical property and widely applications. Many of the multi-stimuli responsive polymers are block copolymers. Among the various stimuli, thermo-responsiveness has been focused on. Recently, our group showed carboxylated poly-l-lysine (PLLSA) shows lower critical solution temperature (LCST). On the other hand, poly-sulfobetaine (PSPB) has been reported to exhibit upper critical solution temperature (UCST) behavior in water and inhibit protein aggregation. In order to get the polymer with all these properties, we prepared a diblock copolymer of PLLSA and poly-SPB.

[Experimental]
The diblock copolymers were synthesized by a three-step reversible addition fragmentation chain transfer (RAFT) polymerization. First, PLLSA was obtained by substituting different degree of substitution of succinic anhydride (SA) to PLL. The addition of the RAFT agent to PLLSA was followed. The formed macro-chain transfer agent can be used to control the degree of polymerization of SPB. The diblock copolymers were obtained after dialysis and freeze dry. All the diblock copolymers were characterized by NMR. UV-Vis spectroscopy and dynamic light scattering (DLS) were employed to analyze the dual-thermo-responsive property.

[Results and Discussion]
From the NMR spectroscopy, the characteristic peak of the two blocks was clearly seen (Fig1a). From the graph we can clearly see the diblock copolymer solutions showed turbid at lower and higher temperature, indicating the dual-thermo-responsive property (Fig1b). Furthermore, the DLS result showed the diblock copolymers showed aggregation at low and high temperature (Fig1c).

[Conclusion]
The diblock copolymers were successfully prepared by RAFT polymerization. And the diblock copolymers exhibited dual-thermo-responsive property.
POLY 328: Phase behavior and structural determinants of multifunctional tripedal mesogens prepared via the Passerini three-component reaction

Shuang Song\textsuperscript{2}, songdashuang@gmail.com, Dipankar Sahoo\textsuperscript{2}, Manoj Kumar\textsuperscript{2}, Deborah A. Barkley\textsuperscript{2}, Paul A. Heiney\textsuperscript{1}, Jonathan G. Rudick\textsuperscript{2}. (1) Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Department of Chemistry, Stony Brook University, Stony Brook, New York, United States

Mesogens are molecules that promote liquid crystalline phases. The anisotropic molecular order in the mesomorphic state maintains mobility and can be responsive to external stimuli such as voltage and temperature. This makes liquid crystalline materials widely used in optoelectronic areas. Heterolithic star-branched mesogens combine two or more different types of mesogenic arms into a single molecule, providing a way to diversify and manipulate the structures and the corresponding properties of liquid crystals. As a result, each arm contributes to the phase behavior of these multifunctional materials. However, being able to predict how combined multifunctionalities in star-branched scaffolds affect the final phase behavior remains a challenge due to the complex structural motif.

In this work, a series of mesogenic tripedes are prepared and their mesomorphism is investigated to elucidate the structure-property relationships. A library of homolithic, heterolithic AB\textsubscript{2}, and heterolithic ABC tripedes are designed and synthesized exploiting the Passerini three-component reaction. Their phase behaviors are analyzed by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction techniques. This work shows that the presence of terminal groups that promote smectic mesomorphism dominates the phase behavior of heterolithic tripedes in the presence of other groups that prefer nematic phases. These results provide a theoretical basis for engineering liquid crystalline materials with novel structural and functional properties through molecular design.
Human transport to Mars and deep space explorations demand developing new materials with extraordinary high performance to mass ratios even more than the state-of-art carbon fiber reinforced polymeric composites (CFRPs) or metallic alloys. In order to fulfill these requirements, Ultra-High Strength Lightweight (UHSL) materials are promising candidates. Pristine Carbon nanotubes (CNTs) exhibited significantly favorable mechanical properties in compare to carbon fibers. Investigations showed that with increase in CNTs diameter, after a certain value, they have another preferred structure rather than circular form that can be obtained in high pressure or tension conditions which is the dumbbell-like shape. ReaxFF reactive force field can provide detailed information of interactions since it can observe chemical reactions based on the bond order concept. Therefore, it has been trained to capture the proper structure of flattened carbon nanotubes (flCNTs), i.e. dumbbell-like shape CNTs, against available DFT data. In addition, we investigated a study revealing the effect of the curvature on reactivity properties of the flCNTs; thus, we calculated the oxidation barrier and reaction energies correlated to the curvature. Moreover, we developed ReaxFF against various sets of DFT data for hardener/epoxy/polymer molecules. Using the developed ReaxFF, we studied the interactions and reactions of flCNTs with variety of solvents and polymers providing detailed observations of crosslinking/polymerization of these components in the presence of the CNTs.
Here we introduce a method for creating oriented block copolymer domains in electrospun nanofibers using solvent annealing. Monodisperse poly(methyl methacrylate)-block-polystyrene (PMMA-b-PS) and poly(methyl methacrylate)-block-poly(butyl acrylate) (PMMA-b-PBA) block copolymers with various volume fractions of PMMA were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. The nanofibers were obtained by single-needle electrospinning. We investigated the effects of PMMA volume fraction, solvent and annealing time on the self-assembly behaviors of the block copolymers in nanofibers. After solvent annealing, the block copolymers formed nanostructures including cylinders and lamellae depending on the volume fraction of PMMA. The nanostructures strongly depended on the solvent and solvent annealing time. Surprisingly, the cylindrical nanodomains were perpendicular to the fiber axis. This study provides a simple and efficient route to manipulate the periodic nanostructures of block copolymers in nanofibers.
POLY 331: Effect of MFC size-concentration in the structure of PVA hydrogels

Washington E. Magalhães³, washington.magalhaes@embrapa.br, Gabriel G. Goetten de Lima²,¹, Bruno Ferreira³,⁴, Mailson de Matos², Caroline Jordão², Francine Claro². (1) Athlone Institute of Technology, Athlone, Ireland (2) Programa de Pós-Graduação em Engenharia e Ciência dos Materiais - PIPE, UFPR, Curitiba, Brazil (3) Embrapa Forestry, Colombo, Brazil (4) Chemistry Department, UFPR, Curitiba, Brazil

Microfibrillated cellulose (MFC) is obtained by the high energy mechanical homogenization of the wood pulp, which promotes the exposure and opening of surfaces that were covered inside the material, commonly named as fibrils/microfibrils. This superficial modification generates a larger area of contact and connection between the microfibrils leading to an increase of the material resistance. Given its high strength, dimensional anisotropy and natural source of MFC, the use of nanocellulose as a functional and renewable reinforcing agent for polymer composites and hydrogels has attracted significant research interest. This cellulose can be used in hydrogels to stabilize the reinforcing agent and to interact with other components of the gel via electrostatic or hydrogen bonding, to lower the effective limit for the gelation or adjust the physical properties. However, due to the mechanical process in obtaining MFC there is a variation in the sizes of the fibrils depending on the degree of defibrillation; therefore, this work investigates the effect of synthesizing MFC in freeze-thawing Polyvinyl alcohol hydrogels while varying the sizes of MFC and its volume. To obtain MFC, eucalyptus wood pulp was defibrillated achieving different size based on the energy of the supermasscolloider used; they were further synthesized with PVA by varying concentration of cellulose. Thermal properties DMA, SDT and TGA were performed with SEM; TEM with investigation to the molecular structure using FTIR. Concentration had a major effect on the hydrogel properties, swelling decreased and the crystallinity measured at the Tm increased as the concentration increases. There was an overall increase in mechanical properties with a decrease in size and increasing of MFC's concentrations, these were also correlated with its thermal properties and kinetics.

DSC and swelling values of various MFC concentrations into PVA hydrogel
Synthesis of well-defined multiblock polymers with high molecular weight via controlled radical polymerizations is a challenge for the accumulation of dead chains through the polymerization. Herein, we developed a one-pot synthesis strategy for producing multiblock polymers via reversible addition-fragmentation chain transfer (RAFT) emulsion polymerization. Firstly, a "dodecablock" polystyrene with high degree of polymerization (DP, \(\sim 100\) per block), acceptable reaction time (2h per block) and low polydispersity (PDI<sub>MW</sub><1.5) was synthesized as a template. The dead chains generated through the polymerization were negligible ascribed to the extremely low initiator concentration, resulting in the excellent agreement between experimental and theoretical molecular weights. Then we synthesized a decablock copolymer containing polystyrene and poly(n-butyl acrylate) blocks via the same strategy. A series of block copolymers from diblock (PS-P<sub>n</sub>BA)<sub>1</sub> to decablock (PS-P<sub>n</sub>BA)<sub>5</sub> were obtained during the polymerization, while the molecular weights of PS and P<sub>n</sub>BA block were 15kg/mol and 30kg/mol respectively. All block copolymers showed significant microphase separation. According to tensile tests, the mechanical property could be improved greatly simply by increasing the block numbers.
Thin block copolymer films can form a variety of nanostructures and provide a versatile toolbox for the bottom-up fabrication of nanodevices. To use block-copolymers in the bottom-up fabrication of these devices, it is critical to characterize the nanoscopic internal morphology of the thin films. However, currently available techniques for subsurface characterization such as grazing incidence small angle x-ray scattering (GISAXS) is limited in spatial resolution; while tapping mode atomic force microscopy (AFM) and scanning electron microscopy (SEM) can be difficult in chemical identification. Here we show that, by combining scanning near field optical microscopy (SNOM) and AFM mechanical measurements, we can probe the subsurface composition of block copolymer thin films with nanoscale spatial resolution. Using this method, different subsurface morphologies, such as perpendicular and parallel lamellae of a poly(tert-butylacrylate)-block-polystyrene thin film was revealed. Our method, therefore, enables non-destructive characterization of block copolymer subsurface structures with nanoscale spatial resolution.
External regulation of atom transfer radical polymerization (ATRP) allows for fine tuning of the activity of the copper catalyst, and asserting spatiotemporal control. Temporal control in ATRP was investigated using various external stimuli including zerovalent metals, light irradiation, and chemical redox agents. The activity of the catalyst had a profound effect on the behavior of the system in the presence/absence of stimuli. For example, in more active complexes, due to the very low concentration of L/CuI, a perfect temporal control was obtained. However, less active catalysts resulted in high concentration of L/CuI activator that drove the reaction to higher conversions even in the absence of stimuli.

Moreover, a chemical approach was developed to affect the redox properties of the Cu catalyst. Ascorbic acid was used as a reducing agent to (re)generate L/CuI activator. A ferrocenium salt or oxygen was used as oxidizing agents to oxidize L/CuI catalyst, and switch the polymerization off. Therefore, ATRP was successfully switched between on and off states using redox agents, which efficiently modulated the redox state of the catalyst without sacrificing control over the polymerization.
POLY 335: Accelerated CuAAC coupling reaction fulfilled the synthesis of ultrahigh densely grafted polymers by grafting-onto strategy

Weiping Gan¹, wgan@nd.edu, Yi Shi¹, Benxin Jing², Xiaosong Cao¹, Haifeng Gao¹. (1) Chemistry and Biochemistry, University of Notre Dame, Mishawaka, Indiana, United States (2) Engineering, Wayne State University, Detroit, Michigan, United States

An acceleration effect that benefits from the complexation of triazole with Cu was first confirmed in two model copper-catalyzed azide-alkyne cycloaddition (CuAAC) reactions in this work: a) 1:1 molar ratio of a diazide compound and an alkynyl-terminated poly(ethylene oxide) (ay-PEO₁₈ with average degree of polymerization DP = 18) and b) 1:1 molar ratio of a dialkyne compound and an azido-terminated N₃-PEO₁₈. It was resulted that both model reactions produced ditriazoles as major products, although the former reaction exhibited a higher yield of PEO-PEO dimers, demonstrating better CuAAC acceleration effect. Illustrated by this acceleration effect, we developed a new method to synthesize molecular brushes with polymethacrylate backbone and ultrahigh densely grafted side chains (SCs) applying accelerated CuAAC grafting-onto strategy. Polymethacrylate backbones with multi-azido dangling groups were designed and subsequently applied for grafting-onto reaction with ay-SCs (including PEO₁₈, PEO₁₁₃, poly(methyl acrylate) (PMA₃₁) and polydimethylacrylamide (PDMA₄₆)) to prepare an array of molecular brushes with high grafting densities. Within our investigation, all these CuAAC grafting reactions finished within 10 minutes and the grafting density was affected by the composition of SCs and the initial molar ratios of ay-SCs to azido groups. The highest grafting density was obtained (1.34 SCs per backbone carbon atom) on both longer polymethacrylate backbone and shorter backbone when applying linear SCs with thinner structure, such as ay-PEO₁₁₃.
Elemental sulfur waste is produced in vast quantities by the petroleum refining process. Sulfur has limited solubility and is hard to process in its elemental state. Recently, inverse vulcanization was developed using vinylic or allylic monomers to cross-link the polysulfides, adding stability and allowing easier processing. Inverse vulcanized polymers have been used to create cathodes for lithium-sulfur batteries, IR lenses, and filters for metal binding. Metal binding is of particular interest, since industrial waste streams often contain heavy metals that are toxic to living organisms and expensive to treat. The majority of these polysulfides have limited solubility, which makes characterization challenging and restricts applications. Here, charged monomers such as diallyldimethylammonium chloride (DADM) were reacted with various amounts of sulfur at 160°C to enhance solubility. The increased solubility enables more accurate solution-based characterization such as NMR and gel permeation chromatography (GPC), to examine the polymer structure and molecular weight. The polymers were also characterized using TLC to confirm the complete reaction of sulfur and FTIR to ensure the integrity of the monomer structure. Additionally, these polymers can be used as an inexpensive material for metal binding. Enhanced water solubility of charge polysulfides allows for better interaction between the metal ions and the polymer. Metal salts, such as ZnCl₂, were added to aqueous polymer solutions and analyzed using UV-Vis to measure the change in absorbance due to the metal binding.
High surface area polymers have been applied in a variety of applications. The unique property of capturing/releasing molecules establishes them as molecular sieves for separations, column stationary phases, and carriers for targeted-release medicines. Recently, we have reported the fluoride-catalyzed hydrolysis of Me-Si(OEt)\textsubscript{3} with Bis-triethoxysilylethane (BTSE). The resulting hydrophobic gels possess surface areas up to 1300 m\textsuperscript{2}\textperkg, thermal stability >200 °C, and tunable pore sizes. This innovative method has short reaction times (<24 hr) in air at RT, opening possibilities for novel microporous polymers. Since the properties and texture of the resulting polymers largely correlate to the silane bridge, various materials applications can be specified. From these initial findings, photoreactive high surface area porous gels have been developed. By incorporating cis-trans isomerizable bridging molecules, the gel functions as a light-switchable solvent capturing/releasing agent for hydrocarbons, with further implications as a photo-reactive pump or artificial muscle.
Biological composites, such as bone and ivory, consist of hierarchically organized hard and soft phases that allow the structure to be tough without being too flexible. Self-assembled films of cellulose nanocrystals (CNCs) can have high toughness, due to their hierarchically helicoidal (Bouligand) structure that effectively dissipates energy, making them ideal for advanced materials. Incorporating a thermoresponsive polymer as the soft phase can improve the tunability, flexibility and strength of the resulting CNC nanocomposite. The incorporation of poly(diethylene glycol methyl methacrylate) (PMEO₂MA) can be accomplished through physical absorption or covalently bonding the polymer to the surface of CNCs. In an aqueous solution, PMEO₂MA has a lower critical solution temperature (LCST) value of 26 °C. Below this temperature, the polymer chains are hydrophilic coils that expand, but the chains contract to hydrophobic globules above that critical temperature. This reversible thermoresponsive process can tune the pitch of the CNC self-assembled films simply by varying temperature and moisture content due to the configuration of the polymer chains. Nanocomposite films of PMEO₂MA/CNC with 5, 15, 30 wt% polymer were prepared via controlled evaporation-induced self-assembly. This resulted in the peak reflectance wavelength (a measure of the pitch) to transition from blue, to green-orange, to red as the polymer concentration increased, respectively. Optical and mechanical properties were studied as well as how the self-assembly of CNCs differed in the presence of PMEO₂MA in the helicoidal structure. Understanding how thermoresponsive polymer can be tuned to influence physical properties of CNC composite can allow mimicry of nature’s design for tough materials.

The wood Na-CNC was blended at different concentration of PMEO₂MA in an aqueous solution and the films were formed at room temperature through evaporation-induced self-assembly. As the polymer concentration increased, the pitch increased due to polymer infiltration - red shifted due to the higher pitch.
Optogenetics combines optics and biology to control living tissues by light-sensitive proteins and radiative energy. Typically optogenetics is studied using invasive optical fibers, consequently, the conventional method has negative side effects such as localized heating and surgical scars. In this presentation, a radioluminescent rare earth oxyorthosilicite nanoparticle is proposed as a noninvasive approach to study optogenetics. The material of interest requires temperatures above 1000°C and thus particle-particle contact and sintering is detrimental to the final size. Polymerization and crystal growth are coupled together to expand the possible chemistry for nanoparticle synthesis. A base catalyzed core-shell approach is used to develop the nanoparticle template for a chemical reaction and is sterically protected with poly(divinylbenzene) (pDVB). The inorganic core-shell particulate was modified with 3-(Trimethoxysilyl)propyl methacrylate followed by precipitation polymerization of divinylbenzene to pDVB. The carbonization of pDVB to amorphous carbon, in an inert environment, prevents particle-particle contact of the core-shell sub 100 nm inorganic particulates at extreme temperatures thus acts as a nano reaction vessel. The work presented here suggests that carbonized pDVB can expand the current chemistry for nanoparticles and provide greater control on the structural-radioluminescent properties that can be used to study optogenetics.

Figure 1: Polymerization and carbonization process of pDVB onto a core-shell particulate for isolated sub 100 nm nanocrystals at temperatures above 1000°C.
The transport of ions through polymer matrix is essential in a wide variety of technologies such as microfluidic, batteries, fuel cells, and desalination/water purification. Conventionally, the transport properties of ions are correlated with the total water content in the swollen polymers. However, water in the polymer exists in three states: non-freezable, intermediate water, and free water. While it is intuitive to expect that water molecules at different states would contribute to the ion sorption and diffusion differently, there lacks systematic studies of the relationship between the state of water and ion transport properties. In this study, we prepare three polymer networks: non-charged cross-linked poly(ethylene oxide) from poly(ethylene glycol) diacrylate (PEGDA) and poly(ethylene glycol) methyl ether acrylate (PEGMEA), zwitterionic polymers from sulfobetaine methacrylate (SBMA) and PEGDA, and polyelectrolytes from 2-acrylamido-2-methyl-1-propanesulfonate sodium (AMPS, CX) or [2-(acryloyloxy)ethyl] trimethyl ammonium chloride (AETMAC, AX) and PEGDA. The effect of polymer composition on the state of water was systematically investigated using the Differential Scanning Calorimetry (DSC). The number of non-freezable water molecules was 1.9 per ethylene oxide unit, 17 per SBMA, 15.1 per AMPS, and 9.1 per AETMAC. Increasing the PEGDA content increases the cross-linking density and thus the amount of free water. In contrast to conventional studies based on the total water content, the \( T_g \) of the hydrated polymers is correlated with the content of the non-freezable water using the Gordon-Taylor equation, and the salt solubility is correlated with the content of the freezable water. Interestingly, the salt diffusivity is related to the total water content (instead of the freezable water content) using the free volume model. This work is one of the very few elucidating the effect of the states of water on physical properties of polymers.
POLY 341: Vapor-phase infiltration of metal oxides into microporous polymers for solvent stable nanofiltration membranes

Fengyi Zhang\(^1\), fengyi.zhang@chbe.gatech.edu, Emily McGuinness\(^2\), Yao Ma\(^1\), Mark Losego\(^2\), Ryan P. Lively\(^1\). (1) Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

Owing to their high surface area and hierarchical porosity, microporous polymers, such as polymers of intrinsic microporosity (PIMs), have shown great potential in heterogeneous catalysis, adsorption, and membrane separations, among other applications. Linear microporous polymers (e.g., solution-processable PIM-1), can be easily manufactured into form factors consistent with large-scale separations (e.g., hollow fibers). However, linear microporous polymers can be dissolved, swollen, or plasticized by various solvents, which restricts their application in aggressive operating environments. Two of the most prominent post-fabrication methods for improving the stability of polymers are pyrolytic carbonization and crosslinking. These are both promising approaches to rigidifying polymeric materials, but require a near-complete transformation of the precursor in the former case and chemical/thermal treatments in the latter case.

Here, we develop a novel post-fabrication modification technique for improving the stability of microporous polymers without damaging the microstructure and macroscale form factors. Cyclic vapor phase infiltration of metal-organic precursors and water into the structure of PIM-1 creates monolayers or bilayers of sub-nanometer metal oxide structures on the surfaces of the interconnected PIM-1 micropores. The resulting interpenetrating atomic-scale networks of metal oxide and PIM-1 retain the microporosity and exhibit excellent solvent resistance to strong solvents for PIM-1 (chloroform, dichloromethane, and tetrahydrofuran). While PIM-1 membranes cannot effectively reject polystyrene oligomers below 1200 g/mol from ethanol, the hybrid PIM-1 membranes reject polystyrene oligomers larger than 400 g/mol. Besides, the interpenetrating aluminum oxide networks inhibit the interaction between membranes and solutes, increasing the Rose Bengal rejection from 45% to 86%. Since the vapor phase infiltration process can be directly applied to state-of-art membrane modules, this treatment has the potential to be adopted into the large-scale manufacturing of advanced membranes.
POLY 342: Design and synthesis of functional sugar poly(orthoester) nanomaterials with ultra-low immunogenicity

Sampa Maiti1, maiti1s@cmich.edu, Saikat Manna2, Aaron Esser-Kahn2, Wenjun Du1. (1) Chemistry, Central Michigan University, Mount Pleasant, Michigan, United States (2) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Polymers have been widely used in a variety of biomedical and clinic applications ranging from suture, urinary catheters, vascular stent and as carriers for drug delivery. A large number of synthetic polymers, such as poly(tetrafluoroethylene) (PTFE), poly(L-lactic acid) (PLLA), poly(ethylene glycol) (PEG), poly(L-glycolic acid) (PLGA), as well as their co-polymers such as PEG-PLGA have been employed for various applications. However, there are still challenges ahead, namely, the high immunogenicity of polymers can result in their neutralization and elimination and can cause long-term toxicity. Further, even though “non-immunogenic” materials like PEG have become the hallmark of development of pharmaceuticals, there are detectable anti-PEG antibodies in as much as 40% of the population. In this context, carbohydrate-based polymers are generally considered low immunogenic and their biomedical application have been extensively studied. Hence, to address the challenges of polymer induced immunogenicity, we have developed sugar poly(orthoester) (SPOE) polymers, where sugar monomers are linked by locked alpha-glycosidic bond similar to the natural glycosidic linkage. The synthesis of the polymers were performed by copolymerization of a novel alkyne-functionalized glucose monomer to a non-functional glucose monomer in varying ratios to achieve random co-polymers. The co-polymerization went smoothly to give the polymers of molecular weights of $M_n^{GPC} = 6.3$ kDa. After conjugation with biocompatible long chain oleyl azide, followed by deprotection of the acetate groups, an amphiphilic polymer was obtained. The polymer was further subjected to self-assembly to give the sugar-coated nanoparticles (NPs) with TEM sizes of about $30 \pm 4$ nm and DLS sizes of about $100 \pm 16$ nm. In-vitro and in-vivo studies with the NP system demonstrated very favorable cell viability, and most importantly, ultralow immunogenicity. When compared with the commonly-used NP systems, such PCL-PEG and PLA-PEG, the novel NP system exhibits much lower immunogenicity, as evaluated by the level of a series of pro-inflammatory cytokines. Thus, SPOE polymers do not cause any aberrant immune activation and hence have a huge potential in various biomedical applications.
Nylon 6,6 is a versatile engineering thermoplastic with high strength, stiffness and thermal stability. These properties make it widely applicable in the automotive, electronics, and food packaging industries, amongst others. However, despite its widespread use, Nylon 6,6 is moisture-sensitive which results in undesirable softening, dimensional instability and susceptibility to corrosive environments. Therefore, there are unmet needs for hydrophobic variants of Nylon 6,6.

Due to the great interest in green alternatives to petroleum-based polymers, here, we present a value opportunity for “bioenabled” polymers that can be derived from biologically-produced intermediates such as muconic acid. In this study, we demonstrate the introduction of mono-unsaturated \( \text{trans}-3 \) hexenedioic acid (t3-HDA) as a platform that provides unique advantages in differentiating Nylon 6,6 through copolymerization. Specifically, a new family of hydrophobic “BioAdvantaged” Nylon 6,6 (BAN-H) have been prepared from mixtures of alkyl-chain-derivatized \( \text{trans}-3 \) hexenedioic acid, adipic acid (AA) and hexamethylenediamine (HMDA).

The resultant BAN-H polyamides were fully tested for moisture absorption and characterized using a broad set of techniques including TGA, DSC, WAXS, DMA, and SEM. Our results illustrate the utility of unsaturation sites in polymer property customization by demonstrating a reduction in hygroscopicity by up to 93% without deleterious effects on the thermal and mechanical properties. Moreover, the chemical stability of BAN-H against aggressive corrosive agents such as zinc chloride is dramatically improved (Figure 1).

Scanning electron micrographs comparing the surface of conventional Nylon 6,6 and Bioadvantaged Nylon 6,6 after exposure to a zinc chloride solution.
Cross-linked Polyethylene (XLPE) has emerged as an outstanding insulator for high-voltage direct current power transmission cables due to its favorable dielectric properties, low water permeability, structural integrity at high temperature and chemical resistance. Dicumyl peroxide (DCP) is the most commonly used peroxide agent for the crosslinking of polyethylene for high voltage power cables. However, DCP-initiated crosslinking leads to the formation of different byproducts which remain in the final product and may have adverse effects on cable function and its long-term properties. Currently, our knowledge of the effects of the byproducts and chemical reactions involved during the crosslinking procedure on the properties of the final XLPE product is limited. By understanding how the crosslinking byproducts change the XLPE properties, improvements may be formulated relative to conventional XLPE cables. In order to design and optimize XLPE cables, it is crucial to obtain detailed, atomistic-scale insight of XLPE chemistry since every byproduct in XLPE affects differently the electrical properties of the polymer and thus the effect of each of the byproducts should be investigated. Quantum mechanic (QC) methods are considered the most accurate technique among atomistic simulation methods, however, these methods are prohibitively expensive, making them impractical for larger systems. The ReaxFF reactive force field method can model chemical reactions based on the bond order concept without the full expense of QC methods, and it has been successfully applied to a wide range of systems such as covalent and metal oxide/hydride/carbide materials. In this study, we developed a ReaxFF force field validated against DFT data obtained for XLPE chemistry. Using this force field, we studied the effects of different parameters such as temperature, density, type of peroxide, and the ratio of peroxides to polyethylene on the formation of byproducts, distribution of functional groups, and cross-linking.
Many house paints are marketed today as containing low or “0” volatile organic compounds (VOC). This can set an expectation from consumers that the materials are also low odor (and are often labeled as such). We and others have found that the level of VOC may not directly correlate with the odor, much more important can be the contribution of specific odorants. Malodorants with a very low odor threshold can have a much larger impact on odor than their relative quantity would predict.

A range of coatings materials were evaluated through the use of analytical tools such as GC-Olfactory analysis and a number of the malodorants in the headspace of a typical low VOC latex paint have been identified and categorized by potency, functional group and source. These results, combined with an understanding of the human olfactory system, have led to a better understanding of how to develop low odor coatings. The structure of the malodorants often have similar local structure and functional groups as many of the formulation materials which are critical to paint performance. Any method to reduce the undesirable materials must be selective as well as time and cost effective. Methods to control these contaminants include biocatalysts, adsorbents and others have been studied. The results of these studies will be discussed.
Iatrogenic tissue damage is a common side effect of current techniques in soft tissue repair, often results in scarring from either the cytotoxicity or inflammatory response of the original suture/adhesive or from secondary surger for removal. It is therefore a necessity to find new bioadhesive materials that can be implanted into the body, which can fully degrade without causing an inflammatory response or cytotoxicity in its surrounding tissue. We have developed a hybrid polycarbonate/polypeptide copolymer network of completely degradable composition through the sequential ring-opening polymerisation (ROP) of cyclic carbonates subsequently followed by N-carboxyanhydrides (NCAs) to form ABA block copolymers. Through the crosslinking of the polycarbonate block, the material exhibits mechanical durability and flexibility similar to soft tissue. The polypeptide blocks contain catechol-functional L-DOPA amino acid repeat units, which in nature are used by mussels for wet adhesion in sea water. Herein, we demonstrate the ability of the hybrid copolymers to adhere to wet soft tissue as well as their ability to undergo degradation and exhibit low cytotoxicity.
POLY 347: Pyrrole-based donor-acceptor conjugated molecules for organic electronics

Prabhath L. Gamage¹, plg150030@utdallas.edu, Anna K. Fiedler¹, Mihaela C. Stefan², Michael C. Biewer³. (1) Chemistry & Biochemistry, University of Texas at Dallas, Dallas, Texas, United States (2) Dept Chem UT Dallas, Richardson, Texas, United States (3) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States

The synthesis of various pyrrole based small molecules and polymers is reported as semiconducting materials. But the lower stability of pyrrole containing materials has limited their usage in various electronic applications. Therefore, the fused ring systems with pyrrole such as thieno[3,2-b]pyrrole and dithieno[3,2-b:2′,3′-d]pyrrole are designed and they have shown better stability and are promising building blocks for organic electronic applications. The inherent electron donating nature of these fused ring systems can result in the formation of p-type polymers with various acceptor units like benzothiadiazole (BTD) and diketopyrrolopyrrole (DPP). Herein, different donors based on pyrrole such as furo[3,2-b]pyrrole, thieno[3,2-b]pyrrole, thieno[3,2-b:4,5-b′]dipyrrole, furo[3,2-b:4,5-b′]dipyrrole are polymerized with BDT, DPP and isoindigo acceptors using stille coupling to generate donor-acceptor polymers to be used in Organic field effect transistors (OFETs). The photo-physical and electrochemical characteristics of these polymers are determined and used in organic electronics.
POLY 348: Interpenetrating polymer networks consisting of poly vinyl pyridine and poly phenylene oxide for use in organic electronics

Tariq Hussain, Brittany Parody, Gregory D. Phelan, gregory.phelan@cortland.edu. Chemistry, State University of New York College at Cortland, Cortland, New York, United States

There is considerable interest in finding functional materials to be used in the next generation of organic electronic devices. These functional materials are needed to help with issues including being able to increase stability, processibility, and conductivity. A series of interpenetrating and semi-interpenetrating polymers and were synthesized using poly (2,6 dimethyl 1,4 phenylene oxide) and poly 4 vinyl pyridine. The networks were synthesized by mixing polymers as well as by starting from monomers and polymerizing in situ. The compositions of the networks were based on weight percent of each polymer used in the mixture and ranged between 0 - 100%. The resulting materials were characterized using differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. Thermal decomposition temperatures were found to vary from 391C to 460C. Materials were found to have a single glass transition temperature that vary from 125C to 210C. Details of the synthesis and morphological results including microstructures created will be presented.
Materials adapting their shape reversibly to external stimuli have gathered increasing attention for a range of applications in medicine and robotics. Photoresponsive systems especially have shown promise through the facile and benign nature of their trigger. In this work we present a new light-responsive polymer system and use this platform to compare a range of different photoswitches from the well-established azobenzene’s to the novel Donor-Acceptor Stenhouse adducts. These studies focus on evaluating the ability of photoswitches to create mechanical force in a polymer network upon exposure to light. Choosing different photoswitches and their respective derivatives enables activation using wide range of wavelengths between 300 nm and 700 nm.
Approximately 20% of the world’s population lacks access to sanitary drinking water, the majority of which is contaminated with metals such as copper and lead. While current technologies can effectively remove metals, methods such as membrane filtration suffer from biodegradation and oxidation. Polyarylene ether sulfones, however, are not subject to biodegradation or oxidation and can be easily tailored to suit the needs of a given application. We have developed a series of sulfonamide-based metal chelators that can be easily modified to improve metal selectability and withstand the harsh conditions associated with water treatment. We have generated multifunctional monomers capable of sequestering metals from aqueous solution. Additionally, polymacrocycles were prepared by exploiting the differences in activation energy required for the aromatic substitution of difluorinated benzenesulfonamide derivatives. The polymerizations were monitored using $^1$H NMR spectroscopy, and characterized using GPC, DSC, TGA. The binding affinities of the polymers and monomers to metals were evaluated using ITC.
Polysulfone-based (PSU) polymers are thermoplastic stable materials characterized by their strength and stiffness. These types of polymers also maintain their integrity when exposed to mineral acids, alkaline conditions, electrolytes, and oxidants in pH ranging from 2 to 13. PSU allows the easy manufacturing of membranes with reproducible properties and controllable size of pores. In order to modify the chemical and physical properties of PSU we employ the synthesis of chloromethylated polysulfones (CMPSUs). The CMPSUs were synthesized by reacting commercial PSU (Mn ~22,000 by MO) with paraformaldehyde in an equimolar amount of chlorotrimethylsilane (Me₃SiCl) as chloromethylation agent, and stannic tetrachloride (SnCl₄) as a catalyst. The reaction was performed in dry chloroform under N₂ atmosphere, the mixture was refluxed at 50 °C for 72 h. The product was used for the addition of alkylated, aminated, hydroxylated or azidated pendants to the PSU backbone via SN₂ reactions. Each PSU-derivative were used for the preparation of polymeric membranes with an approximated thickness of 150 µm via the phase inversion (PI) technique. The prepared membranes were later tested for forward osmosis applications. The characterization of each material was performed using nuclear magnetic resonance spectroscopy (¹H-NMR, ¹³C-NMR), Fourier transform-infrared spectroscopy (FT-IR) and energy dispersive spectroscopy (EDS). The thermal properties were studied using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The membrane surface was evaluated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The complete syntheses, characterization, surface evaluation, and water purification studies will be presented.
In fuel cell system containing anion exchange membrane fuel cell (AEMFC) system, polymer electrolyte membrane is a key part. In case of AEMFC, anion exchange membrane is used as a poly electrolyte membrane. Anion exchange membranes have disadvantages of low thermal stability, which are solved by using poly(ether ether ketone) (PEEK) polymers with excellent thermal stability. In order to solve the problem of low ion conductivity of the anion exchange membrane, the polymer electrolyte membrane with improved ionic conductivity was prepared by polymerization using a monomer introduced with a conductive group. So, we synthesized the PEEK polymer based polymer with different imidazole contents as follows: membranes were fabricated using a process that involves the evaporation of a cast solution. Next, thermal, chemical and mechanical properties of membranes were analyzed by using various evaluation methods.
In this study, hybrid membranes were prepared using polystyrene particles and poly(styrene-ethylene-butylene-styrene)s with ion exchange group. First, polystyrene particles were prepared by emulsion polymerization and cation/anion ion exchange groups such as sulfonic acid group and quaternary ammonium were introduced into the prepared polystyrene particles. Also, cation/anion exchange groups were introduced into poly(styrene-ethylene-butylene-styrene). In order to prepare the hybrid membranes, polymers were dissolved in a solvent, and the particles were dispersed. These solution were poured into petri dish and the solvent was volatilized to prepare hybrid membranes. The performance of the hybrid membranes was verified through various characterization.
A series of new semifluorinated sulfonated copolyimides (PTPQSH-XX) was synthesized by the click polymerization of bis-N,N’-(prop-2-ynyl) pyromellitic diimide (TP) with a mixture of two diazide monomers: 4,4-bis [3-trifluoromethyl-4 (4-azidophenoxy) phenyl]biphenyl (QAZ) and 4,4’-Diazido-2,2’- stilbenedisulfonic acid disodium salt hydrate (SAZ). The degree of sulfonation (DS) of the copolyimides was controlled by variation of the ratio of SAZ to QAZ. The structures of the copolyimides were confirmed by FTIR and ¹H NMR spectroscopy. The copolyimides exhibit high molecular weights, good solubility, and film-forming capabilities. The copolymer films showed good thermal stabilities and mechanical properties depending upon their chemical compositions. Transmission electron microscopy (TEM) images of the copolymer membranes showed phase separated morphology which suggests the formation of hydrophilic and hydrophobic domain throughout the membrane. The proton conductivities of PTPQSH-XX (XX-50, 60, 70, 80) membranes were found in the range of 12-56 mS/cm at 30 °C and 26-131 mS/cm at 80 °C.
A series well-defined AB and ABA PVDF block copolymers with styrene, vinyl acetate, (meth)acrylates, dienes, etc. were synthesized via the Mn$_2$(CO)$_{10}$ mediated quantitative activation of PVDF-I chain ends of obtained from the Mn$_2$(CO)$_{10}$ mediated iodine degenerative transfer controlled radical photopolymerization of vinylidene fluoride (VDF). The dependence of the block properties including thermal transitions, contact angles, surface roughness and morphology on the block Mn, PDI, as well as comonomer nature and composition was studied, and indicated the ability to manipulate the hydrophilic/hydrophobic properties.
New high molecular weight, aromatic fluorinated ladder polymer has been obtained by superacid catalyzed non stoichiometric step-polymerization of xanthenediol with trifluoroacetone. The polymerizations carried out at room temperature in a mixture of trifluoromethanesulfonic acid (CF₃SO₃H, TFSA) with methylene chloride resulted in a polymer completely soluble in acetone, methylene chloride, chloroform, THF, methanol, DMFA, NMP, DMAC. The chemical composition of the ladder polymer has been confirmed by the complementary experimental and calculations studies of the $^{13}$C and $^{19}$F NMR spectra and the calculations of reaction pathways. Flexible, elastic films were obtained by casting. According to gas permeation experiments, the ladder polymer falls above the Robeson 2008 updated upper bound.

![Diagram](image.png)

*Figure 1: General reaction.*
Polycarbodiimides are a class of synthetic helical polymers that have received attention based on their chiral nematic phases. They can be synthesized into single-handed helices that form cholesteric mesophases with special optical properties, such as selective reflection of light. These polymers have potential applications in liquid crystals. In this study, we have prepared a series of cholesteric polydicarbodiimides to correlate their backbone conformation and behavior as liquid crystalline materials. More specifically, we are using dicarbodiimide linkers in combination with carbodiimide monomers to produce a helical backbone for comparison with polymers made from monocarbodiimides. We have extended the living polymerization approach of monocarbodiimide polymerization using Ti(IV) based initiators. The goal of this project is the rational synthesis of polymers with new architectures and targeted properties. In this presentation, the structural rationale, synthesis, backbone conformations, optical properties and liquid crystalline behavior of the resulting polymers will be discussed.
Bottlebrush polymers are a type of polymers with a linear backbone and long side chains attached to each repeat unit of the backbone. The unique architecture leads to a number of special properties and applications, e.g. low solution viscosity compared to linear polymers with the same molecular weight due to the absence of chain entanglement; super soft materials; adsorption-induced scission of C–C bonds; large self-assembly domain sizes lead to photonic crystals; low critical micelle concentration compared to linear diblock copolymers, etc. In this study, macromonomers with AB type functional groups or with AA and BB type functional groups at one chain end, where A means alkyne and B means azide, were synthesized, and subsequently polymerized into bottlebrush polymers via copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) "click" polymerization of the macromonomers. By using this method blocked brush polymers, star-shaped brush polymers, Janus armed brush copolymers, etc. could be synthesized easily via a one-pot reaction.
This poster describes our recent efforts at utilizing flow reaction conditions to perform ring opening metathesis polymerization (ROMP) reactions. These reactions can be easily conducted on the benchtop under air using simple syringe pumps and commercially-available Grubbs-type initiators. These reactions are shown to be fast (in some cases no more than one minute is required) and allows for the polymer to be directly isolated without the need for any sophisticated glassware. This process is amenable to (i) monomers with moderate to high levels of ring strain (i.e. norbornene derivatives, cyclooctadiene, and oxanorbornene derivatives) and (ii) the preparation of homopolymers and copolymers (block and random) alike. Interestingly, we found that mixtures of endo and exo norbornene-based monomers can also be polymerized in which the exo isomer is almost exclusively polymerized while the endo remains untouched. This allows for mixtures of the two to be used without previously being separated. A comparison of molecular weight distribution, as compared to typical batch polymerizations, is also presented.
Semi-rigid building blocks suitable for materials synthesis are uncommon. One such class of structures is cyclobutane-containing building blocks (CBBs). They bridge the gap between their flexible aliphatic chain and rigid aromatic counterparts. The unique blend of rigidity and flexibility, due to the presence of one or more conformationally strained four-membered aliphatic rings in CBBs, make them a viable option in the design and synthesis of novel materials. In addition, their stability towards thermal cycloelimination and near UV radiation substantiate their candidacy in developing materials of choice. One such example is cyclobutane diacid (CBDA). Various types of CBDAs were readily synthesized from olefins derived from agro-residues via environmentally friendly [2+2] solid-state photoreactions. A diverse array of polymers were synthesized by polycondensation of CBDAs and biomass-derived diols to demonstrate the potential applications of CBDAs in material synthesis and to study their thermal and mechanical properties. Despite the presence of the strained cyclobutane ring, these biobased polyesters showed promising thermal, chemical, and photo stability.
POLY 361: Development of an initiator with post-polymerization photo-cleavage capabilities

Matthew S. Baker, matthew.baker@oswego.edu, Cory Ludwig. Chemistry, State University of New York at Oswego, Oswego, New York, United States

Stimuli-responsive materials have garnered a great deal of attention over the past few decades due to their versatility and wide range of applications. A more recently explored area of responsive materials includes polymers with reactive end-caps. We have developed a new reagent capable of initiating radical polymerizations with an additional ability to be cleaved off in the presence of UV light. At first, in the presence of heat, our reagent initiates a radical polymerization. Subsequently, when the resulting material is exposed to UV-light, the end-cap of the polymer will undergo bond-cleavage resulting in a new terminal site for our polymer. This poster will focus on the development, synthesis, polymerization, and photo-cleaving response of our reagent.
POLY 362: Synthesis of acid-degradable star polymers by chain-growth CuAAC polymerization of AB monomers from active core

Weiping Gan, wgan@nd.edu, Xiaosong Cao, Haifeng Gao. Chemistry and Biochemistry, University of Notre Dame, Mishawaka, Indiana, United States

All polymerizations are classified into two mechanisms, step-growth polymerization and chain-growth polymerization. With decades’ development of controlled living polymerization, it is a general consensus that chain-growth is better to obtain polymers with defined molecular weight, structure, architecture and narrow distribution. Our newly developed chain-growth CuAAC polymerization only suitable for AB$_2$ type monomers. This poster presents our new progress on the chain-growth CuAAC polymerization of AB type monomers by applying active cores in the polymerization to construct star polymers with well-defined molecular weight and polydispersity. By using this method, acid-degradable hyperstar polymers with molecular weight $M_n = 2.31 \times 10^5$ and polydispersity $M_w/M_n = 1.04$ was achieved and further degraded to linear polymer with molecular weight $M_n = 5.1 \times 10^3$ and polydispersity $M_w/M_n = 1.64$. 

![Diagram of polymerization mechanisms](image)
First prepared in the 19th century, s-tetrazines undergo Inverse Electron Demand Diels Alder (IEDDA) reactions to yield dihydropyridazines and pyridazines making them popular for ‘Click’ functionalization of activated alkynes and alkenes. We have discovered that s-tetrazines can be used to modify more mundane alkene groups in polybutadiene and alkene-functionalized polysilsesquioxanes. When liquid polymers are used, the reaction converts the polymers into solids while the nitrogen gas released from the IEDDA reaction turns the solidifying polymer into a flexible foam. Furthermore, the dihydropyridazine groups react with one another, crosslinking the foam, effectively vulcanizing elastomeric versions and converting thermoplastic forms into thermosets. Dihydropyridazine groups from some tetrazines reacting with alkene groups in polymers also show excellent UV absorbance and act as free radical inhibitors making these materials attractive as inherently UV and oxidation resistant materials. Furthermore, because the dihydropyridazine groups are generally fluorescent while pyridazine groups are not, consumption of the antioxidant can be visually monitored. In this poster, our current progress on the application of s-tetrazines as a polymer modifier and enhancer will be presented.
POLY 364: Simple toolbox for building dendritic and polyisoprene based multidentate phosphine ligand structures and their Pd(0) complexes

Jonas Christopher C. von Irmer, j.vonirmer@mc.tu-darmstadt.de, Matthias Rehahn. Ernst-Berl-Institute, TU Darmstadt, Darmstadt, Hessen, Germany

Dendritic catalysis has proven to be a potent modern tool for different reactions like hydrogenation and a variety of cross-coupling reactions such as the Heck and Suzuki reaction. The construction of such branched and highly functionalized architectures proved to be challenging and requires endurance and precise synthetic protocols. Therefore, the development of a convenient and robust toolbox to synthesize phosphine-terminated branched or linear multi-substituted structures is of great interest. In this work we present an atom-economic and facile way of introducing phosphine moieties into branched and/or highly functional polymer-based scaffolds utilizing the terminal double-bond motive of allyl groups or 1,2-polyisoprene respectively. The degree of functionalization, solubility and morphological aspects can be targeted by varying the polymer composition, i.e. introducing a second block segment or by the generation of star-shaped polymer architectures. Additionally, the successful introduction of the phosphine motive can be validated by its characteristic and scaffold-independent fingerprint in 1D- and 2D-NMR spectroscopy experiments. As the binding of the catalytically active metal, i.e. palladium(0) and the resulting stoichiometry of the formed complexes is crucial for the efficacy of the resulting catalyst, the binding kinetics are investigated by NMR spectroscopy studies. The presented multivalent ligand systems could be utilized in manifold applications like dendritic or (pseudo)micellar catalysis due to nano-confinement with great potential in the field of multi-phase reactions by showing a simultaneous catalytic and phase-mediating activity.
Approximately 60 million tons of elemental sulfur are produced each year from crude oil in the petroleum refining process. Inverse vulcanization was created to utilize the abundance of elemental sulfur by reacting it with vinyl or allyl monomers to form functional polymers. Modification of these polysulfides is a possible means to broaden the versatility of sulfur based polymers. Utilizing the inverse vulcanization method, a 30:70 ratio of sulfur: divinylbenzene (DVB) were combined on a 5 g scale at 185 °C for 1 hour to create poly(S-DVB). Next, maleimide was grafted onto poly(S-DVB). This reaction occurs at 100 °C at varied time trials ranging from 15 min to 48 hours. The reaction occurs because the S-S bonds within poly(S-DVB) cleave forming free radicals, which bind to maleimide, incorporating it into the prepolymer. To aid miscibility between maleimide and poly(S-DVB), a small amount of dimethylformamide was added to the reaction. In an effort to make this reaction solvent free, a terpolymer was created by combining S8, DVB, and styrene in a 30:35:35 ratio. The addition of styrene allows the prepolymer to have a more fluid consistency. Using poly(S-DVB-styrene) improved miscibility between maleimide and the prepolymer without the need for solvent. Polymers were characterized before and after completing the reaction by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR). The NMR spectra revealed that as the reaction time increases, more maleimide is incorporated. Examining changes in the molecular weight revealed a substantial drop after 24 hours indicating that the backbone of the poly(S-DVB) is intact as the maleimide is incorporated initially, but the structure begins to degrade after 24 hours. Overall, we were able to create graft polymers by reacting maleimide using dynamic S bonds within polysulfides. The ability to modify these polymers demonstrates their versatility for future applications.
The kinetics and mechanism of the thermally activated dynamic covalent exchange of thiol-Michael adducts is investigated. A model system of thiol-Michael adducts between thiophenol and phenylvinylketone derivatives and adducts between 2-mercaptoethanol phenylvinylketone derivatives in N, N-dimethylformamide (DMF) at elevated temperatures is used to probe the underlying exchange mechanism. The kinetic data show negligible free Michael acceptor, which is consistent with the highly efficient thiol-Michael reaction being a “click”-like reaction that significantly favors the adduct form. At elevated temperatures of 90 °C in DMF the thiol-Michael adducts reach equilibrium after 24 h, although equilibration did not occur within 24 h at 60 °C or 75 °C, and negligible exchange occurs under ambient conditions. A kinetic model was developed to describe the dynamic covalent exchange and equilibration. The experimental and simulation kinetic data of dynamic covalent exchange are consistent with the thiol-Michael adducts undergoing a retro-Michael reaction, followed by subsequent addition of a free thiol to the liberated Michael acceptor. Kinetic analysis is consistent with the fragmentation, or retro-Michael reaction, being the rate-determining step in the dynamic covalent exchange. This suggests that the key step in dynamic covalent exchange is not enhanced by addition of free thiol or free Michael acceptor, since the addition reaction is much faster than the retro-Michael reaction. This fundamental study will guide the design of organic compounds, materials, and bioconjugates that utilize the thermally activated dynamic covalent thiol-Michael bonds.
POLY 367: Synthesizing laccol polymer and its copolymers using lacquer sap *Toxicodendron succedanea* for radiation hard applications via cationic polymerization and characterizing the materials

**Imalka H. Marasinghe Arachchilage¹, imalka@mail.usf.edu, Milly Patel¹, julie harmon². (1) Chemistry, University of South Florida, Tampa, Florida, United States (2) usf, Tampa, Florida, United States**

In recent years lacquer chemistry stimulated more attention from scientific community due to its environmental friendly applications. A novel approach is introduced to develop polymers using 'laccol' extracted from Vietnamese lacquer sap (*Toxicodendron succedanea*). In nature, lacquer polymerization is induced via enzymatic radical initiation. Herein, lacquer polymer was synthesized via cationic polymerization with aluminum chloride-ethyl acetate (AlCl₃.EtOAc) initiator complex. This approach was further improved by copolymerizing laccol-styrene and laccol-limonene designed for use in radiation hard materials. The Infra-Red (IR) Spectroscopic data clearly evidence reactions with trans conjugated double bonds present in long side chains (988 cm⁻¹ and 966 cm⁻¹ characteristic peaks) of laccol monomer accompanying the polymerization. This was further verified with proton Nuclear Magnetic Resonance (NMR) analysis by indicating the disappearance of peaks around δ 5.6 and δ 6 which were correlated to *trans* conjugated double bonds. GPC, TGA, DSC and Rheometry were used to characterize the synthesized materials. Further, an increase in hardness was observed for all the compositions; after the gamma Co-60 irradiation without deteriorating the material. The properties such as thermal stability and hardness were improved after irradiation due to a possible increase in crosslinking. Therefore, the developed laccol polymer and its copolymers are suitable candidates to produce radiation hard polymer and copolymer coatings for aerospace operations, nuclear reactors, medicinal and automobile sectors.

Pathway of making radiation hard polymers
A new polymer click platform has been developed utilizing readily available and inexpensive starting materials. This system unites the high reactivity of cyclopentadiene in Diels-Alder cycloadditions with the high stability commonly observed with less reactive dienes, allowing for incorporation into a number of polymer systems. To highlight the potential of this chemistry, we demonstrate that this new system may be included into polymer chains through functionalized initiators and monomers in both ROP and RAFT polymerizations. In addition, the new click platform is compatible with acrylates via a post-polymerization method. The potential of this click platform to conjugate traditionally incompatible polymers into complex architectures is especially exciting and may be accomplished by functionalizing polymers of interest with this new approach.
Polyimide is one of the most important high-performance polymers, which is widely used due to its excellent mechanical performance and thermal stability. Unlike the conventional synthetic approach, hydrothermal polymerization enables the synthesis of polyimides without any toxic solvent and catalyst. Herein, we report the synthesis of polyimide microparticles (PIMs) through one-pot hydrothermal polymerization using precursors of mellitic acid (MA) and three isomers of phenylenediamine (PDA) (o-, m-, and p-PDA). Interestingly, the chemical composition of PIMs was highly tunable with the choice of the PDA isomers, leading to considerable morphological differences between PIMs. The molecular dynamics simulation and density functional theory calculation of the polymeric segment of the respective PIMs suggested that the relative ratio of amide to imide influenced the rotational freedom of the polymeric chains, resulting in the well-defined structures of respective PIMs. Considering the highly tunable nature of PIMs coupled with the facile synthetic protocol, we anticipate prospective potentials of PIMs in materials, energy, and composite applications.
Brush Polymers have seen use in many applications such as drug carriers, photonic crystals, surface modifiers, and nanolithography. The application of ring opening metathesis polymerization (ROMP) in grafting through approaches is a highly efficient way to achieve brush architectures. However, there remains a limited number of ways to synthesize the norbornene-functionalized macromonomer precursors reducing the possible number of brush polymers with unique chemical composition. Through anionic polymerization, previously challenging or inaccessible monomers have been polymerized with a norbornene pendant group.
Two novel and renewable benzoxazine monomers that include structures of vanillin and phenol were synthesized by Mannich reaction using (5,5’-methylenebis(furan-5,2-diyl)) dimethanamine (DFDA) obtained by coupling furfurylamine using formaldehyde. Both benzoxazine monomers show low melting temperature (about 100°C) and low cure onset temperature (about 150°C). Polybenzoxazines that were cured at 200°C have a glass transition temperatures of ~250°C, and 62% char yield at 800°C in Argon atmosphere. In addition the chemorhelological behavior of these systems was investigated using dynamic mechanical analysis (DMA) and dynamic viscosity measurements. The molten benzoxazine monomers have low viscosity and a broad temperature and time processing window allowing for facile molding and infusion.
Elemental sulfur is produced as a byproduct of petroleum refinement, but sulfur has limited uses in its elemental state. Sulfur-based polymers such as poly(sulfur-random-divinylbenzene) [poly(S-r-DVB)], have been produced by a new method, inverse vulcanization. Inverse vulcanization occurs under solvent free conditions, where sulfur acts as the initiator and solvent when copolymerizing with the monomer DVB. The polysulfides produced are tunable, high in sulfur content, low cost, and being investigated for uses in applications such as lithium sulfur batteries, mercury capture, and IR optics. Several inverse vulcanization procedures have been published that can produce these polysulfides including varied reaction times and reaction scales, as well as the use of inert gas. Some samples also use post-polymerization curing or ramp the temperature during the reaction. Here, these varied synthetic procedures to generate poly(S-r-DVB) were replicated in order to: determine if they were reproducible, analyze the fundamental differences amongst them, track the occurrence of the autocatalytic effect, and determine a schematic representation of the polymeric structure created. Various synthetic procedures displayed distinct microstructures, solubility, and molecular weight data. $^1$H NMR determined that increasing reaction scales effects HC-C bonding. Solubility testing of the polysulfides determined that increasing reaction scales increased the solubility in dichloromethane. Gel permeation chromatography (GPC) data collected indicated that reaction time affects Mw and solubility. Additional testing performed on the polysulfides were $^{12}$C NMR, FTIR, differential scanning calorimetry (DSC), and TLC. Overall, the data collected thus far has determined: poly(S-r-DVB) can be produced by various synthetic procedures that have varied microstructure and physical properties.
To obtain lower chain length dispersity in surface-initiated (SI) polymer brushes, brushes were grown by ATRP in the presence of an end-capping group. Growing the SI brushes on high surface area nylon filters provided sufficient polymer for characterization after surface cleavage. SI grafting-from brushes are reported to exhibit a concentration gradient with the monomer concentration increasing with increasing distance from the surface. This gradient has been proposed to increase the growth rate of longer chains at the expense of shorter ones, as the active polymer ends move further from the surface. Limiting the DP of the polymer chains by the addition of a monomer that is known to propagate very slowly, such as α-methyl styrene (αMS), might be expected to limit the growth of fast-growing chains, giving the shorter chains a chance to catch up. As a comparison, we synthesized solution-grown polymers with the same monomer to αMS ratios. GPC and NMR analysis of the cleaved brushes showed a decrease in dispersity in both systems, but with the DP tending to higher in the SI system. The proposed mechanism and prospect of the approach to SI brush growth will be presented.
Unlike the well-studied ATRP of styrene and (meth)acrylates, the metal mediated ATRP of conjugated dienes remains underdeveloped. We have recently carried out in-depth investigations of the butadiene (BD) ATRP mediated by group 8, 10 and 11 transition metal ATRP catalysts, which highlighted the superiority of Cu vs. Ni, but also the good potential of Fe systems towards polymerization control. In the current study, a comprehensive examination of the similarities and differences between the Group 8 Fe and Ru catalysts is presented, and highlights the high sensitivity of this polymerization to the nature of otherwise similar metal and ligand systems.
Polyethersulfone (PESU), due to its high temperature stability, modulus, toughness, and hydrolytic stability, is used in a wide range of high performance applications. These properties are also desirable for thermoplastic composites, however, the high melt viscosity and processing temperature of PESU present challenges for its widespread adoption. Polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals have been shown to reduce viscosity in a range of lower temperature polymers when added at low weight percent loadings. In this study, we demonstrate reductions in the torque during melt extrusion and reductions in the complex viscosity during rheological analysis for PESU blends with small concentrations of POSS molecules of specific composition. The PESU-POSS blends show no significant changes in mechanical (tensile and impact) and thermal (Tg and T_{degradation}) properties. DMA, dielectric spectroscopy, and surface analysis indicate potential mechanisms for this unusual viscosity reduction, which occurs without changes in bulk mechanical properties.
Benzoaxazine-based resins afford non-toxic, environmentally friendly plastics that possess enhanced mechanical and thermal properties, which are desirable for creating safe and reliable parts in the aerospace industry. High temperature resins are often made from highly crosslinked polymers which complement the thermal properties of benzoaxazine-based materials. Resins bearing phenylacetylide units have proven useful in the synthesis of high temperature resins. By attaching phenylacetylide substituents to a benzoaxazine molecule, we hypothesize that we can create a highly crosslinked phenylacetylene-based benzoaxazine resin that will consolidate the properties of both classes of materials. The structure and purity of the monomer, determined by NMR and IR, will be presented. The resin will be made into films for characterization. Primary thermal ring-opening polymerization and secondary crosslinking reactions of the phenylacetylide-based benzoaxazine will be studied via DSC and will also be presented. TGA and TGA-FTIR studies for thermal stability will also be discussed. The tensile mechanical properties of the fully cured films, including modulus, tensile strength, and toughness, are also studied.
Hybrid polymers composed partially of inorganic elements likely represent the next generation of thermoset materials that can outperform state of the art organics. Typical challenges to their implementation include poor manufacturability and synthetic difficulties. Thermally robust and synthetically accessible boron-containing structures can be introduced into polymer systems to serve as lightweight inorganic scaffolds. Dioxaboroles featuring strong boron-oxygen bonds are being studied as monomers for condensation and retro Diels-Alder polymerizations with chemistry necessary for cross-linked thermosets. This presentation will discuss the synthesis and polymerization of dioxaborole monomers, strategies for overcoming hydrolytic instabilities, and characterization by TGA, DSC, FTIR, and multinuclear NMR.
Nowadays, there is a problem associated with the use of dyes in different industries because they generate toxic wastes that can cause ecological problems and health problems in humans such as skin irritations and allergic reactions. For that reason, some researchers presented hydrogels as a new alternative to deal with this problem in an efficient way due to the low costs of fabrication and the potential of being reusable. The main objective of this study was to evaluate the applicability of new hydrogels based on N,N-dimethylacrylamide and 2-oxazoline macromonomer as removal agents of methylene blue dye and also with the particularity that the dimethylacrylamide can self-crosslink without the necessity of employing a conventional crosslinker. Those polymeric materials were structurally characterized by proton nuclear magnetic resonance ('H-NMR) and infrared spectroscopy (FTIR) identifying the presence of the main functional groups. Furthermore, the sensitivity to pH of hydrolyzed hydrogels was tested and we obtained high values of water absorption at basic pH values. In addition to that, we evaluated the different synthesized hydrolyzed hydrogels as adsorbent materials of a variety of methylene blue solutions (with different concentrations) and it was obtained that the hydrolyzed hydrogels showed high values of adsorption capacity (mg/g) owing to the presence of polar carboxylate groups. Finally, it was determined that the adsorption isotherm of the process fit with Freundlich model and it could be related to a physisorption process due to the interaction of the carboxylate groups (COO⁻) of the hydrogel (specific from macromonomer) and the cationic groups (N⁺) of the dye.
High internal phase emulsion (HIPE) polymerization approach allows to obtain macroporous polymers. If the volume fraction of the internal phase (dispersed phase) is increased above 74%, than it gets surrounded by a thin film of the continuous phase (external phase). Polymerization of the continuous phase containing monomers results in locking in of the HIPE structure. After removal of the internal phase, the obtained cross-linked polymer networks possess a macroporous structure (called polyHIPE). Poly(2-oxazoline)s are obtained by living cationic ring-opening polymerization of 2-oxazolines. This process provides easy access to a wide variety of well-defined polymers, in which the endgroup functionality can be varied by appropriate initiation and termination steps. Moreover, the properties of poly(2-oxazoline)s can be tuned by changing the side chain of the 2-oxazoline monomer.

In the present work, we have obtained porous poly(2-oxazoline)s using HIPE polymerization. The porous structures were obtained by crosslinking short poly(2-oxazoline) oligomers possessing methyl ester groups in their side chains using an amidation reaction catalyzed by triazabicyclodecene (TBD). The HIPE conditions were provided by using a mixture of cyclohexane and acetonitrile. The obtained polymers were characterized by scanning electron microscopy and N₂ sorptometry. Furthermore, they were used for adsorption of phenolic compounds, namely 2,4-dichlorophenol, bisphenol S and 2-naphthol from aqueous solutions. Combination of these polymers with ambient plasma mass spectrometry allowed to quantify the content of these phenolic compounds in aqueous solutions.
Despite that the cationic polymerization of 2-oxazolines is commonly denoted to be living, a clear high molar mass fraction appears in the size exclusion chromatography traces, especially when performing the polymerization at higher temperatures. This formation of the higher molecular weight fraction still remains a puzzle, albeit it has recently been proposed to be due to a combination of intrinsic chain transfer based on the β-elimination\(^1\) and oxazolinium chain end-tautomerisation.\(^2\) But, the high molecular weight formation during the polymerization of 2-phenyl-2-oxazoline (PhOx) remains unanswered.

In the quest to understand the puzzle we investigated the effect of the polymerization time (at 140 °C) of various 2-oxazoline monomers on the high molecular weight formation. We observed gradual increased in intensity of the high molecular weight fraction in the SEC traces with prolonged time. Here we propose another possible mechanism for chain coupling: the attack of the active chain ends onto already formed polymer amide nitrogen atoms, which becomes sterically hindered with the increased polymerization and becomes reactive as observed in case of sterically hindered amides.\(^3\)
POLY 381: Synthesis and characterization of thiol and aldehyde functionalized poly(2-oxazoline)s

Martin Purino, martin.purino@ugent.be, Ali Tigrine, Victor R de la Rosa, Richard Hoogenboom. Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

The rich chemistry of poly(2-alkyl-2-oxazoline)s (commonly abbreviated as PAOx, POx or POZ) allows tailoring the properties of these biocompatible materials and offers a great degree of freedom to explore multiple conjugation chemistries with potential applications in drug delivery or as biomaterials. Thiol and aldehyde groups represent some of the most important functional handles for bioconjugation, playing a key role in the covalent conjugation of PAOx with (bio)molecules but also surfaces and nanoparticles.

In the present contribution, a straightforward strategy was applied to synthesize thiol functionalized poly(2-oxazoline)s by using potassium ethyl xanthogenate as a terminating agent on the living polymer. The free thiol group was obtained by dialysis of the polymer solution in hydrazine/H₂O, which allows the deprotection of the xanthate group and avoids oxidation of the free thiol group. The quantification of free thiols is performed via Ellman’s methodology, which is very useful as a sulfhydryl assay reagent due to its specificity for -SH groups at neutral pH, high molar extinction coefficient and short reaction time.

On the other hand, the synthesis of aldehyde groups at the α chain end was carried out by using 2-(2-bromoethyl)-1,3-dioxolane as the initiator. The free aldehyde polymer can be obtained by dialysis of the corresponding 1,3-dioxolane-PAOx in an aqueous solution of trifluoroacetic acid (TFA). The aldehyde-functional polymer was treated with benzophenone hydrazine in order to quantify end-group fidelity by ultraviolet-visible spectroscopy (UV-Vis).
Star polymers have attracted great attention in the polymer field because of their special properties such as solubility, decreased viscosity and prolonged blood circulation. Poly(2-oxazoline)s (PAOx) are a synthetic class of polyamides, that are obtained by living cationic ring-opening polymerization of 2-oxazoline monomers. The polymers are characterized by narrow distributions and various functional groups can be easily introduced to both initiation and termination ends. Star shaped poly(2-oxazoline)s have already been reported and prepared by: i) “core first” method using a variety of multifunctional electrophilic initiators method, and ii) “arm-first” method using multifunctional amines, as terminating agents. However, up to now it has been impossible to prepare uniform high-molar mass star PAOx, regardless the method used. Herein we report the synthesis of well-defined star-shaped PAOx with an overall degree of polymerization of 300. Moreover, the PAOx star polymers were further used to obtain thermo and/or photoresponsive hydrogels.
If properly designed, poly(ester amide)s (PEA) represent polymers that can be hydrolytically degraded yielding biogenic degradation products. Such materials can be obtained via ring-opening polymerization (ROP) of substituted morpholine-2,5-diones. The ROP of such monomers was realized at room temperature in tetrahydrofurane using benzyl alcohol as initiator and 1,5,7-triazabicyclo[4.4.0]dec-5-ene as a catalyst.[1] The replacement of the initiator by a hydroxyl end-functionalized poly(2-ethyl-2-oxazoline) (PEtOx) enabled access to a range of amphiphilic PEtOx-b-PEA block copolymers from morpholine-2,5-diones based on l-valine and l-isoleucine. The PEtOx macroinitiator was obtained via end-capping of the cationic ROP by acetic acid and subsequent cleavage of the acetate end group. Aiming towards nontoxic and biodegradable nanoparticulate drug delivery vehicles, the degree of polymerization (DP) of the PEtOx was kept as 20, whereas the DP of the hydrophobic PEA was varied between 20 and 100. The well-defined block copolymers (D < 1.4) assembled into a range of morphologies depending on the DP of the hydrophobic PEA block.

Bis(2-oxazolines) represent alternative starting materials for the synthesis of PEAs, as the 2-oxazoline ring can be opened by nucleophilic attack of a carboxylic acid. The resulting polyaddition of bis(2-oxazolines) with a range of bifunctional carboxylic acids hence yielded a library of PEAs that are easily accessible and suitable for nanoparticle preparation via nanoprecipitation.
POLY 384: Synthesis of laccase polymer hybrids

Marina Kovaliov¹, marina.kovaliov@ahn.org, Saadyah Averick². (1) Neuroscience Research Institute, Allegheny Health Network, Pittsburgh, Pennsylvania, United States (2) Neuroscience Institute, Allegheny Health Network Research Institute, Pittsburgh, Pennsylvania, United States

Laccase is an essential biocatalyst with many potential applications, including degradation of pollutants, chemical synthesis, biosensing, chemical processes of the textile, and wine stabilization. Due to inherent enzyme sensitivity to environmental challenges the conditions at which this versatile tool may be employed are limited. There have been many efforts in the literature to improve laccase stability, including immobilization on to solid supports either using simple adsorption, encapsulation, covalent binding, and self-immobilization. These attempts at enzyme stabilization come at a significant cost to enzyme activity. Herein we present a method to enhance the stability and activity of laccase by grafting polymers from the surface of laccase using ATRP.

![Diagram of laccase polymer hybrid](image-url)
POLY 385: Sub-7 nm patterning platforms through directed self-assembly of metal conjugated biopolymers

Gayani Pathiraja, gcpathir@uncg.edu, Klinton Davis, Hemali P. Rathnayake, Daniel Herr. Nanoscience, University of North Carolina at Greensboro, Greensboro, North Carolina, United States

With a growing demand for continuous miniaturization and functional scaling, the complementary metal-oxide semiconductor (CMOS) platform continues to drive advances in integrated circuits (IC), nanoelectronics and information processing technologies. Directed self-assembly of block copolymers is the current state-of-the-art which yields patterns with various morphologies and could reach minimum feature size up to 8 nm. In order to continue Moore’s Law further to take new nodes into production, consequently, there remains an enormous research space to be explored emerging research materials (ERMs) that show potential for extending the feature size below sub 8 nm. Utilizing hydrophilic-hydrophobic interactions as driving force for self-assembly, we developed a method to fabricate atomic patterning platforms using different metal cation-conjugates biopolymers. With this method, we were able to develop ordered line patterns with the feature size down to 7±0.58 nm using metal cation-conjugate biopolymers. These directed self-assembly of metal cation-conjugates biopolymers line patterns could serve as a cheap and effective way for manufacturing of high resolution features, both in the semiconductor electronics industry and in high density magnetic media, enabling wide applicability in 21st century emerging technologies.

Sub-7 nm Random line patterns made from directed self-assembly of a metal ion conjugated biopolymer
Optimal protein-polymer conjugates should have intact biological function of the protein combined with the processability of the polymer. With this work, we aim to capture these qualities and generate solution-stable protein-polymer conjugates using the recombinantly expressed human carbohydrate-binding protein, galectin-3 (gal3). Conjugates are synthesized using both full gal3 and a truncated sugar-binding domain-only construct. Cysteines substituted into gal3 using site-directed mutagenesis will be the reactive handles for grafting-to polymer conjugations. Proteins will initially be conjugated with polyethylene glycol (PEG) as a model polymer to test for solution stability and ligand-binding ability. These will serve as preliminary studies for future applications of surface-immobilized gal3-polymer conjugates.
In this work we seek to exploit site-specific genetic incorporation of biorthogonal “click” handles or initiating species to generate “grafting-to” and “grafting-from” bioconjugates. Proteins of interest include a robust super-folder green fluorescent protein (sfGFP) and the biologically active, neuronal-targeting protein tetanus toxin fragment C (Hc). Utilizing mutant Methanococcus jannashii synthetase/tRNA pairs specific for non-canonical amino acids (ncAAs) of unique functionality, allows for facile expression of mutant proteins with site-specific handles in E. coli. Azide-bearing ncAA mutant proteins are used to generate unique, dually-functionalized protein-polymer materials via a mild, catalyst-free cycloaddition with bisDBCO-PEG. In contrast to the “grafting-from” method, genetic installation of an ATRP-initiating ncAA allows for growth of block-polymers from the surface of proteins in a similarly site-specific manner. Self-assembled structures can then be made from the mutant protein via polymerization-induced self-assembly (PISA). These techniques, aided by genetic manipulation, produces protein-polymer materials of superior homogeneity. Currently, we are developing protocols for bioconjugation, using both grafting to and grafting from, and ultimate study of mutant sfGFP and Hc-polymer systems.
Water pollution by heavy metals presents a pervasive environmental problem. One of the most prevalent heavy metals found in drinking water is lead. Lead enters drinking water when pipes that contain lead corrode, especially where the water has high acidity or low mineral content. Currently, there are a number of methods focused on the removal of lead from drinking water, however, functionalized chitosan nanoparticles show promise as eco-friendly decontaminants.

Chitosan is a nitrogenous polysaccharide that is derived from the deacetylation of chitin and has high adsorbent properties (modifiable positions) that allow it to bind to heavy metals, such as lead. This nanoparticle has hydroxyl and amino groups which gives it an affinity to interact with other pollutants. In this study, modified chitosan nanoparticles (mCSNPs) were produced via ionotropic gelation, and then characterized using several analytical techniques. Scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM) confirmed surface morphology and that the mCSNPs were uniform in size (<100 nm) and shape. Fourier transform infrared (FTIR) spectroscopy confirmed formation of the mCSNPs. Loading studies using inductively coupled plasma mass spectrometry (ICP-MS) determined the concentration of lead adsorbed onto the surface of the mCSNPs. Briefly, various solutions with different concentrations of lead (II) ions were prepared. The mCSNPs were then submerged in the various solutions for 24 hours to determine the loading capacity of the mCSNPs and to test the threshold of the chitosan nanoparticles. The mCSNPs show promising applications in water decontamination.
Purpose: the aim of this study is to synthesize lipid-hybrid nanoparticles (LPHNs) loaded with a mixture of two antiretroviral drugs for the treatment of human immunodeficiency virus (HIV). This system which is composed of a polymeric core and a lipid shell, combines the advantages of both polymeric nanoparticles and liposomes, these advantages include the synthesis of nanoparticles from biodegradable materials with high drug loading, relatively small size and low polydispersity, adding ligands to the surface of the LPHNs for active targeting, the drug release can be easily be controlled and the produced particles have high stability.

Method: nanoprecipitation method was used, where 1.5 mL of 2.5 mg/mL solution of poly (lactic-co-glycolic acid) (PLGA) in acetonitrile, is slowly added to a stirring preheated 4% ethanol solution of soybean lethicin (150 µg/ml), the mixture is then vortexed for 3 minutes and left stirring for 2 hours, the mixture is then freeze dried for further assessment.

Results: The synthesis method is reproducible and the Z-average of the produced nanoparticles was around 120 nm with PDI of 0.3 before freeze drying, increasing the amount of the drug did not affect the size, even when the drug loading % increased from 0 % in case of the blank LPHNs to 50% in case of the drug-loaded LPHNs. Adding PEG (Mn 2050) as a cryoprotectant during freeze drying reduced the aggregation of the particles and made them easy to re-disperse. The drug loading and encapsulation efficiency were relatively high compared to other drug delivery systems.

Discussion: new aspects include designing LPHNs system to treat HIV which hasn’t been mentioned in the literature before, using a mixture of two antiretroviral drugs, the lipid nature of the surface of the particles enhances the uptake of the particles by Peyer patches to reach HIV reservoir sites.
POLY 390: Investigation of the tumor penetration capability of PVCL/OEGA/GMA nanogels using a multicellular tumor spheroid model

Changchang Zhang¹, cczhang_bme@163.com, Elisabeth Gau²,³, Wenjie Sun¹, Andrij Pich²,³, Xiangyang Shi¹. (1) Donghua University, Shanghai, China (2) RWTH Aachen University, Aachen, Germany (3) DWI–Leibniz-Institute for Interactive Materials e.V., Aachen, Germany

Current nanomedicine suffers a big challenge due to the fact that most of the nanocarrier systems such as nanoparticles (NPs), liposomes and copolymer micelles lack desired tumor penetration depth, thereby limiting their clinical translation. Unlike the nanomaterials with similar size or shape, nanogels (NGs) display excellent softness, fluidity and deformability, as well as stimuli-responsiveness under the tumor microenvironment. Herein, we report the synthesis of poly(N-vinylcaprolactam)/oligo(ethylene glycol) acrylate/glycidyl methacrylate nanogels (PVCL/OEGA/GMA NGs) with different sizes (100-500 nm), crosslinking densities, 2-methoxyethyl acrylate (MEA) contents and OEGA chain lengths by precipitation polymerization in aqueous solution and the investigation of the NGs in terms of their tumor penetration capability using a multicellular tumor spheroid (MCTs) model. The prepared NGs were well characterized with different techniques. We show that regardless of the sizes, crosslinking densities, MEA contents and OEGA chain lengths, all NGs display desired cytocompatibility in the given concentration range. In vitro cellular uptake data reveal that similar to the 2-dimensional (2-D) adherent cells, NGs with a smaller size display more enhanced cellular uptake than those having a larger size in the 3-D MCTs model. Likewise, 3-D MCTs penetration results indicate that the PVCL/OEGA/GMA NGs with the smallest size of 100 nm exhibit the deepest penetration length. We then selected the NGs with a size of 200 nm but with different physicochemical parameters to investigate their cellular uptake and tumor penetration behavior. Our data show that NGs with varying crossing densities, MEA contents and OEGA chain lengths do not have appreciable changes in terms of their cellular uptake in both 2-D and 3-D models and the penetration in the 3-D MCTs model. Our study is beneficial for the design of different PVCL-based NG systems for further cancer theranostics applications.

(a) Schematic illustration of the penetration behavior of NGs with different sizes (100-500 nm).
(b) Fluorescence intensity profile of Cy3-labeled PVCL/OEGA/GMA NGs within HeLa MCTs.
pH-triggered macromolecules are typically defined as weak basic or weak acidic structures. The acidity or basicity has been adopted by the functional groups such as tertiary amines, pyridine, phosphate and carboxylic acids are name few. These stimuli responsive polymers are potential candidates for biomedical applications. Here we are reporting for the first time pH responsive chiral amphiphilic polycarbodiimides. Polycarbodiimides are helical polymers. Each repeat unit of these polymers has amine and imine nitrogen atoms, attached to the different side groups. By changing the functional groups, we can tune the properties of the polymers. Thus, we introduced polar side groups like piperazine, morpholine and dimethylamine to the polymer backbone to induce solubility in water (Figure 1). These polymers self-assembled to form spherical micelles in water and different buffer solutions. These micelles can be used as molecule cargo and as surfactants. Furthermore, the formed micelles displayed pH dependent swelling properties. The changes occurred in the volume of the micelle with respect to the different pH and this behavior will be useful as pH responsive nanocarriers for targeted site control release molecules. The results reported here are from the Dynamic Light Scattering (DLS), Electronic Circular Dichroism (ECD), Polarized Optical Microscopy (POM), Fluorometer and Transmission Electron Microscopy (TEM).
Enteric polymers have been long used in oral drug delivery. They have been viewed as "pH-dependent" in the sense of utilizing the pH gradient along the intestine to target drug release to different intestinal segments based on the polymer's dissolution pH threshold, with the dosage form delivering the drug to the most proximal segment where the pH value exceeds that dissolution threshold. However, it has been overlooked that it is the surface pH that directly controls an enteric polymer's dissolution rate, and that this surface pH is not a function of solely the bulk pH. In this study, we investigated the effects of bulk pH and bicarbonate molarity (bicarbonate being the buffering species in the intestinal fluid in vivo) on the performance of different enteric-coated (EC) products utilizing various polymers. Our results showed that an enteric polymer's dissolution rate (and so its surface pH) is more strongly affected by bicarbonate molarity ([HCO₃⁻]) than by bulk pH, with [HCO₃⁻] seeming to be the intestinal fluid parameter limiting the in vivo performance of these polymers. This is because of the effective pKa of bicarbonate in the diffusion layer surrounding the dissolving polymer being lower than the value of ~6.1 (at physiological temperature and ionic strength) commonly encountered in literature. This is attributed to the interconversion between carbonic acid and carbon dioxide not being sufficiently rapid to maintain equilibrium in this layer under ordinary hydrodynamic conditions. These findings shed a new light on reports concerning the failure of various EC products to deliver drugs to the intestinal segments they are supposed to target. In addition, these results pose the question whether referring to enteric polymers as pH-dependent or bicarbonate molarity-dependent (with a [HCO₃⁻] gradient also existing along the intestine) would be more practical from a pharmaceutical development point of view.
The current methods of functionalization of the polyesters involve the coupling of the polyesters with the single ligand. We, herein, describe the design and development of dual-headed nanosystems for improved drug delivery across the biological barriers. The chemical modification of the commercially available polylactide-co-glycolide (PLGA) having one terminal carboxylic end with linkers with two functional heads which permits coupling with two similar or different ligands. These functional polyesters upon emulsification lead to submicron sized particles encapsulating a wide range of drugs with different physicochemical attributes. These dual-headed polymer based nanosystems show better bioavailability of the encapsulated compounds as compared to single-headed systems.

Figure showing dual-headed polymer nanosystems: a) UV-vis spectrum. (b) SEM image. (c) DLS spectrum.
POLY 394: Adipose-derived stem cell delivery system using temperature-responsive biodegradable injectable hydrogel

Yuta Yoshizaki1, y-yoshi@kansai-u.ac.jp, Hiroki Takai2, Soichiro Fujiwara2, Masaaki Ii3, Hiroaki Uchida3, Shintaro Nemoto3, Akinori Kuzuya2, Yuichi Ohya2. (1) Organization for Research and Development of Innovative Science and Technology, Kansai University, Suita, Japan (2) Dept of Chemistry Materials Eng, Kansai University, Suita, Japan (3) Osaka Medical College, Takatsuki, Japan

Polymer solutions exhibiting sol-to-gel transition in response to temperature increase can be used as injectable polymers (IPs). We previously reported tri-block copolymer constituted of poly(e-caprolactone-co-glycolic acid) (PCGA) and poly(ethylene glycol) (PEG), PCGA-b-PEG-b-PCGA (tri-PCG) as temperature-responsive biodegradable IP systems. In addition, we recently reported the biodegradable temperature-triggered covalent gelation systems exhibiting longer durations of gel state using tri-PCG attaching acryloyl groups at both termini (tri-PCG-Acryl). A mixture of tri-PCG-Acryl micelle solution and tri-PCG micelle solution containing dipentaerythritolhexakis(3-mercaptopropionate) (DPMP) as a hydrophobic hexa-functional polythiol exhibited an irreversible sol-to-gel transition by formation of covalent cross-linking. On the other hand, adipose-derived stem cells (AdSCs) attracted much attention as easily available resource of stem cells. In this study, we investigated the utility of the IP formulation as AdSC delivery system to retain administrated cells for regeneration of damaged tissues by paracrine effects of cytokines secreted from AdSCs. We investigated cell viability, mRNA expression and cytokine secretion of AdSC cultured in the IP hydrogel. AdSCs were cultured in physically cross-linked IP hydrogel (tri-PCG) or chemically cross-linked IP hydrogel ([DPMP/tri-PCG + tri-PCG-Acryl]), and then cell viability were evaluated by Live/Dead assay. Both IP hydrogels retained a certain number of viable cells. RT-PCR and ELISA analyses suggested that mRNA expression and secretion of vascular endothelial growth factor (VEGF) of the AdSCs cultured in the chemically cross-linked IP hydrogel were larger than the physically cross-linked IP hydrogel. Longer in vivo retention of the IP hydrogel injected in ischemic heart muscle were also confirmed using mice ischemic heart model compared with physically cross-linked IP hydrogel or intact AdSCs.

We report on a facile capsule-based platform for efficient encapsulation of a broad spectrum of hydrophilic compounds with molecular weight less than 1,000 g mol$^{-1}$. The encapsulated compounds extend from low-molecular weight anionic Alexa Fluor dye and cationic anticancer drug doxorubicin to FITC-dextrans with $M_w$ ranging from 4,000 to 40,000 g mol$^{-1}$. The pH-sensitive hydrogel capsules with interpenetrated network shell are synthesized by multilayer assembly of poly(methacrylic acid) (PMAA, $M_w = 150,000$ g mol$^{-1}$) and poly(N-vinylpyrrolidone) (PVPON, $M_w = 1,300,000$ g mol$^{-1}$) on 5 µm silica microparticles followed by chemical crosslinking of the PMAA multilayers. Following core dissolution, the result is a hollow microcapsule with PVPON interpenetrated in the PMAA network. The capsules exhibit reversible change in diameter with a swelling ratio of 1.5 upon pH variation from 7.5 to 5.5. Capsules crosslinked for 4 hours display high permeability toward molecules with molecular weight under 1,000 g mol$^{-1}$ at pH = 7.5 but exclude dextran molecules with $M_w \geq 40,000$ g mol$^{-1}$. Encapsulation of small molecules was achieved at pH = 7.5 followed by sealing the capsule wall with 40,000 g mol$^{-1}$ dextran at pH = 5.5. This approach results in negatively charged molecules such as Alexa Fluor being entrapped within the capsule cavity, while positively charged molecules such as DOX are encapsulated within the negatively charged capsule shell. Considering the simple post-loading approach, ability to entrap both anionic and cationic small molecules, and the pH-responsiveness of the interpenetrated network in the physiologically relevant range, these capsules offer a versatile method for controlled delivery of multiple hydrophilic compounds.
Polymeric vehicles assembled via multilayer deposition of polymers on sacrificial templates have shown promising potential as the next generation of advanced biomedical materials due to their controllable shape and stimuli-responsive properties. Multilayer microcapsules of the polyphenol, tannic acid (TA), and poly(N-vinylcaprolactam) (PVCL) are particularly interesting due to their large capacity for drug loading and ultrasound-triggered release of payload. However, there is the need for spatial localization of the delivery vehicles in the body after administration. Magnetic resonance imaging (MRI) is a powerful tool for medical diagnostics and the de-facto standard for precision imaging in medical settings. A multilayer assembly using a (PVCL-transition metal complex) copolymer that enables MRI has been developed. Currently, there is no common MRI contrast agent that can be tuned to increase contrast on demand within the human body. However, the transition metal complex tris(2,2'-bipyridine)ruthenium(II), [Ru(bpy)3]⁺² has been shown to oscillate between oxidation states that are either para- or diamagnetic as part of the Belousov-Zhabotinsky (BZ) reaction, resulting in “on/off” MRI contrast. Motivated by this capability, a series of copolymers consisting of PVCL with pendant [Ru(bpy)3]⁺² complexes with PVCL to [Ru(bpy)3]⁺² ratios of 1:1 and 2:1 were created through free radical polymerization. The ability of the copolymers to participate in redox reactions was demonstrated with 2,2-Azinobis(3-ethylbenzothiazoline-6-sulfonic acid) and a version of the BZ reagent system. We showed that these copolymers can be used to fabricate multilayer microcapsules of (PVCL-Ru/TA)n through multilayer polymer deposition onto sacrificial silica templates followed dissolution of the template. Our results indicate that these capsules may provide multimodal imaging through MRI contrast representing a step forward in the field of advanced therapeutic carriers.
POLY 397: Porous polymeric microparticles for delivery of agents to control myopia progression

Motahareh Mohammadiroudbari¹, motimhmd@uab.edu, Veronika A. Kozlovskaya², Eugenia P. Khizhniak³. (¹) Chemistry, The University of Alabama at Birmingham, Birmingham, Alabama, United States (²) Chemistry Department, University of Alabama at Birmingham, Birmingham, Alabama, United States (³) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States

Myopia is the most common refractive error of the eye that has affected more than 40% of adults in the United States. For a myopic eye, axial elongation of the eye globe causes light focusing in front of the retina instead of on it. Despite being the most effective therapy to control myopia, the direct use of atropine can exert severe systemic side effects. Conversely, scleral crosslinking of the eye backside is one of the ways to control the retina elongation; however, its clinical procedure involves the application of UV light that can damage corneal cells. Herein, we report on the synthesis of biocompatible porous poly(lactic-co-glycolic acid) (PLGA) microparticles using an oil-in-water emulsification for utilization in the delivery of atropine, or genipin, a non-toxic biocompatible scleral crosslinker. The porous microstructure, size, and shape of the microparticles obtained were analyzed using scanning electron microscopy. We have synthesized two types of porous PLGA microparticles and studied their loading with genipin or atropine. We explored a sustained release of these agents from the microparticles at pH = 7.4 and 34 °C (the eye backside temperature). Our results show that the sustained release of genipin and atropine can be achieved through both diffusion and degradation mechanisms and can be tuned by controlling the ratio of lactic-to-glycolic acid in the copolymer structure.
POLY 398: Efficient pro-oxidant cancer therapy using ROS-responsive thioether-based polymeric nanoparticles

Yoon-Seok Kim¹, Sumin Kim², Min Shim¹, min.shim@case.edu. (1) Division of Bioengineering, Incheon National University, Incheon, Korea (the Republic of) (2) Department of Pharmacy, The Catholic University of Korea, Gyeonggi-do, Korea (the Republic of)

Pro-oxidant therapy using chemical agents that can lead to cytotoxic oxidative stress in the cells has attracted great attention to cancer-specific therapy. Piperlongumine (PL) is a new class of pro-oxidant agent and has triggered cancer-selective cytotoxicity. Despite the therapeutic potency of the PL, its poor water-solubility hampers its in vivo use. Therefore, development of drug carriers that can effectively deliver the hydrophobic PL into cancer cells is highly required for efficient pro-oxidant therapy. Here, ROS-responsive thioether-bearing polymer (TEP) was developed as an effective carrier for the controlled delivery of PL into cancer cells that over-produce ROS. PL-loaded TEP nanoparticles (PL-TEP NPs) showed ROS-sensitive degradation, resulting in ROS-sensitive drug release. In addition, PL-TEP NPs exhibited higher cytotoxicity in human breast cancer cells (MCF-7) than in normal human dermal fibroblast cells (hDFB), demonstrating their cancer-specific pro-oxidant therapy. This study demonstrates that ROS-responsive TEP NPs have high potential for efficient intracellular drug delivery into cancer cells undergoing oxidative stress.

Thioether-based polymers were synthesized for the delivery of pro-oxidant piperlongumine for cancer-targeted therapy
POLY 399: Magnetic molecularly imprinted polymer nanovectors as targeted delivery systems for breast cancer treatment

Maria Nerantzaki2, maria.nerantzaki@upmc.fr, Claire Wilhelm1, Jérôme Fresnais2, Christine Ménager2, Nébéwia Griffete2. (1) Matter and Complex Systems laboratory (MSC), Paris Diderot University, Paris 07, CNRS UMR 7057, Paris, France (2) Physicochemistry Laboratory of Electrolytes and Interfacial Nanosystems (PHENIX), UMR CNRS 8234, Sorbonne University, Faculty of Science and Engineering, Paris, France

Breast cancer is the most common malignancy in women worldwide and the second most common cancer overall. It includes 1.7 million new cases per year and it is predicted that it will reach up to 22 million new cases in two decades. Surgical approaches, chemotherapy, hormonal therapies and radiotherapies can all improve breast cancer patients’ survival but when applied systemically these therapies show detrimental side effects due to their lack of tumor targeting specificity and the emergence of tumor multidrug resistance. Hence, an intense emphasis needs to be placed on the development of new technologies that allow targeted destruction of tumours by localising the delivery of therapeutic agents to the tumour region, while avoiding side-effects. In this regard, in PHENIX laboratory N. Griffete and C. Ménager developed recently an innovative magnetic delivery nanoplatform for triggered cancer therapy, showing active control over doxorubicin release by using local effect of hyperthermia. Here, we propose to take advantage of this development to design a novel magnetic system, loaded with a powerful cytotoxic anticancer agent, directed and guided towards the tumor site and preferentially fixed to the tumor to destroy it. The nanovector will combine for the first time the controlled drug release ability under alternating magnetic field (AMF) of the magnetic molecularly imprinted polymer and the excellent vitamin-tumor-targeting offered by surface-grafted biotin and folic acid molecules (Figure 1). We believe that the use of magnetic molecularly imprinted polymers, surface-decorated with tumor-targeting molecules, for drug delivery under AMF, will be a major advance in the development of multifunctional targeted drug delivery nanotechnologies and may become important theranostic tools in nanomedicine for cancer therapy.

Figure 1. Synthetic strategy for the fabrication of Vitamin (biotin/folate) decorated magnetic imprinted polymer nanoparticles containing doxorubicin, for drug release under AMF
POLY 400: Well-defined pH-responsive PEG-b-PHEMA-b-PBA based micelles for targeted delivery of doxorubicin

Mohamed Alaa Mohamed1,3, mm446@buffalo.edu, Ajay Singh1, Ahmed El-Sokkary3, Magda Akil3, Paras N. Prasad2, Chong Cheng1. (1) Department of Chemical and Biological Engineering, The state University of New York at Buffalo, Buffalo, New York, United States (2) Department of Chemistry, The State University of New York at Buffalo, Buffalo, New York, United States (3) Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Dakahlia, Egypt

pH-Responsive micelles hold substantial promise for drug delivery, but achieving tunable drug release with enhanced bioavailability remains challenging. Herein, targeted pH-responsive micelles with tunable size and crosslinking density at core-shell interface are reported for anticancer drug delivery (Figure 1). Well-defined triblock copolymer, poly(ethylene glycol)-b-poly(2-hydroxyethyl methacrylate)-b-poly(butyl acrylate) (PEG-b-PHEMA-b-PBA) functionalized with thiol-reactive olefin groups at the middle PHEMA block, was used as the building unit for micellar assembly. Covalent stabilization of the micelles was achieved through UV-induced thiol-ene crosslinking using different molar amounts pH-sensitive crosslinker. A series of doxorubicin (DOX)-loaded crosslinked and non-crosslinked micelles (CMs and NCMs) with average hydrodynamic sizes of 95.1-135.5 nm were prepared, and their in vitro DOX release at pH 7.4 and 5.5 demonstrated pH-sensitive features. Moreover, regulation of DOX release was achieved by controlling the permeability of the interfacial micellar layer via different thiol-ene ratios. The targeted CM was readily prepared using tumor targeting ligand Cyclo(Arg-Gly-Asp-D-Phe-Cys) (cRGD) through in situ conjugation during crosslinking. In vitro MTT assay revealed that NCM and CM samples are biocompatible with MCF 10A cells, and the samples exhibited significant therapeutic efficiency as compared to free DOX. Relative to the non-targeted DOX-loaded CM, cellular uptake studies demonstrated higher uptake of cRGD-decorated CM by MCF 10A cancer cells. Overall, these results indicate that crosslinking and RGD-conjugation are promising strategies to enhance the applicability of pH-responsive crosslinked polymeric micelles in anticancer drug delivery.

Figure 1: Synthesis of pH-responsive PEG-b-PHEMA-b-PBA based crosslinked micelles.
A supramolecular hydrogel system was prepared by the host-guest interaction between the α-cyclodextrin (α-CD) and poly (ethylene glycol) (PEG) chains of the poly (ethylene glycol)-block-poly (lactic acid) (PEG-b-PLA) micelles. The formation of inclusion complex (IC) crystals between α-CD and the PEG chains of the micelles was verified by different techniques. Rheological studies indicated that the gelation kinetics and the mechanical strength of the hydrogels could be modulated by the α-CD concentration. Also, the shear-thinning and self-healing properties of the hydrogels were confirmed. Doxorubicin (DOX) could be encapsulated into the hydrogels via the micelles and be released from the hydrogels sustainably, with the release rate dependent on the α-CD concentration. The released DOX showed higher inhibition efficacy against HeLa cells compared with the free drug. These attractive features, together with the superior biocompatibility, make the present hydrogels an potential injectable drug delivery system for tumour treatment.
POLY 402: Non-viral genome editing based on polymer-derived CRISPR conjugates

Wardah Ejaz, wejaz@umass.edu, Mine Canakci, Francesca Anson, Benjamin Laliberte, Jeanne A. Hardy, Barbara Osborn, Sankaran Thayumanavan. Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States

CRISPR-Cas9 (clustered regularly interspaced short palindromic repeats) has emerged as a cutting-edge genome editing technique during the past decade. Viral vectors have been commonly utilized for the delivery of Cas9-sgRNA ribonucleoprotein (RNP) in-vitro. However, their ability to integrate within the host genome and limiting packing space issue limits their use for practical purposes. That is why we envision that our polymeric platform can serve as a robust non-viral vehicle for Cas9-sgRNA RNP delivery and traceless release. To achieve this goal, we have formulated protein-polymer assemblies that are formed due to covalent self-assembly of a random copolymer, templated by Cas9 protein. Our hypothesis is that the surface exposed lysine functionalities on Cas9-sgRNA RNP can covalently react with a few polymer chains to form self-assembled structures with Cas9 at the core. A secondary crosslinker can react with remaining side-chain moieties on the polymer to form a protective sheath around the RNP, the function of which can only be revealed upon specific structural modification of the polymer because of intracellular trigger application. We have optimized several conjugation parameters to achieve ~60% encapsulation efficiency. The turn on/off feature of the assemblies has been investigated via cell-free editing assay. We have successfully shown the uptake of polymer-CRISPR conjugates inside HeLa and HEK-293 cells with final localization inside nuclei. The genome editing ability of released RNP has been shown via loss of fluorescence in GFP expressing HEK 293 cells.

Redox sensitive amphiphilic polymer to covalently conjugate CRISPR-Cas9 and proposed release mechanism
Tuning enzyme diffusion and reaction on temporal hydrogel stiffening

Hung-Yi Liu¹, liu1808@purdue.edu, Chien-Chi Lin². (1) Biomedical Engineering, Purdue University, Indianapolis, Indiana, United States (2) Indiana University-Purdue University Indianapolis, Indianapolis, Indiana, United States

Hydrogels with spatiotemporally regulated mechanics are increasingly used for studying the impact of matrix stiffness on cell behaviors. To mimic dynamic stiffening of a tumor tissue, we have reported a temporal stiffening hydrogel system via enzymatic reaction. Herein, a mathematical model was proposed to describe enzyme diffusion and reaction kinetics within a hydrogel to elucidate the critical influence of enzymatic reaction on gel stiffening. Fick’s 2nd Law of Diffusion was used to predict enzyme diffusion in a highly swollen hydrogel, whereas the Michaelis-Menten equation was harnessed to estimate enzyme-mediated stiffening. To experimentally verify model predictions, we designed a one-dimension (1D) diffusion/reaction system (Figure 1A) where a poly(ethylene glycol)-peptide (i.e., CYGGGYC) gel was crosslinked by thiol-norbornene photochemistry in a channel slide. Enzyme (i.e., tyrosinase) was supplied only in one chamber to allow for 1D diffusion/reaction. The results suggested that tyrosinase concentration, gel permeability, and diffusion path length determined stiffening profiles. Through adjusting these parameters, we predicted gel stiffening in a spatiotemporally tunable manner (Figure 1B).

![Figure 1A and 1B](image_url)
In recent years, pH-sensitive materials have drawn attentions owing to their comprehensive applications in biotechnology, medicine and pharmaceutical technology. In general, acidic or basic functional groups are employed in these materials. For instance, weak polyacids, they release protons at higher pH, forming a negatively charged polymer chain which in turn causes the structure to swell and can release cargos embedded within. At lower pH, they accept protons, leading to an uncharged polymer chain and can retain cargos. In other words, the change in charge density is the key to its pH sensitivity and it is desirable to be able to tailor the charge density at a given pH hence the swelling can be triggered at will. By mixing variable ratio of acidic and basic functional groups that cancel the charge of each other, charge-tunable surfaces can be realized. Using this concept, charge-tunable polyelectrolytes were synthesized by free-radical polymerization of methacrylic acid (MAA) containing carboxylic group and N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA) containing tertiary amine group in this work. The ratio of functional groups in the synthesized polyelectrolytes were determined using Nuclear Magnetic Resonance (NMR) and the molecular weight was determined using Static Light Scattering (SLS) with Debye plot. The charge density and the swelling behavior of polyelectrolytes with different ratios of functional groups were characterized by measuring the surface zeta-potential and mean hydrodynamic radius as a function of pH using Dynamic Light Scattering (DLS). It was found that the hydrodynamic radius increased with the zeta-potential, which indicated the charge of polymer controlled its swelling behavior. Furthermore, with increasing loading of methacrylic acid, the pH where the polymer swelled systematically increased and the surface showed more negative zeta-potential at a given pH. On the other hand, increasing loading of amine groups let the polymer swell at lower pH and higher iso-electric point. In other words, through adjusting the ratio of acidic and basic functional groups, charge-tunable polyelectrolytes were prepared and the pH that triggered the swelling can be tailored for desired applications.
POLY 405: Characterizing the structure and dynamics of styrene-maleic acid copolymer-lipid nanoparticles (SMALPS) as a membrane mimetic

Kevin Burridge¹, burridkm@miamioh.edu, Indra Sahu¹, Benjamin Harding¹, Avnika P. Bali¹, Gunjan Dixit¹, Madison T. Dolan¹, Richard Edelmann², Carole Dabney-Smith¹, Dominik Konkolewicz¹, Gary Lorigan¹. (1) Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States (2) Biology, Miami University, Oxford, Ohio, United States

The lipid nanodisk morphology is an increasingly attractive platform for spectroscopic characterization of membrane proteins, and has seen use in obtaining pure protein for X-ray crystallography, as well as NMR characterization. Lipid disks can be formed using various copolymer formulations such as peptides, or here, a copolymer of styrene and maleic acid (SMA). Due to the cost of the commercially available material, there has been interest in synthesizing materials of equal quality. Our approach has been to use Reversible Addition Fragmentation chain Transfer (RAFT), a method of controlled radical polymerization that generates polymers with a narrow size distribution. Recently, we extensively characterized the structure of lipid nanodisks made from RAFT-synthesized polymers, as well as the structure and dynamics of membrane proteins suspended therein. DLS and TEM analysis reveal comparable quality to nanodisks formed using commercial material. Analysis of line shape in CW-EPR reveals that the spin label incorporated into the transmembrane domain of a model peptide becomes more rigid after the vesicle-to-disk transition.
POLY 406: On-demand softening of hydrogels through SrtA-mediated transpeptidation

Dustin Moore\textsuperscript{2}, Matthew Arkenberg\textsuperscript{1}, markenbe@purdue.edu, Chien-Chi Lin\textsuperscript{1,2}. (1) Purdue University, Indianapolis, Indiana, United States (2) Indiana University-Purdue University Indiana, Indianapolis, Indiana, United States

The extracellular matrix (ECM) provides dynamic biophysical cues to influence cell behavior. Physiological events such as fibrosis regression and stem cell differentiation are associated with gradual softening of the ECM. In this study, we developed a cell encapsulation system capable of undergoing on-demand matrix softening independent of regular protease activity (Fig. 1A). PEG-peptide hydrogels were fabricated using peptide crosslinkers that are both sensitive and insensitive to enzymatic cleavage. Specifically, sortase A (SrtA), an enzyme widely used in molecular labeling and modification, was utilized to cleave the peptide crosslinkers containing a SrtA substrate, LPRTG. The degree of softening was tuned by adjusting the ratio of SrtA-sensitive (G: LPRTG) and SrtA-insensitive (A: LPRTA) linkers (Fig. 1B). The rate of softening was also tuned by changing the enzyme concentration. Importantly, we demonstrated that on demand softening promoted spreading of human mesenchymal stem cells (hMSCs) in 3D. Specifically, hMSCs exhibited rounded morphologies in both non-dynamic stiff and pre-softened hydrogels. On the other hand, significantly more cell spreading was observed in the dynamically softened hydrogels.

Figure 1. (A) Schematic of SrtA-mediated softening of hydrogels. (B) Effect of the ratio of nondegradable (A) and degradable (G) peptide crosslinkers on softening of PEG-A/G peptide hydrogels.
POLY 407: Robust and transparent superhydrophobic surfaces with high thermal resistance

Yeon Hee Park, Ho Sun Lim, limhs@sm.ac.kr. Department of Chemical & Biological Engineering, Sookmyung Women's University, Seoul, Korea (the Republic of)

Nanostructured superhydrophobic surfaces, inspired by the surface of the lotus leaf, are attracting interest for applications in many fields such as water repellent, anti-icing coatings. In particular, the combination of surface micro/nanostructures and materials with low surface energy is an essential prerequisite for maximizing the performance of the anti-wetting about water. In this study, we demonstrated robust and transparent superhydrophobic surfaces with high thermal resistance. We introduced silane groups into the polydimethyl siloxane (PDMS) with high heat resistance through hydrosilylation, followed by sol-gel reaction to prepare a clear coating solution. As a result, the transparent superhydrophobic surface was obtained after coating on the clean glass substrate. The water contact angles and sliding angles exhibited above 150° and below 5°. It was confirmed that the water repellency was maintained even after the heat treatment at a high temperature of 400 °C. This type of the superhydrophobic surface would provide a promising candidate as a functional coating material in a wide range of applications such as mobile glasses, heat exchange pipes, etc.
Molecularly Imprinted Polymers (MIP) are a class of polymeric materials applied in the selective identification of different types of molecules and they have thermal resistance, low cost and can be modified in order to increase their performance. Core-shell type MIP are polymers modified with a solid core that increase the ratio surface area/volume, allowing selective cavities to be more exposed and, consequently, MIP has better binding capacity. Another modification consists in remove the core to obtain hollow porous MIP; which has faster kinetic binding to analyte once the absence of core increases the analyte diffusion to the recognition sites by both outer and inner interface of the polymer layer. Therefore, the aim of this research consists in synthesis and characterization of different types of MIP; besides to compare their efficiency to identify tetracycline antibiotic. The synthesis of tetracycline MIP was conducted as follows: tetracycline interacted with acrylic acid in methanol for 3 hours to form the analyte-functional monomer complex. Then it was added ethylene glycol dimethacrylate as structural monomer and, after purge the system with N₂, benzoyl peroxide was added as radical initiator. MIP with the core of SiO₂ (MIP@SiO₂) was obtained according with the protocol above described, with the addition of 300.0 mg of vinyl modified SiO₂ nanoparticles previously synthesized. To obtain hollow porous MIP, 100.0 mg of MIP@SiO₂ where shaken in NaOH 2.0 mol L⁻¹ aqueous solution. As control were synthesized Non-Imprinted Polymers, whose synthesis were performed in the same way without adding the analyte. The materials were characterized by techniques as Scanning Electron Microscopy and Fourier Transform Infrared (Figure 1) to evaluate their physical surface. Currently, we are evaluating the efficiency of materials using HPLC and the results should be show further up. However, it is expected that the more porous the material the greater the amount adsorbed due to favouring the mass transfer in these materials.
Conventional polymer brushes consist of surface-grafted random coil polymers, typically synthesized via the grafting from method using a living radical polymerization technique. While successful, this technique still primarily limits the preparation of polymer brushes from vinyl-based monomers. Recently, there has been increased interest in the development of more rigid-rod character using aromatic rings in the backbone. However, synthesis of this type of polymer brush was not possible until the discovery of the chain growth condensation polymerization technique. Previously published research from our research group was the first demonstration of aromatic polyamide brushes synthesized using the chain-growth condensation technique. While these initial studies were very useful in developing a fundamental understanding of these new types of polymer brushes, they were limited to one monomer with a side chain of little practical interest.

The next step is focused on creating new monomers for the preparation of aromatic polyamide brushes with side chain functionalities that will allow for rigid rod polymer brushes with new properties and lead to new applications. One of the potential applications for new aromatic polyamide brushes would be in reverse osmosis (RO) distillation membranes for water desalination. Current desalination membranes are coated with aromatic polyamides, but these membranes have problems with stability and fouling. We hypothesize that using a covalently attached aromatic polyamide brush with multiple functional groups will lead to improved stability and better antifouling properties. To obtain a polymer brush with these properties, new monomers must first be synthesized, and their polymerization behavior then explored. As such, a monomer containing a protecting group, for the secondary amide proton, and an ethylene glycol monomer were successfully synthesized and characterized. Once polymerized this protecting group can be cleaved to provide the amide proton, which will provide improved physical properties via hydrogen bonding.
A polymeric membrane is widely studied for gas separation. In CO$_2$ separation, membrane process has a great advantage due to its simplicity in installation and operation. However, one major setback is the presence of minor gases. In pre-combustion carbon capture, H$_2$ is obtained as a byproduct, while syngas also contains various minor gases such as H$_2$S. The effect of minor gas has been reported by a number of research. Nevertheless, a fundamental investigation for the interaction between them has not been thoroughly studied. This study will focus on the investigation of interaction between minor gases and a popular polymeric membrane. In this study, PEBAX 2533 membrane is mainly tested for permeability of CO$_2$ and structural change. PEBAX 1657 and PDMS membranes are compared to evaluate the impact on different molecular structure. CO$_2$ are used as a feed with trace amount of H$_2$S (5-100ppm). H$_2$ and N$_2$ are added for further evaluation. Permeability test is conducted by various gas mixtures and temperature (15-70°C). Every test is triplicated and measured at steady state. Gas composition is controlled using mass flow controller and GC. Surface analysis tools, such as AFM, FT-IR, XRF, and XPS, are used to analyze the membrane surface before and after the permeability test. At low concentration of H$_2$S (less than 10ppm), the CO$_2$ permeability increases, whereas high concentration of H$_2$S causes decreased permeability. More H$_2$S added, higher activation energy of CO$_2$ permeation is observed. On the surface of the membrane which has less than 100 µm thickness, there is no sign of sulfur. However, qualitative analysis using XRF which requires a membrane thicker than 200µm shows the presence of sulfur. Therefore, the length of gas permeation path might affect the accumulation of sulfur on the membrane. In XPS analysis, bond energy of C-O bond shows notable change after 12 hours of CO$_2$ permeation inferring that C-O bond might have changed. However, with 100ppm H$_2$S, the change in bond energy is lessened compared to pure CO$_2$ result, possibly due to the competitive permeation.

![Permeability of CO2 by different H2S concentration](image-url)
In this study, we investigate the molecular diffusion of carbon dioxide through hyperbranched polyethyleneimine (HB-PEI) membrane using quantum mechanics and classical molecular dynamics simulation. The effect of various conditions are analyzed. Especially, the effect of water on the dynamics of HB-PEI and the CO2 diffusion is pursued. For this purpose, we design the HB-PEI model according to the experimental observations, and build the 3D model of HB-PEI membrane. The atomic partial charges are assigned using Mulliken population method with B3LYP and 6-31G** and the numbers of primary, secondary, and tertiary amine are determined to have the values from experiments. 3D structures are modeled to have amorphous phase. Using annealing procedure to obtain equilibrium state, the volume compression and expansion with heating and cooling are repeated 5 times, and subsequently the equilibrium MD simulation is performed. CO2 diffusion is evaluated using the mean-square displacement analysis. Then, the correlation of CO2 diffusion with the structure of HB-PEI membrane is elucidated.
Polyamide thin film composite (TFC) membranes are the most applied membranes for desalination of seawater or brackish water. However, biofouling control remains one of the greatest challenges for membrane technology. Chlorine, as a conventional disinfectant, is effective in inhibiting microbial growth, but is also detrimental to membrane performance by destroying the cross-links of polyamide layers. In the past years, efforts were focused on increasing polyamide resistance to chlorine by incorporating cycloaliphatic or aliphatic diamine monomers, coating membrane with protective layers (e.g., graphene oxide), and functionalizing polyamide layer with electron withdrawing groups. While successful, chlorine resistance was obtained at the expense of performance loss. In this work, we examined the stability of polyamide nanofiltration membranes in the presence of a novel disinfectant: peracetic acid (PAA)/hydrogen peroxide (H$_2$O$_2$) mixture. PAA/H$_2$O$_2$ mixtures have shown comparable microbial inactivation performance as chlorine, and are likely to induce less damage to polyamide membranes. The commercial DOW FILMTECH NF90 membrane was used as a model polyamide membrane, and its water flux and salt rejection were compared before and after exposure to PAA/H$_2$O$_2$ (20 -20000 ppm h). Additionally, the role of chloride concentration and pH of the feed stream in the interaction between polyamide and PAA/H$_2$O$_2$ was examined. Membrane characterization was carried out regarding surface chemical structure (FTIR and XPS), morphology (SEM and AFM), and wettability (contact angle) to provide mechanistic insight. Lastly, a cross-flow system was used to evaluate the performance of PAA/H$_2$O$_2$ mixture in terms of controlling biofouling while maintaining water flux and salt rejection.
Polyimides are widely used in many fields including semiconductor processing, gas separation/water purification, and aerospace applications. Synthesis of block-co-polyimides has been widely used to obtain materials with tailored properties despite of complex synthesis routes. Polyimide blending can be useful in replacing these complicated synthesis procedures. Most polyimides are immiscible with each other regardless of the structural similarities among them which makes the blends less attractive. Herein we report a novel technique for compatibilization of 4,4’-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA)-based polyimides. An immiscible polyimide blend can be converted into a miscible blend by using this simple technique. Scanning electron microscopy and differential scanning calorimetry were utilized to detect the miscibility of these blends.
Block polymer (BP) electrolytes are attractive alternatives to liquid, gel, or homopolymer systems because the mechanical, thermal, and conductive properties are decoupled such that enhanced stability and performance are attainable. However, as the polymer blocks are covalently bonded together, the ionic conductivity of the BP is limited in comparison to homopolymer alternatives because the polymeric segmental motion is hindered. As a method to increase conductivity, polystyrene-b-poly(oligo-oxyethylene methacrylate) [PS-b-POEM] BP was blended with more mobile, ion-conducting POEM homopolymer; the blends then were doped with lithium salts. By adding homopolymers of different molecular weights, wet brush or dry brush regimes were achieved, as confirmed via neutron reflectometry. The wet brush polymer blends increased the mobility of both the polymer and lithium as suggested by the reduction of $T_{g, \text{POEM}}$ (determined by differential scanning calorimetry) and via line narrowing in variable temperature Li-7 solid-state nuclear magnetic resonance measurements, respectively. However, the dry brush blend demonstrated an overall higher ionic conductivity (via alternating current impedance spectroscopy), likely due to the presence of homopolymer-rich ion channels. By connecting the structure of the blended BP electrolytes to their physical properties, improved designs can be developed to create safer, faster-charging, and more energy-dense lithium-ion batteries.
In this work, we consider the effect of the addition of functionalized clay particles to a polyether based polyurethane that is a candidate to be used as for flexible storage containment for a variety military fuels. We have synthesized urethanes and fully incorporated functionalized layered silicate inorganic nanoclay with concentrations varying from 0% to 15% by weight. The clays were functionalized with polar hydroxyl groups (-OH) and nonpolar long alkyl chains (-CH3-(CH2)14-CH3) and the permeation properties of commercial and military fuels were evaluated. The rate of diffusion and permeation are found to be heavily dependent on the concentration as well as the nature of the functionality of the functionalized particles. Nanoclays functionalized with nonpolar groups were found to increase the transport of fuel through the urethane membranes, while polar functionalization decreased transport.
Li-Air batteries are a unique fit for electric aircraft due to their high theoretical energy densities and their potential to leverage on-board oxygen systems. The electrolyte and cathode are the limiting factors for advancing this technology. We are investigating novel "electrolyte and cathode engineering" concepts to enable Li-Air batteries with high practical energy densities, rechargeability and safety. New stable electrolytes and cathodes are being designed and fabricated for Li-Air batteries and tested in an electric flight. An array of various electrolytes were screened and analyzed using NMR and GC-MS techniques to understand the fundamental decomposition mechanisms at the cathode surface and within the porous polymer separator. This work integrates predictive computation with the experimental screening approach to elucidate the electrolyte decomposition mechanisms.
Both Kevlar\textsuperscript{TM} and bisphenol-A based polycarbonate are leading impact resistant materials; Kevlar\textsuperscript{TM} by high tensile strength and polycarbonate by $\beta$-transition vibrational modes. The goal is to synthesize a material that combines the desirable characteristics of both Kevlar\textsuperscript{TM} and polycarbonate by engineering a repeat unit structure with both amide groups and notable beta-transitions.

Polymers from 1,4-cyclohexanedicarboxylic acid isomers and hexamethylenediamine were prepared via interfacial polymerizations. The \textit{cis} and \textit{trans} isomers of this cyclic carboxylic acid have different thermal and mechanical properties. The properties of the pure materials were investigated along with blends of \textit{cis}/\textit{trans} isomers. The properties of each isomer are markedly different; \textit{cis} is fully amorphous while \textit{trans} is highly crystalline. The data is supported by solid-state NMR molecular mobility experiments and thermal analysis. The \textit{cis} isomer was polymerized into the \textit{trans} at loadings of 1-10 mol\%. The \textit{cis}/\textit{trans} polyamides were characterized by Fourier-transform infrared spectroscopy and differential scanning calorimetry. These analyses highlight differences in hydrogen bonding, bond strength, and crystallinity with increasing \textit{cis} content.
Bicyclic guanidines are a potent class of organocatalysts that mediate ring-opening polymerization (ROP) of lactide and other lactone monomers. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) is a bicyclic guanidine that mediates ROP of lactide at room temperature and can complete polymerization in a matter of seconds (Scheme 1). However, the relative rate of transesterification can compete with the rate of polymerization, broadening molecular weight distributions of the formed polymers. A related bicyclic guanidine, TBO, has been compared with TBD in ester aminolysis and ROP reactions and shown to require higher temperatures and longer reaction times to reach complete monomer conversion. The aim of this study is to synthesize a homologous series of bicyclic guanidines in which the ring size is systematically varied. It is hypothesized that the active site geometry of TBD explains its high reactivity, and one-carbon deletion in the ring structure of the related guanidine TBN will result in diminished catalytic rates. Polymerization data for these catalysts are presented, in addition to screening data for various lactone monomers.

Scheme 1: Ring-opening polymerization of lactide with bicyclic guanidine organocatalysts.
Small molecules capable of molecular recognition have been heavily employed for sensing and remediation of chemical warfare agents and biological/environmental analytes. For these types of applications, it is useful to incorporate the sensing moiety into a composite or polymeric material for on-site ease of use. Utilizing perfluoropyridine (PFPy) as an orthogonal building block, a bio-based trifunctional monomer with integrated hydrogen bond-mediated sensing capabilities, was realized. Furthermore, straightforward polymer development was envisioned through the incorporation of click-able end groups. This work will highlight monomer design and synthesis, as well as, the results of the initial binding studies. The use of the monomer in polymeric materials was also investigated and will be discussed in more detail.
Poly(ethylene terephthalate) (PET) and poly(ethylene) (PE) are among the most common plastics produced today. Together, they are often used in multilayer film for food wrappers and other gas/water vapor barrier products and constituent one of the largest offenders insofar as oceanic waste is concerned. Unfortunately, multicomponent systems such as these are challenging to recycle due to the difficulty in separating the layer components and the immiscibility that exists between the components during the recycling process. Towards this end, we have prepared several compatibilizers that could be utilized in improving the recyclability of mixed plastic waste streams such as PET-PE. Synthetic details and characterization of the compatibilizers will be discussed as well as data supporting the notion that these materials can help to improve the miscibility of PET and PE during reprocessing.
Polyhedral oligomeric silsesquioxane (POSS) containing compounds have become increasingly prevalent in both academic and functionality-based pursuits. With the addition of fluorine, these nanostructures have shown the ability to be valuable additions to polymers and composites for their unique properties, which include low surface energy, increased surface roughness, chemical stability, and mechanical robustness. In this work, perfluorocyclopentene (PFCP)-POSS monomers of differing side chain length were synthesized utilizing PFCP as building block for monomer design. Polymers of varying weight percent of PFCP-POSS were prepared via radical initiated chain growth polymerization techniques and characterized using TGA, DSC, GPC, and $^1$H/$^{19}$F NMR. Furthermore, in order to fully understand the effects of the POSS cage and side chain length on the PFCP-POSS polymers and their properties, model compounds were also prepared and polymerized. The results of these studies will be further discussed.
Most starting materials used to synthesize commercial polymers are sourced from petroleum. However, there is a movement in the chemical industry towards new bio-based starting materials as these are increasingly more attractive on a cost and performance basis for industrial use. For example, the four-carbon diacid, succinic acid (SA) has been identified by the Department of Energy (DoE) as a potential large volume sustainably-produced starting material that could replace the six-carbon petroleum-based diacid, adipic acid (AA), in polymers. In this work, we compare the properties of copolymers and blends made from SA with BDO and HDO at 2000 Da ($n=11$) and 1000 Da ($n=6$) to explore the role of repeat length on solubility, crystal structure, and melting point. We find both co-crystallization and the uncommon occurrence of double crystallization in these systems. We use this information to understand the role of average repeat length and percent co-monomer composition for the properties of these systems.
POLY 423: Preparation of perfluoropolyether-modified nanoparticles for improved fluoropolymer filament compatibilization for 3D-printed structural energetics

Bradley Martin¹, C19bradley.martin@usafa.edu, Joseph Mates², Jena McCollum³, Scott T. Iacono¹. (1) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (2) Air Force Research Laboratory, Edwards AFB, California, United States (3) Department of Mechanical and Aerospace Engineering, University of Colorado, Colorado Springs, Colorado, United States

Perfluoropolyethers (PFPEs) serve as an oxidizer when blended with micro- or nanometer sized aluminum fuel and have previously been shown to produce energetic composites in pour-molded epoxy resins, electrospun fibers, and foamed poly(urethane)s. However, various heated and/or solvent processing conditions have been shown to physio-desorb the PFPE from the aluminum particles thus lowering potential energetic performance. In order to circumvent this, we have utilized the chemical bonding of carboxylic acid functionalized PFPE to the oxide monolayer on aluminum particles. This work will discuss the preparation, characterization, and thermal properties of this system and their potential application in fused deposition for 3D printed structural energetic components.
Since the 1950s, metal-containing fluoropolymer composites have been used in military applications as thermites for pyrolant flares and rocket propellants. While metal powders are traditionally used as the fuel component in almost all conventional flagrant-based energetic materials, recent efforts have focused on optimizing fuel/matrix interface in order to accommodate a higher weight percent loading of nanoaluminum (n-AL). In this work, partially fluorinated perfluorocyclobutyl aryl ether (PFCB) fibers loaded with an energetic blend of n-Al pre-coated with perfluoropolyether (PEFE) were successfully fabricated via electrospinning producing energetic non-woven mats. Microfibers of consistent diameter were successfully generated with loadings up to 60 wt% n-Al/PFPE (18 wt% n-Al content) incorporated into the fiber. The prepared metalized fibers were more consistent in diameter and possessed n-Al loadings an order of magnitude higher than our previously reported polystyrene-based electrospun fibers. Other details of these metalized fiber composites including their fabrication, characterization, and thermal properties will be presented.
POLY 425: Polysilazane preceramic polymer formulations of differing crosslink densities

Nicholas L. Williams¹, Nicholas.Williams@usafa.edu, Timothy Pruyn², Abby R. Jennings¹. (1) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (2) Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, Ohio, United States

Previous work with polysilazane polymers has demonstrated that additive manufacturing can be used to obtain unique structural preceramics via radical initiated 3D printing techniques. However, once the structures are converted into ceramics via pyrolysis at temperatures above 1000 °C, they are often plagued with brittleness, low rigidity, and non-uniform volume loss. In an effort to understand and combat these issues, this work aims to investigate the network properties of both the pre- and post-pyrolyzed polysilazane networks as a function of crosslink density. These studies focus on thiol-ene networks formed between vinyl polysilazane oligomers and various multifunctional thiols. Samples were characterized by TGA, DSC, DMA, and SEM. Preliminary rheology studies were also performed. The results of these studies will be discussed in further detail.

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\text{Thiol-ene Networks}
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Supramolecular molecules can be implemented in a variety of ways, but this research focused on the ability of chiral, helical polymers to act as an enantioselective catalyst. To conduct this research, benzene 1-monourea-3,5-bisamide (BUBA) monomers were synthesized. Then the monomers self-assembly properties were characterized, and chiral amplification was achieved. The amplification was tested by putting an achiral BUBA ligand with small amounts of chiral BUBA monomer. This led to the formation of chirally amplified supramolecular helical scaffolds. The tests to observe the self-assembly and the chirality amplification properties of the BUBA monomers were done using circular dichroism (CD) and infrared spectroscopy (IR). The helices were then coordinated to copper to act as an enantioselective catalyst. The capability of the copper catalyst to conduct enantioselective reactions was tested in a reaction of reference: the hydrosilylation of prochiral aromatic ketones.
This research explores the synthesis of a polymer based on cyclopentadithiophene (CPDT) and difurodiketopyrrolopyrrole (DFDPP) comomers. This work differs from previously published compounds due to an ethynyl spacer between the comomers, which will provide less steric interactions between the alkyl chains. The DPP comomer will be synthesized via published methods and then brominated with NBS. The dibromodihexylcyclopentadithiophene comomer will be treated with trimethylsilylacetylene under Sonogashira conditions to yield the ethynyl comomer. The final polymer will be produced via another Sonogashira reaction of the deprotected CPDT ethynyl and dibromoDPP comomers. This polymer will be characterized via FTIR, 1HNMR, and GPC. The optical band gap will be determined from solid UV-Vis absorbance. This organic polymer will be employed in the construction of bulk heterojunction hybrid solar cells with a colleague at South Dakota State University.
A new class of easily synthesized, tunable organic photochromic materials, termed Donor-Acceptor Stenhouse Adducts (DASAs), has recently been developed. Upon irradiation with non-invasive visible to near-infrared light, these materials switch from a colored, hydrophobic extended form to a colorless, hydrophilic compact form. These light responsive molecules have set into motion a new and potentially powerful way to harness mechanical work controlled by visible light. Our group is currently exploring their equilibria, reactivity, optical properties and switching ability based on environmental factors. Guided by these studies, we aim to expand upon the already diverse range of applications by designing new functional polymers.
POLY 429: Investigating optimal reaction conditions for the synthesis of Polylactic Acid (PLA)

Edward Garza, earsha79@mail.stmarytx.edu, Richard Bui, rbui@mail.stmarytx.edu, Jose Tormos. Department of Chemistry/Biochemistry, St. Mary's University, San Antonio, Texas, United States

Polylactic acid (PLA) is a biodegradable polymer that has gained attention for its potential uses in mechanical engineering (3-D printing), as well as in the biomedical field. PLA has been described as an aliphatic polyester and can be synthesized on an industrial scale via fermentation and polymerization using agricultural materials, such as cornstarch. Polymerization processes include ring opening polymerization (ROP), prepolymer chain coupling, and azeotropic dehydrative condensation. Because methods such as ROP have toxic components and byproducts, this project was mainly focused on polymerization via azeotropic dehydrative condensation. This project was carried out in collaboration with Dr. Amber McClung from the Department of Engineering at St. Mary’s University. Our research was focused in synthesizing PLA while controlling the temperature of the reaction. This was done in two ways, one by varying the addition of catalyst and solvent, while keeping the reaction time and temperature constant. The other by incorporating graphene (a semimetal of flat polycyclic aromatic hydrocarbons), and lignin (a complex organic polymer found in plants) into the PLA to determine if their changes would cause any changes in viscosity or in the structural integrity of the polymer.

From left to right, we have a cube or normal PLA, PLA infused with lignin, and PLA infused with graphene
Making microfluidic devices or chips to be used in biological systems from three-dimensional printers is a new and evolving field in research. In order to find the best method for making the devices, different molds and gels are being used to evaluate which system works best. Instead of working with a single chip, the idea for this project is to create and build a three-dimensional in-vivo system where cells can have more freedom as they grow. This helps to specialize the device, meaning cells from one particular tissue system or organ system can be cultivated and tested for biomarkers, proteins, etc., in relation to that specific organ. To create this device, an inverse LEGO® will be printed using a three dimensional printer and PDMS will be used to fill the mold. The use of PDMS will allow the flow of liquid to be visually seen inside the device. Once multiple LEGO® systems are built, they can be stacked together in different ways to generate a specific region for cell cultivation with passage for fluid to flow. Sample collection on the other side of the channel for off-line analysis can then take place. This ability to stack is vital for the proper evaluation of cell placement within the device so that optimal results are able to be observed. The development of designing the device in Tinkercad, printing the inverse LEGO® mold, the process of making the PDMS blocks, assembling the blocks, and testing the flow within the device will be presented.
POLY 431: Poly(4-vinylpyridine-N-oxide) as an oxygen atom transfer reagent

Gretchen Fata, gretchen.fata@hope.edu, Chloe Hutchison, chloe.hutchison@hope.edu, Chris R. Turlington. Chemistry, Hope College, Holland, Michigan, United States

Pyridine-N-oxide is an oxygen atom transfer (OAT) reagent used as a stoichiometric oxidant in metal-catalyzed oxidation reactions. A polymer derivative of the N-oxide, poly(4-vinylpyridine-N-oxide), was discovered in the 1960’s, but has not been investigated in OAT reactions. Could the insoluble poly(4-vinylpyridine-N-oxide), here called PVP-N-oxide, offer advantages over the molecular pyridine-N-oxide? PVP-N-oxide was synthesized and its reactivity compared to pyridine-N-oxide in the oxidation of phosphines and phosphites. Metal-catalyzed reactions were attempted with PVP-N-oxide. Recycling and reuse of the polymer backbone are described.
Traditional archetypes for radical polymerization catalysts and organic group transfer polymerization catalysts offer poor control of tacticity in the polymerization of methacrylates. Here, chiral organic catalysts and chiral organic additives are employed in order to evaluate their influence on poly(methacrylate) tacticity. Methyl methacrylate was polymerized with chiral N-heterocyclic carbenes or in the presence of chiral thioureas. The tacticity of poly(methyl methacrylate) samples was determined by NMR spectroscopy and differential scanning calorimetry (DSC). Effects on molecular weight and dispersity are also discussed.
Sulfur is fairly inexpensive and abundant because of its production as a by product in oil refining. In this experiment, elemental sulfur is polymerized with divinylbenzene, creating a highly cross linked polymer via inverse vulcanization. Inverse vulcanization is a solvent free and fast reaction method to form polysulfides. The sulfur is heated, breaking the sulfur ring into radicals, where DVB is then incorporated, producing poly(S-DVB). Poly(S-DVB) is then reduced using sodium borohydride as the reducing agent and dichloromethane as the solvent. The reduction of poly(S-DVB) creates thiol functional groups as a result of cleaving the disulfide bonds. This reaction also eliminates the need for protecting groups to prevent other compounds from binding during polymerization. The poly(S-DVB) is characterized using gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) to examine the polymer molecular weights and structure respectively both before and after reduction. Poly(S-DVB) with different ratios of elemental sulfur and DVB will be made and analyzed using GPC to test for different starting molecular weights and observe changes to the molecular weight after it has been reduced. NMR data indicates a new peak growing in after being reduced indicative of thiol formation. Thiol groups can react with a variety of different functional groups via click chemistry. This will allow the structure of the poly(S-DVB) to be easily modified. Model compounds such as bromoanthracine were bound to reduced poly(S-DVB). This reaction was characterized using UV-Vis spectroscopy.
POLY 434: Synthesis and characterization of networked fatty acid based polymers

Mitchell Maw, mitchellmaw1@gmail.com, Robert W. Kopitzke. Winona State University, Winona, Minnesota, United States

Bio-based polymer features of biodegradability and compostability are desirable to combat the harmful environmental effects of petroleum-based polymers. Versatility of fatty acids derived from plant oils have been displayed in the production of polyesters, polyamides, and polyurethanes. With an objective to successfully utilize whole natural oils in the synthesis networked polymers, a three-fold procedure was investigated. High oleic sunflower oil was subjected to fatty acid methyl ester (FAME) synthesis. Subsequently, the FAME’s were oligomerized by transesterification with molecules of variable hydroxyl functionalization. Lastly, these oligomers were networked via the radical polymerization of the unsaturation in their hydrocarbon tails. The oligomers were characterized by Mass Spectroscopy (MS) and $^{13}$C Nuclear Magnetic Resonance (NMR) spectroscopy. The networked polymers were characterized by Differential Scanning Calorimetry (DSC) and thermal stability by Thermogravimetric Analysis (TGA).

Scheme 1. Networked Fatty Acid based biopolymer synthesis
Additive manufacturing, or 3D printing, allows users to explore the design and production of highly complex and specific custom parts with ease. However, traditional additive manufacturing employs time consuming layer-by-layer processes, leading to structural defects throughout the printed part. Additionally, the scope of materials is limited to a single chemistry at a time unless the ink/resin is changed in the middle of printing. To alleviate these issues, we have developed a one-pot, wavelength selective resin for the simultaneous curing of multiple chemistries in a single part. By design, these resins have highly connected interfaces more robust than those produced through more standard multi-material techniques (e.g. direct write). In this work, we present compositional and mechanical studies to demonstrate the strength of this new class of multi-material resins.
Thiol-ene ‘click’ photopolymerization was utilized to prepare a series of phosphonium-containing, covalently crosslinked poly(ionic liquid) networks. Several bis-phosphonium-containing ‘ene’ monomers were prepared with variable alkyl chain linkers (R = C4 or C12), ‘ene’ end-groups (allyl vs. hexenyl) and/or R groups on the phosphorous atom (alkyl vs. phenyl) in order to determine how changes in the monomer structure effected the thermal, mechanical and conductive properties of the resulting networks. Conductivity, as determined from dielectric relaxation spectroscopy (DRS) measurements, indicated that glass transition temperature (Tg) plays a major role in determining the ionic conductivity. Preliminary results concerning using these PILs as binders in lithium ion batteries will be discussed.
The seeds of *Brassica carinata*, more commonly known as Ethiopian Mustard, contain oil that can be utilized in advanced jet fuel and bio-diesel. In some places, crops of this plant are being grown in large quantities for this purpose, but large amounts of waste material remain post-production. Extracting a useful starting material from this waste material that can be functionalized and polymerized to yield materials with similar properties to commodity plastics provides a viable option for “greener” plastics, as the majority of feedstock chemicals used for plastic production are petroleum-based. Through simple base hydrolysis, a biorenewable monomer is extracted from plant matter, modified, and polymerized. By controlling the ratios of modified monomers and reaction conditions, copolymers with tunable thermal properties similar to those seen in commercial plastics are obtained. Identities of monomers are confirmed by NMR spectra, and molecular weights are confirmed by HFIP GPC. Thermal properties are shown by DSC thermograms.
Polyimide (PI) aerogels are highly porous, lightweight materials with excellent thermal properties, due to the highly porous network structure, high surface area, and nanoscale pore size, ideal for insulation applications in extreme environments. Recently, PI aerogels were synthesized with a fluorocarbon backbone resulting in greater optical transparency, which could be used for insulated window applications or as alternative substrates for electronic screens. Fluorinated PI aerogel developed by the NASA Glenn Research Center Aerogel Research Team were studied using novel thermal carbon analysis (TCA). This method quantifies carbon mass through temperature ramp evolution and pyrolysis first in inert atmosphere of helium followed by heating in presence of oxygen. The evolved/pyrolyzed products are converted to methane and detected by flame ionization detector. The TCA was employed to investigate thermal properties of the transparent PI aerogels and provide quantitative evolution profile matching qualitative thermal desorption pyrolysis gas chromatography mass spectrometry (TD-Py GC-MS). TCA quantified carbon mass correlated with predicted values based on formulated carbon mass percentages for all aerogel samples with an R2 value of 0.98. The analysis also showed that increase in fluorine monomer fraction of tested polymers resulted in decreased carbon mass loss during the He atmosphere temperature ramp. This decrease was most apparent in PI aerogels with the median chain length between crosslinks (50 dimer units). TD-Py GC-MS analysis showed reduced variation in pyrolysis products, as fluorination in the polymer chain increased.
Metal-organic frameworks (MOFs) are three-dimensional networks comprised of metal clusters, regularly spaced and adjoined by rigid organic linker molecules. MOFs have emerged as a versatile class of crystalline materials with ultra-high porosity and large specific surface areas. However, MOFs have seen limited commercial use due to poor longevity in atmospheric conditions. Polymer-MOF hybrids (polyMOFs) have been developed to circumvent this issue by adjoining carboxylate-containing linker molecules along a polymer backbone, protecting the framework from moisture contamination. This work sought to elucidate the role of connectivity in polyMOFs, especially how blocky polyMOF architectures could span across multiple crystalline domains. To that end, we synthesized a poly(2,5-dihydroxy-benzenedicarboxylate) (polyDHBDC) by sequential modification of DHBDC via Williamson ether synthesis and subsequent polymerization via acyclic diene metathesis. We confirmed the formation of a polymer by $^1$H NMR and size-exclusion chromatography. The parent-MOF UiO-66 was fabricated and X-ray diffraction (XRD) patterns were collected to confirm appropriate crystalline structures. Future work will include the copolymerization of DHBDC in the presence of various soft $\alpha,\omega$-alkene-terminated oligomers and the study of copolymerization kinetics, as well as the optimization of the DHBDC polymerization conditions to form the expected polyMOFs. We anticipate that the resulting materials will afford more robust and ultimately more versatile MOF hybrids.
POLY 440: Synthesis of thermosensitive copolymers for the modification of polysaccharides

Charles Barrios¹,³, cjbarrios@bsu.edu, Courtney Jenkins², Rachel Auzely-Velty³. (1) Chemistry, Ball State, Muncie, Indiana, United States (2) Chemistry, Ball State University, Muncie, Indiana, United States (3) CERMAV-CNRS, Grenoble, France

Stimuli responsive polymers can undergo drastic changes in properties by responding to subtle changes in the environment. One specific type is thermoresponsive polymers, which are soluble in water but rapidly precipitate when heated to a specific temperature. The lower bound of this phase change is called the lower critical solubility temperature (LCST). Typically an LCST of lower than room temperature is targeted. This project focuses on synthesizing terminally functionalized thermosensitive polymers that allow for the grafting natural polysaccharides. This is particularly interesting because grafting natural polysaccharides such as hyaluronic acid onto the polymer forms a hybrid polymer that retains properties of both the synthetic and natural polymers. This can potentially form thermosensitive hydrogels that can release drugs in a controlled manner. Norbornene (NB) derivatives, all difunctionalized at the 2 and 3 carbons, were used as the monomers to control of the polymer architecture enabling the size and polarity to be easily controlled. The polymers were synthesized using ring opening metathesis polymerization with Grubbs’ 1st generation catalyst. The target LCST was a max of 25 ºC. Polymers of different molecular weights with various monomers were synthesized to optimize the LCST. A homopolymer of NB functionalized with methyl carboxylate (NBDMC), a homopolymer of NB functionalized with triethylene glycol (NBTEG), and a copolymer of both species were explored. The polymerizations were terminated with 4-penten-1-ol. A variety of terminating agents were studied to find the optimal terminating agent for grafting the polysaccharide. The polymerization of NBDMC achieved a Mn of 12000 g/mol and was not soluble in phosphate buffer solution. The homopolymer of NBTEG achieved Mn’s of 35,000 and 14,000 and an LCST of 27 ºC and 28 ºC respectively. The copolymer consisted of a 2:1 ratio of NBTEG: NBDMC. This achieved a Mn of 30,000 and an LCST of 17 ºC. The polymers were characterized via 400 MHz ¹H NMR, gel permeation chromatography, dynamic light scattering, and TLC.
Our group has recently developed a method for the synthesis of block copolymers incorporating diallylammonium blocks. This method involves the use of a functionalized photoiniferter to produce end-functional polydiallylammonium oligomers, which are then copolymerized with polysulfone comonomers in a step-growth reaction. We have continued to explore this method for making multiblock copolymers in order to investigate the synthesis of a variety of copolymers. Amine and carboxylic acid functionalized photoiniferters have been prepared with the goal of producing polyamides and polyesters. The presentation will describe the synthesis and characterization of the functionalized oligomers and the preparation of new multiblock copolymers.

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\[A^- = \text{anion}\]

linking group between the hydrophobic polymer and the diallylammonium polymer repeated structure to represent multiblock copolymer
Siloxane polymers, or silicones, are widely used materials found in a variety of applications owing to their excellent thermal, chemical, and physical properties. However, silicones themselves also have a few undesirable properties, including thermal degradation via back-biting depolymerizations and significant reactivity with Lewis acids and bases. In order to overcome these limitations as well as incorporate additional attributes, such as improved mechanical or optical properties, “hybrid” silicones are necessary. Herein, we describe the preparation of polymers prepared by the copolymerization of divinyl-terminated and dihydridosilyl monomers via platinum-catalyzed hydrosilylation reactions in a one-pot process. The copolymers produced are perfectly alternating and can incorporate organic segments into the silicone backbone. Of particular interest is the presence of cyclic aromatic and non-aromatic repeat units on the physical, thermal, and optical properties. Thermal and optical characterizations of these polymers show increased thermal stability as well as changes in refractive index and UV absorption depending on comonomer and ratio.
Poly(quinoline)s, and derivatives thereof, have been of both academic and industrial research for decades owing to their incredible chemical stability, optical and electrical properties, as well as their robust mechanical qualities. However, while these polymers are well-known to have amazing properties, synthesis of these polymers has generally been tedious, with difficult multi-step procedures, limited monomer selections, and poor solubilities. Over the last several years, the use of [4+2]-cycloadditions, the so-called Povarov or aza-Diels-Alder reaction, has been utilized for the preparation of small molecule quinolines and diazaanthracenes, but has seen only limited use in polymer synthesis. Herein, we describe the preparation of polymers from simple, commercially available monomers in a one-pot synthesis utilizing cycloadditions of diimines and divinyl compounds. Inclusion of alkyl side groups is shown to improve solubility of the resulting polymers and improve degree of polymerizations. Chemical structures are analyzed via FTIR and NMR. UV-Vis analysis reveals extended π-conjugated systems with excellent absorptions within the UV range (sub-400 nm).
Nanotechnology based drug delivery systems have been used and developed widely in recent years. Pseudo-polyrotaxane, polyrotaxane, and their supramolecular structures are the results of host-guest interactions. The host in his study is β-cyclodextrin (β-CD) and the guest is poly(ethylene glycol) (PEG). Previous studies that were initiated by Harada et al in 1993 suggest that PEG does not form inclusion complex with β-CD. But our recent studies suggest that β-CD forms crystalline inclusion complexes or pseudo-polyrotaxane structures with poly(ethylene glycol) of two molecular weights MW= 600 and 1500 supporting the first PEG–β-CD single crystalline structure reported by Udachin et al in 2000. The complexation of β-CD with the hydrophilic PEG increases the solubility in water thus overcoming restrictions on biomedical applications. This study is to investigate different molecular weights of PEGs, and to examine the results of the end capping of the PEGs once included within the β-CD.
Today, bacteria are becoming increasingly resistant to antibiotics. Additionally, the formation of biofilms on medically implanted devices, such as catheters and vascular patches, almost certainly calls for treatment through use of antibiotics or other means. Considering biofilms are already very difficult to fully remove, a non-antibiotic solution is needed to ensure biofilms will not be formed in the first place. Covalent attachment of bacteriophages to polymer surfaces allows polymeric-based medical devices to maintain their bulk properties while preventing biofilm formation of selective pathogenic bacteria strains, thus not affecting the patient's natural bacterial flora. Bacteriophages work by injecting their host bacteria with genetic material and using the host for replication resulting in the release of many progeny bacteriophages and an amplified antimicrobial effect. These studies utilize microwave generated plasma reactions in the presence of maleic anhydride to create carboxylic acid groups on medically relevant but inert polytetrafluoroethylene (PTFE) and ultra-high molecular weight polyethylene (PE) surfaces. Φ11 bacteriophages are then covalently attached using carbodiimide coupling chemistry. The PTFE and PE surfaces exhibiting Φ11 bacteriophages display antimicrobial activity against Staphylococcus aureus human pathogen and prevent biofilm formation.
Chitosan-based drug delivery systems show great potential in the treatment of various diseases over the past few decades. Chitosan is a natural based cationic polymer that is produced from alkaline deacetylation of chitin. This polymer has attracted much attention in the area of drug delivery due to its muco-adhesive, nontoxic, biodegradable, and biocompatible properties. Despite its many advantages, however, chitosan has limitations in sustained drug release because it has a high tendency to swell in an aqueous environment resulting in a fast release (burst effect) of the drug during drug delivery. In this study, chitosan was complexed with polyethylene glycol (PEG), polyacrylic acid (PAA), polylactic acid (PLA) in order to extend the release of bovine serum albumin (BSA) under physiological conditions. Modified chitosan nanoparticles (mCSNPs) were prepared via crosslinking. The mCSNPs were then characterized via scanning electron microscopy (SEM) and atomic force microscopy (AFM) for surface morphology and size (<100nm). Fourier Transform Infrared Spectroscopy (FTIR) confirmed the formation of the mCSNPs. Loading and release studies were then carried out to test the loading capacity of the mCSNPs as well as the release time of BSA under physiological conditions. We discovered that the PEG mCSNPs showed a greater decrease in release of the BSA than the unmodified CSNPs. These mCSNPs have potential applications in sustained drug release.
POLY 447: Effect of hydrogenation on conductivity and glass transition temperature in novel oxanorbornene dicarboximide based polymers

Andrew Riedl¹, riedlaj@plu.edu, Dean A. Waldow². (1) Chemistry, Pacific Lutheran University, Graham, Washington, United States (2) Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

Solid polymer electrolytes are a promising alternative to small molecule organic electrolytes to increase safety in lithium ion batteries. Two polymers have been synthesized by ring opening metathesis polymerization (ROMP) to study the decoupling of segmental motion and ion conductivity with an increase in backbone rigidity due to pi stacking. These polymers have an oxanorbornene dicarboximide backbone where one polymer has a side chain with three units of ethylene oxide and the other polymer has a xylene group between the backbone and the same ethylene oxide side chain. Additionally, these polymers have been hydrogenated using Wilkinson’s catalyst to produce potentially more stable electrolytes. Conductivity measurements using dielectric spectroscopy of these polymers will be presented. The influence of pi stacking on segmental motion and changes to the glass transition temperatures will be used to interpret the conductivity results.
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and light-activated ATRP was utilized to incorporate DA linkages at various locations within the polymer backbone and side chain. By utilizing different DA linkages, polymer composition and topology were controlled upon the application of a thermal stimulus, including inversion of composition and variation in topology.[figure1]
POLY 449: Degradable imine-containing core-crosslinked star polymers

Michael B. Sims¹, Johann Rapp¹, johann.rapp@ufl.edu, Sofia Goodrich¹, Mingrui Li¹, Brent S. Sumerlin². (¹) University of Florida, Gainesville, Florida, United States (²) Department of Chemistry, University of Florida, Gainesville, Florida, United States

Branched polymeric architectures have attracted considerable research interest due to their distinct physical properties and ability to facilitate unique stimuli-responsive behavior. A subset of this class of architectures, star polymers consist of a densely connected center with linear “arms” radiating from it, providing a large molecular structure that can serve many purposes. Core-crosslinked star polymers with degradable cores have the potential to act as small molecule delivery agents by dissociating into linear arm polymers with an accompanying release of internalized cargo, however means to control this process still remains elusive. In this work, we utilize photoiniferter-mediated polymerization to prepare star polymers crosslinked with degradable imine linkages. Importantly, this approach allows the rate of core degradation to be controlled through modification of the imine N-substituent. Star polymers were prepared through an “arm-first” synthetic approach, in which a linear macroinitiator was chain extended with divinyl imine-containing crosslinkers to form the target star architecture. First, macroinitiator arms were prepared by photoiniferter-mediated polymerization of N,N-dimethylacrylamide, which preserves reactive trithiocarbonate end-groups for subsequent chain extension with multivinyl crosslinkers. Next, these macroinitiators were converted into star polymers via a similar photoiniferter polymerization in the presence of divinyl crosslinkers. We synthesized and evaluated crosslinkers containing oxime, semicarbazone, and hydrazone functional groups to serve as degradable crosslinks which create the core of the star polymer. Various factors such as the time spent irradiating, the addition of a diacetone acrylamide comonomer and crosslinker identities were precisely tuned to optimize crosslinker synthesis. After the synthetic procedure was optimized, the rate at which star polymers degraded under acidic conditions into lower molecular weight structures was analyzed by dynamic light scattering, and the extent to which the measured degradation rates correlated to a release of encapsulated dye cargo was also evaluated.
Many instructors are hesitant to adopt teaching lab experiments that use tin (II) 2-ethylhexanoate (Sn(Oct)$_2$) as a ring-opening transesterification polymerization (ROTEP) catalyst due to toxicity and environmental concerns. Recent literature reported that bismuth (III) subsalicylate (BiSS), the active ingredient in the over-the-counter medication Pepto-Bismol, was an effective catalyst for ROTEP of L-lactide. Previous researchers developed a teaching experiment that employed BiSS as the catalyst in end block formation of a triblock polymer. A pilot run of the experiment in Spring 2018 was encouraging, but several areas of improvement were identified. The objective of the current research is to improve yield and the physical copolymer properties produced in this lab experiment.

The procedure involves synthesizing a poly($\beta$-valerolactone) (PVL) homopolymer on Day 1 and end-blocking it with poly(L-lactide) (PLA) on Day 2 using the BiSS catalyst. Through a series of trials, revisions were made that improved student yield and PLA incorporation when implemented in a laboratory for the second time. Additionally, research to improve the mechanical properties of the copolymer is being done by varying the composition of the midblock. Overall, both data and student feedback indicate a positive development toward creating an effective polymer synthesis teaching lab experiment that instills excitement for sustainable polymers in future chemists.
A polymer’s molecular weight distribution (MWD) has a profound impact on its properties, from material strength and viscosity to changes in the phase behavior of block copolymers. Dispersity is the most common measure of MWD and is described as the ratio of weight-average ($M_w$) to number-average ($M_n$) molecular weights. Importantly, dispersity only provides information on the relative breadth of molecular weights in a sample and is not a comprehensive description of the molar quantities of each chain size. The exact shape of a MWD has been proposed to have a strong influence on polymer properties; however, this hypothesis remains relatively unexplored. This presentation will detail the development of a modular synthetic strategy that provides deterministic control over the $M_n$, breadth, and composition of polymer MWDs. Using this method, the influence of MWD skew on polymer properties will be investigated.
POLY 452: Tuning the effective interaction parameters or dispersity from the short mid-block in PS-b-PMMA based block copolymers

Joona Bang, joona@korea.ac.kr, June Huh. Dept. of Chem. Bio. Eng., Korea University, Seoul, Korea (the Republic of)

Block copolymers (BCPs) are widely used in materials science due to their unique ability to self-assemble into various nanostructures, which is well described by the segregation strength $cN$. Recent advances in BCPs have focused on the development of new systems that can overcome the size limitation of traditional BCPs. Such efforts have been demonstrated with design and synthesis of new type of BCPs, changing the BCP architectures, or introducing the specific junctions between blocks. In this work, we demonstrate that the introduction of short middle block can manipulate the effective $c$ between A and B blocks. For example, in the polystyrene (PS) and polymethyl methacrylate (PMMA) based BCPs, the short middle block of PS-$r$-PMMA (R) was incorporated to prepare the ARB type triBCPs. In this case, the order-disorder transition (ODT) temperatures decreased due to the reduced effective $c$. Moreover, it was also expected that the R block increases effective dispersity via compositional distribution, leading to an increased domain size compared to the AB diBCP with same MW and dispersity. We prepared various ARB type triBCPs and AB diBCPs having the similar dispersity via living-radical polymerization. Consequently, it was shown that the ARB-type triBCP exhibited $\sim$50% increase in the domain spacing compared to the AB diBCPs with same MW and dispersity. As another example, we synthesized AHB-type triBCP, where A and B represent the PS and PMMA blocks, and H represents a short poly(methacrylic acid) (PMAA) that can form hydrogen bonds with the same PMAA (H block) or with PMMA (B block). Due to the hydrogen bonding, we hypothesized the enhanced intermolecular interactions at the domain interface will increase the effective $\chi$, thereby increasing the ODT as compared with AB diblock with the same molecular weight, in contrast with ARB case. This enhanced window for the ordered structure allowed us to fabricate sub-10 nm nanostructures. The results in both systems, ARB and AHB type triBCPs, were also compared with theoretical predictions.
This talk is motivated by the desire to develop first-principles simulations capable of quantitatively accurate predictions for block copolymer melts. Usually, the choice of model involves balancing the complexity needed to faithfully represent an actual experimental system and the simplicity required to make the simulation tractable. Fortunately, block copolymer phase behavior becomes universal in the high molecular-weight limit, which foregoes the need for detailed models. We illustrate how this universality can be used to make accurate predictions for a diblock copolymer melt from simulations using a simple lattice model. However, it is essential to account for polydispersity in order to achieve this quantitative agreement. The take-home message is that even small degrees of polydispersity, which are generally ignored by researchers, have a sizeable quantitative effect on behavior.

Hysteresis loop identifying the ODT in a simulation of a symmetric diblock copolymer with polydispersity. Its position agrees perfectly with experiment to within the statistical and experimental uncertainties.
Block copolymer morphologies formed spontaneously from the melt state lack long range order. Application of external forces, such as shear, electric fields, or magnetic fields, can lead to alignment of microdomains. In this study, a microphase-separated poly(styrene-b-(lauryl acrylate-co-stearyl acrylate)-b-styrene) triblock copolymer, exhibiting a disordered spherical microdomain with randomly oriented spheres, was aligned through the application of oscillatory shear in the nonlinear region. Strain sweep measurements revealed three shear regions: small amplitude oscillatory shear (SAOS), medium amplitude oscillatory shear (MAOS) and large amplitude oscillatory shear (LAOS). Shear alignment experiments were performed in both MAOS and LAOS regions. Highly aligned close-packed spherical morphologies were observed after application of oscillatory shear, independent of the strain amplitude. The presence of close-packed spheres are attributed to the higher dispersity of the midblock. The alignment kinetics were investigated with a combination of rheology and in situ rheo-small-angle X-ray scattering (rheo-SAXS). The degree of alignment was monitored throughout the course of shearing, and fit with a stretched exponential function. With same frequency, application of higher strain resulted in lower characteristic ordering time, indicating faster ordering kinetic. Enhanced macroscopic alignment was achieved in LAOS region.
Numerous recent investigations have focused on the impact of increased segmental molecular weight dispersity (PDI = $M_w/M_n$) on the morphologies and self-assembly thermodynamics of neutral diblock and triblock polymers. These industrially-relevant polymeric materials exhibit a unique combination of broad and continuous composition and molecular weight dispersions, which are not readily captured by multicomponent blends of narrow dispersity polymers. As compared to their narrow dispersity analogs, changes in the self-assembly behaviors of charge-neutral broad dispersity block polymers apparently arise from altered chain packing arrangements and chain stretching entropy. This contribution describes the syntheses and the phase behaviors of poly(styrene-block-ethylene oxide-block-styrene) (SOS) triblock polymers with a broad dispersity center poly(ethylene oxide) segment, in the absence and the presence of varying levels of lithium bis(trifluoromethyl)sulfonylimide. Using small-angle X-ray scattering, we demonstrate that center block dispersity shifts the lamellar phase window to higher than expected O block volume fractions ($f_O$). Furthermore, we examine the impact of O block dispersity on the total ionic conductivities of materials.
Spatial and temporal control are critical properties to advance and optimize functional (macro)molecular materials in order to mimic key features of living systems. In my lecture, I will discuss our methodology in developing non-equilibrium states in thermoresponsive hydrogels using peptide-polymer conjugates. We have expanded our concept of charge regulated β–sheet self-assembly of alternating hydrophilic and hydrophobic amino acids in order to introduce redox-switchable properties. An interplay of pH- and oxidation-stimuli, promoted by the production of reactive oxygen species (ROS) leads to transient supramolecular assemblies of either methionine containing dendritic peptide amphiphiles or amphiphilic ABA and ABA’ triblock peptide-polymer conjugates, with tuneable lifetimes and stabilities of the hydrogels. The incorporation of triethylene glycol chains introduces thermoresponsive properties to the materials, which operates in a biomedically relevant temperature range of 30 - 40 °C. Repair enzymes are able to reverse the oxidative damage in the methionine-based thioether side chains and thus reinitiate supramolecular polymerization. Reactive oxygen species play an important role in signal transduction cascades, and our strategy therefore offers great potential for applications in dynamic biomaterials that operate in redox microenvironments.
POLY 457: Polypeptide and protein-based bioconjugates as innovative functional biomaterials

Sebastien Lecommandoux, lecommandoux@enscbp.fr, Elisabeth Garanger, Bertrand Garbay, Monica Bravo Anaya. LCPO-ENSCPB, University of Bordeaux, Pessac, France

By combining the self-assembly properties of block copolymers together with the richness of function-bearing peptides, protein or saccharide domains, we aim at creating functional nanosystems integrating the advantages of both materials. We developed synthetic strategies for the design of polypeptides and polysaccharide-polypeptide biohybrids with controlled placement of sugar functionality. We were interested in designing copolymers able to self-assemble into well-defined micelles and vesicles that can advantageously be loaded with drugs and present a surface with multivalent presentation of bioactive saccharides or oligosaccharides, such as galactose, galactan that were shown to target specific cell receptors.

In order to be used as model systems for the establishment of structure-bioactivity relationships, they however suffer from some deviation in their chain-to-chain structure and molar masses. If not necessarily an issue for the final purpose, there is still a critical need to develop perfect polymer structures during the development stages, for better understanding and rational design. Our latest development involves the production of protein-like polymers by protein engineering. Recombinant DNA techniques allow fine-tuning of amino acids positioning within the final polymer product, thereby enabling the incorporation of specific biological properties (including degradation), in addition to imparting intrinsic biocompatibility. We especially developed Elastin-Like Polypeptides (ELPs) with methionine functions that allow bio-orthogonal coupling strategies for post-modifications with a large variety of functional groups.
Light-mediated chemistries serve as invaluable tools for the formation and modulation of material properties when and where desired. Providing exquisite control of reaction rate often under mild conditions, such approaches are particularly powerful for probing and directing biological systems. Here, we highlight two biologically-relevant applications of photochemistry: 1) imparting three-dimensional structure to peptides via cyclization followed by orthogonal conjugation for cell targeting and 2) controlling the crosslink density and modulus of materials initially and temporally with the rate of photopolymerization and a dual cure approach (Figure 1). In the first application, we established the use of sequential orthogonal click reactions, specifically a photoinitiated thiol-ene and strain promoted azide-alkyne cycloaddition (SPAAC), for the facile synthesis of a functionalized cyclic peptide (i.e., azido cyclic RGD) and subsequent conjugation to hydrogels and small molecules with application in 3D cell culture and in cell targeting, respectively. In the second application, we established a rate-based, dual cure approach for controlling the crosslink density and elasticity of materials. Specifically, hydrogels first were formed using visible light (455 nm LED) with the photoinitiator lithium acylphosphinate to initiate the polymerization of bioinert multi-arm poly(ethylene glycol) norbornene with linear dithiol. This photopolymerization using thiol-ene click chemistry with was less efficient with 455 nm light than with typical long wavelength UV (365 nm); yet, the slower rate of polymerization allowed facile manipulation of the mechanical properties of the resulting matrix (E ~ 1 – 20 kPa), relevant for mimicking a variety of soft tissues. Further, dangling end group present as defects within these networks were exploited in a second cure to increase crosslink density temporally, ‘stiffening’ these synthetic matrices. Broadly, these approaches highlight the utility of using light for controlling conjugation reactions and related material properties of relevance for the design of biomaterial-based tools to probe and direct the function and fate of cells in culture and in the body.
About hundred years ago, Hermann Staudinger published his “Macromolecular Manifesto” and demonstrated the existence of macromolecules. Today, polymer chemistry still provides a rich research area with many synthetic challenges that still need to be solved to create materials with entirely novel functions. In comparison to natural biopolymers such as proteins, peptides, carbohydrates, or DNA that represent the central framework of all biological processes in Nature, synthetic polymers usually lack precisely defined backbones, distinct monomer sequences of natural diversity that program shapes, 3D architectures and supramolecular assemblies, which is a prerequisite for achieving rich activities of biopolymers. Taking inspiration from Nature, novel synthetic procedures allow preparing polymeric architectures with structural complexity and precision. Such macromolecules resemble natural biopolymers in many aspects and they provide new opportunities for generating efficient and biocompatible polymer biotherapeutics.

Our approaches to solving such challenges will be presented first focusing on the synthesis of precision polymeric architectures based on body’s own biomaterials as templates and scaffolds. The synergistic combination of polymer chemistry and protein or DNA research provides hybrid macromolecules of high structure definition that interact with proteins, viruses and cells in a controlled fashion thereby modulating vital cellular processes.
Microstructured hydrogels offer many opportunities in developing therapeutic matrices for guiding cell behavior. This presentation will outline our recent studies in formulating PEG-based hydrogels with microstructure imparted by the controlled phase separation of PEG-polypeptide solutions. Resulting microstructured hydrogels can be manipulated on the basis of solution conditions and the composition of the polypeptide. The materials exhibit distinct microscale mechanical properties and high cytocompatibility over weeks in static and dynamic culture.
This presentation will describe the preparation of triblock copolymers consisting of a central poly(propylene oxide) (PPO) block that is flanked by zwitterionic polymer blocks. The polymers produced resemble Polaxamers (i.e., PEO-PPO-PEO triblock copolymers) wherein the PEO blocks are replaced with poly(methacryloyloxyethyl phosphorylcholine) (polyMPC) blocks). The synthesis of polyMPC-PPO-polyMPC triblock copolymers is particularly versatile, since inverse zwitterions (i.e., choline phosphates) are easily integrated into the zwitterionic polymer blocks, affording functional versions that can be cross-linked to form robust nanostructures, or utilized in bioconjugation chemistry for the attachment of cancer drugs, peptides, proteins, targeting moieties, etc.
Enzyme properties can be tuned and improved through polymer-based protein engineering, which enables the generation of polymer shell around an enzyme that can rationally tailor its function. Enzymes are characterized by precise and unique structure and function essential for complex biochemical processes. Synthetic polymers, on the other hand, are less precisely structured but can be rationally designed to withstand and respond to chemical, thermal or biological impulses. The synergistic fusion of enzymes and synthetic polymers results in advanced nano-armored enzymes with improved properties such as increased solvent, pH and temperature resistance, and modulated activity. Such bioconjugates are exceedingly useful in areas such as pharmaceuticals, chemical and biofuel industries. Our current work is focused on the development of efficient and scalable combinatorial synthesis method to generate rationally designed bioconjugates and consequently screen them on the presence of desired properties such as temperature stability, solvent stability and other properties relevant to the field of industrial biocatalysis. In this work, polymer modification of lipases is utilized as a case study to demonstrate that enzymes can be successfully functionalized with polymers using our high-throughput approach to gain improved stability. Such approach not only speeds up identification of better performing enzymes but also contributes to the more profound understanding of how polymer conjugation influences enzyme performance and to the development of fundamental knowledge of what kind of enzyme properties can be gained through polymer modification. This method can be further extended to a significantly more extensive area of protein science.
Triptycene-containing polymers are unanimously recognized as the new frontier in membrane material science. Triptycenes are formed by three phenyl rings bound by a central hinge to form a paddlewheel-like three-dimensional structure. Once inserted into a polymer backbone, they provide an extra, internal free volume which greatly enhances gas permeability and provides unprecedented levels of selectivity. Unlike in common glassy polymers, the internal free volume provided by iptycene units is not related to the non-equilibrium conformation, but to the molecular configuration. Such configurational free volume is intrinsic to the polymer structure and, as such, it is non collapsible, like in inorganic sorbents. Although several iptycene-containing polymers have shown separation performance above the 2008 upper bound, fundamental information about small molecule sorption and transport mechanism in this family of polymers is fairly absent in the literature.

In this study, pure gas and vapor (helium, nitrogen, methane, carbon dioxide, ethane, water vapor, alcohols) sorption and diffusion in a novel thermally rearranged co-polymer (TRPBO) prepared from a co-polyimide precursor with controlled triptycene molar content was experimentally measured in a wide range of operative conditions. Experimental data were analyzed in the framework of the Dual Mode and Lattice Fluid models. The dual mode parameters retrieved from the analysis of single penetrant sorption isotherms were used to estimate a priori the sorption behavior in mixed gas conditions. The mixed gas solubility-selectivity is significantly higher than ideal solubility-selectivity. Finally, sorption experiments were run, for selected gases, on samples previously annealed at 220°C under vacuum for 1 week. Remarkably, gas sorption is slightly enhanced upon thermal annealing, thus demonstrating the superior resistance exhibited by these materials to physical aging. The analysis of diffusion coefficients also disclosed precious information about the effect of the polymer structure on small molecule transport in this class of materials.
Polybenzimidazoles (PBIs) are a class of polymer materials that have the potential to improve and expand the applications of commercial gas separation membranes. While many commercial membranes can only perform gas separations up to 100 °C, PBIs are both chemically and thermally stable at temperatures up to 400 °C. A potential application of PBI membranes is the high temperature hydrogen-hydrocarbon separations proposed by the NSF Engineering Research Center for Innovative and Strategic Transformation of Alkane Resources (CISTAR). Two novel aspects of this work are the previously unstudied ethane and ethylene gas separation properties at elevated temperatures and the temperature dependence of gas transport in sub-micron films over an expansive temperature range. Hydrocarbon gas separation properties of Celazole® PBI membranes were characterized at temperatures up to 190 °C. Gas permeabilities, gas selectivities, activation energies of permeation, and physical aging rates differed significantly between thin sub-micron and bulk 20-micron Celazole® films. In particular, the activation energies of permeation were 1.5 to 4 times higher in an aged 450-nm thin film than in a 27-micron bulk film, suggesting a denser membrane structure and greater size-sieving ability. The first known evidence of physical aging in PBIs showed an 80 percent decrease in methane permeability over a 1000-hour period at 190 °C for a 450-nm Celazole® film. This study elucidates the effects of elevated operating temperature on thin films by encompassing a broader and higher temperature range than previous studies of flat, sub-micron polymer membranes.

(a) Gas permeability versus inverse temperature for 27-micron bulk Celazole® film, (b) Gas permeability versus inverse temperature for 450-nm thin Celazole® film aged 1000 hours. Slopes of lines correspond with activation energies of permeation for the gases in the membranes.
POLY 465: H$_2$O and O$_2$ sorption and diffusion behavior in thermoset polymers with temperature

Mathew C. Celina, mccelin@sandia.gov, Erik Linde, Nick Giron. Dept 1853 MS 1411, Sandia National Laboratories, Albuquerque, New Mexico, United States

Many aspects of polymer materials performance and reliability depend on molecular mobility, interactions of the polymer with small molecules, and hence the nature of diffusion processes. These range from sorption and desorption behavior all the way to mass transfer under reactive competitive conditions or through barrier materials, with the fundamentals and mathematics of such processes having been sufficiently described in the literature. Materials may degrade due to ingress of oxygen or water, or may act as the source of off-gassing volatiles and impurities resulting in concerns for materials compatibility in assemblies and overall reliability. Similarly, accelerated aging by nature will involve permeation processes. Unfortunately, diffusion in polymers is not always easy to measure and its temperature behavior is not clearly understood, with free volume and Tg often regarded as key drivers for diffusivity, but comprehensive data sets not being available.

We will present a brief overview of recent approaches towards quantification methods for oxygen and water diffusion in glassy thermosets and other polymers, as well as avenues to expand such studies towards spectroscopic monitoring of small molecule diffusion in polymer films, all as a function of temperature. Data will be discussed in the context of free volume and Tg, and our current understanding of diffusivity. All of these efforts are geared towards quantification of sorption/desorption phenomena and diffusion kinetics for predictive aging of these materials, off-gassing behavior and improved models towards long-term materials reliability.
Some of the best performing polymers for membrane-based gas separations are formed from linear polymers with contorted and rigid backbone structures. Such characteristics enable solution casting to form films, and their extreme contortions and rigidity allow polymeric structures to pack inefficiently, thereby creating ultramicroporosity that can enable ultrahigh permeabilities and good selectivities relative to the polymer upper bound. However, these traditional polymers of intrinsic microporosity (PIMs) have several key limitations, including limited opportunities for structural design, pronounced physical aging, and plasticization effects. Herein, we present an alternative strategy for forming ultramicroporous polymers by using a flexible ring-opening metathesis polymerization (ROMP) backbone with porous side chains attached. This approach enables the design of membrane property sets based on side chain chemistries instead of more difficult-to-control backbone packing structures. Transport properties for two side-chain variants are presented, including a polymer that is the second most permeable linear ultramicroporous polymer to date. This polymer exceeds the H\textsubscript{2}/CH\textsubscript{4} upper bound and has separation performance near the upper bound for H\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} separations. Plasticization and physical aging data are presented relative to the state-of-the-art PIM, PIM-1. By incorporating ultramicroporosity via side chain units instead of the main chain, it is possible to reduce plasticization and physical aging effects.
High performance polymers of intrinsic microporosity (PIMs) have emerged as novel materials with broad applications from gas separation to electronic devices. Sufficiently rigid, even contorted polymer chains show only limited molecular mobility, therefore undergo inefficient packing and give rise to intrinsic microporosity with pore size generally smaller than 1 nm and BET surface areas larger than 700 m²/g. Further performance optimization and long-term stability of devices incorporating PIMs rely on our understanding of structure-processing-property relationships and physical aging, in which glass transition plays a key role. Up to now no glass transition temperature ($T_g$) of PIMs could be detected with conventional thermal analysis techniques before degradation. Decoupling the time scales responsible for the glass transition and the thermal decomposition is a reliable strategy to overcome this. This was achieved by employing fast scanning calorimetry (FSC) based on a chip sensor, which is capable to heat and cool a small sample (ng-range) with ultrafast rates of several ten thousand K/s. FSC provides definitive evidence of glass transition of a series of PIMs with a special consideration on the chain rigidity. The determined glass transition temperature of these PIMs follows the order of the rigidity of their backbone structures. FSC provides the first clear-cut experimental evidence of glass transition of a series of PIMs with a heating rate of $1 \times 10^4$ K/s. Local fluctuations are featured in glass transition of highly rigid PIMs. As conformational changes are prevented by the backbone rigidity, the glass transition must rather be assigned to local small scale fluctuations.
Molecular separation, such as gas separation, is central to many technological innovations and advancements in clean energy (e.g., H2 purification) and environmental remediation (e.g., carbon capture). Membrane technology, which takes advantage of material's selectivity rather than energy to perform separations, represents a simple but powerful separation technology. Particularly, polymers with finely tailored microporosity are highly desirable for gas separation membranes considering the very small size differences between gas molecules—several tenths of an Ångstrom difference. Here we report a new family of molecularly porous polymers with super rigid backbone and facilely-tunable microporosity for gas separation membranes. These new ladder-like polymers exploit the molecular configurations of shape-persistent pentiptycene-based building blocks to construct non-collapsible free-volume-based microporous structure to provide diffusing molecules with a low-resistance transport avenue. The framework profiles defined by the shape of pentiptycene (i.e., S-shaped or C-shaped in Figure 1) provide a convenient way to tune the tortuosity of the ladder backbone and consequent free volume architecture that effectively regulates molecular transport in these membranes for various separation needs. Moreover, varying the content of pentiptycene units provides further tunability in selectivity by introducing internal free volume of iptycene moieties for size sieving. Thin films of these ladder polymers show superb separation performance. For example, a thin film containing only 17 mol% C-shaped pentiptycene units outperformed the 2008 upper bounds for all common gas pairs including CO2/CH4, O2/N2, CO2/N2, H2/N2, and H2/CH4. In this talk, synthesis and characterization of these new ladder polymers will be presented. Discussions will focus on elucidating the fundamental correlations between microscopic structure and gas transport properties for these innovative polymers.

Figure 1. Schematic of pentiptycene-based ladder polymers with S- and C-shaped profiles.
POLY 469: Advancing toward lower energy-intensity gas separations using polymer-derived membranes

William J. Koros, 30085801@acs.org. Chemical & Biomolecular Engr., Georgia Institute of Technology, Atlanta, Georgia, United States

Advanced membrane that minimize energy intensive phase change-driven separations can allow as much as an order of magnitude reduction in energy intensity per unit of product purified. While already used for water purification, more efficient approaches such as reverse osmosis cannot yet be used widely, due to a lack of advanced materials suitable for use with non-aqueous feeds. Recent developments in membrane materials can extend the low energy intensity separation revolution beyond water to include the full spectrum of large scale feeds. Crosslinked glassy polymers, polymer-selective nanoparticle hybrids and carbon molecular sieve (CMS) materials cover different areas in this new separation landscape. This presentation will discuss examples of these new materials, devices based on them as well as their manufacturing and the savings they enable.
POLY 470: Water sorption, dilation, and transport in polybenzimidazoles for gas separation membranes

Joshua D. Moon¹, jdmoon@utexas.edu, Michele Galizia², Hailun Borjigin³, Ran Liu³, Judy S. Riffle³, Benny D. Freeman¹, Donald R. Paul¹. (1) McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States (2) School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma, United States (3) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia, United States

Due to their high chemical and thermal stability, polybenzimidazoles (PBIs) have recently been studied for use as gas separation membranes for aggressive, high temperature applications. A series of sulfonyl-containing PBIs based on the 3,3′,4,4′-tetraaminodiphenylsulfone (TADPS) monomer were recently synthesized and shown to have enhanced solubilities in common organic solvents relative to commercial PBI (Celazole®), thus improving their processability as membranes. Celazole® and TADPS-based PBIs are both hydrophilic and can sorb up to 25% water by mass at room temperature. Since many industrial processes operate with partially humidified gas streams, it is crucial to understand the impact of sorbed water on the membrane’s transport properties.

This study describes water sorption, dilation, and transport in PBIs across a range of humidities to provide insight into how water uptake affects the gas transport properties of PBIs while separating humid streams. Water vapor sorption isotherms and diffusion kinetics were determined using gravimetric analysis, and water-induced dilation was determined using vapor dilatometry. Sorption and dilation isotherms were fit using the dual-mode sorption model. Combined modelling of sorption and dilation isotherms enables prediction of the partial molar volume of sorbed water and the fractional free volume of the polymer/water mixture as a function of vapor activity. Results suggest that water uptake reduces fractional free volume of PBIs by up to 38% while swelling the polymers by up to 21 vol%. Humidified gas permeabilities are correlated with free volume changes to elucidate the roles of competitive sorption and plasticization that result from water uptake.
POLY 471: Thiol-ene networks containing tethered perfluoroalkyl chains:Synthesis and investigation of gas permeation, free volume, and surface properties

Sergei Nazarenko1, sergei.nazarenko@usm.edu, Ramesh Ramakrishnan1, Steven W. Wand1, Vivek Vasagar1, James Goetz2, Bruno M. Ameduri3, James W. Rawlins1. (1) Polymer Science and Engineering, Univ of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Eastman Chemical Company, Kingsport, Tennessee, United States (3) Ecole Nat Sup Chim Montpellier, Montpellier, France

Perfluorinated amorphous polymers display a number of attractive technological properties such as chemical resistance, low surface energy, low water adsorption, optical clarity, and potentially high gas permeability (‘breathability’). This study focuses on preparation and investigation of various physical properties, including free volume, gas/vapor permeation behavior, and surface properties of a new class of UV-curable, thiol-ene based, homogeneously perfluorinated amorphous networks. The homogeneous incorporation of fluorine moieties into such networks is based on the fact that UV-curing kinetics in the thiol-ene systems is extremely rapid, and enable the fluorine containing thiol units (miscible with ene monomers prior to curing) to be covalently “locked in” into the network structure before thermodynamically driven phase segregation develops upon building up the molecular weight. Therefore, after curing is completed, these networks remain thermodynamically “frustrated” and as a result demonstrate rather unusual physical properties. Derivatized thiol monomers were prepared via a nucleophile-catalyzed thio-Michael addition reaction of multifunctional thiols to short chain perfluoroalkyl acrylates (f2-f10). The fX designation reflects the number of carbons in the chain attached to the acrylate ester. Using UV-initiated photopolymerization, cross-linked networks were fabricated from these systematically modified thiol monomers. As the length of the perfluoroalkyl chain was increased from f2 to f10, the free volume hole size increased over 2.5 times and oxygen permeability increased by two orders of magnitude while the networks retained similar glass transition temperatures. Surprisingly, in contrast to oxygen permeability, the water vapor permeability was virtually independent of perfluoroalkyl length. The effect of perfluoroalkyl chain incorporation was compared in this study with that resulted from incorporation of short n-alkyl acrylates.

Two-step’ scheme of perfluorinated network fabrication
The use of natural gas for power generation and seawater desalination, as well as for chemical feedstock, provides opportunities for Saudi Aramco to diversify beyond crude oil. Heavy hydrocarbons (C$_3$+), often referred to as natural gas liquids (NGL), must be separated from natural gas through energy intensive refrigeration processes. Alternatively, commercially available siloxane membranes separate NGL from natural gas using significantly less energy. Due to their high permeabilities, these membranes can reject N$_2$ and concentrate C$_3$+ in membrane permeate streams. However, current state-of-the-art PDMS membranes exhibit lower C$_3$/C$_1$ selectivities due to swelling under aggressive testing conditions. Here, we demonstrate strategies to overcome this limitation by developing more efficient siloxane membranes with improved C$_3$/C$_1$ selectivity for heavy hydrocarbon separation and recovery. Novel PDMS membrane materials comprised of vinylmethylsiloxane terpolymers were prepared via an addition curing or grafting-hydrolysis-polycondensation process by controlling polymer backbone and side-chain structures, crosslinking moieties, and crosslinked networks in the membrane matrix. This talk compares these novel PDMS structures to commercially available PDMS under industrially relevant conditions, including the use of C$_1$-C$_5$ multicomponent hydrocarbons in the presence of N$_2$, CO$_2$ and BTEX contaminants at 800 - 850 psi. These results demonstrate the strong dependence of C$_3$/C$_1$ selectivity on feed compositions, operating parameters and PDMS chemical structure. The results of this study aim to advance the development of these promising siloxane membrane materials for aggressive natural gas separations.
In biosemiotics and signaling theory, sign systems are adopted by organisms to communicate information to predators and peer groups, for eliciting behavior favorable for their survival. Humans have adapted sophisticated sign systems that draw from implicit understanding of material properties and context-driven associations. Polymers that are designed to explicitly display information to humans possess many applications in consumer goods, architecture, and food industries. In this presentation, we will discuss how stimuli-responsive biopolymers and biomimicry can be used to engineer multi-sensory information displays. We will introduce a library of color, odor, and form changing materials called Organic Primitives, which are designed specifically for this initiative. By converting chemical input into human senses, we can represent a wider array of sensory modalities in representing chemical contents, and introduce new methods and applications into the field. Some examples of applications that will be shown include: for climate change activism - an umbrella that bleeds in the presence of acid rain, communicating that the rainwater from the sky is hurting it; and for food safety - an apple that tells you it's been contaminated during transport by producing red spots to communicate it's toxicity. This research is part of an ongoing investigation in molecular design interactions for user experience design.
A stoma (plural stomata) is a pore or opening in the epidermis of plant leaves, through which carbon dioxide is received for photosynthesis and water vapor is transpired. A stoma consists of two guard cells, having thicker and inextensible inner walls and outer walls that are thinner and more extensible. The stomata open and close through the swelling and shrinking of the two guard cells in response to environmental stimuli, e.g. high light intensity and high humidity.

In this study, we are fabricating the pores in a breathable fabric to mimic the structure and function of leaf stomata. In the artificial stomata, a special polymer is coated around a slit (“pore”) of the fabric to form “guard cells”. The polymer will bend asymmetrically toward one side under higher humidity (wet), leading the “pore” to open, while it stays still under normal humidity (dry) which keeps the “pore” close. In both conditions, the fabric maintains a flat surface without buckling, which means little effect on the overall dimension of the fabric.

The process is simple and easy to scale up. The polymer can be coated via digital liquid dispensers, or various industrial printing techniques, like screen printing or 3D printing. The slit can be cut by laser etching technology, and the dimensions can vary from micro- to millimeters. The dimension change of the pore under “open” and “close” states can be easily measured by the length and width change, or observed under optical microscope. The fine structure and morphology can be examined under scanning electron microscope (SEM). The air penetration or vapor transmission through the pores under different states can be measured by air permeability tester (e.g. KES-AP) or moisture vapor transmission rate (MVTR) tester.
Traditional ceramic-based electronics are based on rigid and planar wafer-based 2D technologies. Polymer substrates for electronic devices are of intense interest to offer opportunities to replace these conventional electronic substrates and to yield compliant, stretchable, and 3D electronics. Liquid crystal elastomers (LCEs) have attracted considerable attention as stimuli-responsive materials because they undergo large, reversible strain on heating and because this stimulus-response can be controlled through directed self-assembly. We hypothesized that these materials could serve as substrates for responsive electronics. Here, we discuss using programmable shape-morphing LCEs as substrates for electronic devices that are flat during processing but then morph to 3D shapes for use (Figure 1). We design processes to fabricate a variety of electronic devices on LCEs including conductors, capacitors, antennas, and biomedical microelectrode arrays (MEAs). For example, patterning twisted nematic orientation within the substrate can be used to create a bio-inspired helical 3D geometry in electronic devices that stretch up to 100% with less than a 5% change in electrical performances. Moreover, we discuss self-morphing LCE antennas which can dynamically change the operating frequency from 2.7 GHz (room temperature) to 3.3 GHz (-65 °C). Finally, we describe LCE-based MEAs for in vitro neuronal recordings that demonstrate that LCEs are non-cytotoxic and act as a stable encapsulation over 30 days in physiological conditions.

![Figure 1. Deployed LCE electronic device from 2D flat (processable) to 3D helical (strain tolerant) with photolithographically defined micro-connectors.](image-url)
Motor molecules in nature convert energy inputs, such as a chemical fuel or photons of light, into directional motion and force biochemical systems away from thermal equilibrium. The ability to control directional movements of components in molecules under certain stimuli represents significant advances toward future technological applications. Herein, we demonstrate a wholly synthetic molecular pumping system that allows for a unidirectional translational motion of a small macrocycle passing through a dumbbell-like track molecule. The operation of the system relies on inputs of chemical fuels via redox reactions.
POLY 477: Sequence-defined redox-responsive polymers as artificial molecular muscles

Jonathan C. Barnes, jcbche3@yahoo.com. Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

Nature relies on sequence-defined polymers to carry out a wide range of functions, such as the precise folding of a protein to establish a catalytic active site, or the matching of base pairs in two strands of DNA during replication or transcription for example. Recently, synthetic polymer chemists have devoted a lot of time and resources to coming up with new methods to control the sequence of monomers in synthetic polymers for the purpose of preparing digitally encoded polymers or bioactive macrocycles, to name a few examples. My research group is interested in stimuli-responsive materials that can actuate – i.e., change their size, shape, and mechanical properties reversibly in response to an external stimulus – and more specifically, whether sequence-defined polymers can impact this actuation process. In my talk I will describe the iterative step-growth-like syntheses of oligo- and polyviologens consisting of 4,4′-bipyridinium subunits (a.k.a., viologens) spaced on either side by different polar and non-polar groups that are known to affect the bulk physical properties of a polymer – e.g., crystallinity, Tg, etc. – and how these sequence-defined redox-responsive polymers perform in a series of hydrogel actuators. In each case, I will highlight the ability of each material to function as an artificial molecular muscle.
Syntetic polypeptides can be seen as simplified protein analogues: they are ideal materials to design protein mimics, able to reproduce some properties of natural proteins and to create innovative polymeric structures for materials science applications. In particular, polypeptides can reproduce natural protein secondary structures such as \(\alpha\)-helix or \(\beta\)-sheets and this rare feature is, in polymer chemistry, at the origin of fascinating properties. In marked contrast to proteins, synthetic polypeptides can easily undergo secondary structure transitions that can be easily implemented and tuned by tailoring amino acid side chains. Recent developments in this direction include the elegant use of polypeptide polymers to enable structuring switch upon redox changes or upon metal coordination. In this work, we show that functionalizing simple polypeptide backbones with nucleobases can afford biomimetic structuring switch upon DNA binding and structured polypeptides electrolytes that adopt stable \(\beta\)-sheet conformations.
Biological systems are able to self-repair repeatedly and autonomously on multiple scale lengths, from DNA macromolecules to larger organs, such as veins, soft or hard tissues, and muscles. Leaf plants encode self-healing functions by incorporating viscoelastic responses to their tissue during growth, thus enabling deformations upon mechanical damage to close a wound. While numerous studies have shown that chemical modifications may be successful in achieving self-healing properties, the role of phase morphologies, viscoelasticity-driven shape memory effects and copolymer compositions was only recently explored. At micro scale, the formation of stable interfacial regions between hard and soft segments can facilitate efficient self-healing resulting from reduced chain slippages during damage in polycaprolactam-polyurethane (PCL-PU) polymers. In other studies we have shown that predominantly alternating chain segments create favorable interchain van der Waals forces forming “key-and-lock” interchain junctions within narrow molar compositional range of poly(methyl methacrylate)/n-butyl acrylate [p(MMA/nBA)] copolymer and its derivatives. The perturbation of ubiquitous van der Waals forces upon mechanical damage facilitates energetically unfavorable for interdigitated alternating/random copolymer motifs, thus enabling self-healing under ambient conditions. Although significantly different in terms of scale length, illustrate that self-healing can be achieved by controlling phase morphologies or chain topologies in commodity material and the use of van der Waals forces enables multiple recovery upon mechanical damage without external intervention.
POLY 480: Soft lifters via layered liquid-crystal elastomers

Tyler Guin¹, tylercguin@gmail.com, Timothy J. White². (1) Physical Sciences Directorate, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Materials and Manufacturing Directorate, Air Force Research Laboratory, Centerville, Ohio, United States

Liquid crystalline elastomers (LCEs) are soft, anisotropic materials that exhibit large shape transformations when subjected to various stimuli. Rational design of these materials enables the reversible formation of biomimetic shapes. Here, we demonstrate a facile approach to enhance the out-of-plane shape-changing work capacity of this shape-morphing by an order of magnitude, to nearly 20 J/kg. The enhancement in force output is enabled by the development of a room temperature polymerizable composition used to prepare individual films, organized via directed, photo-patterned self-assembly. The material actuator is shown to displace a load more than 2500× heavier than its own weight nearly 0.5 mm.

Figure 1. Deformation of a four layer LCE laminate lifting 28.7 g more than 2 mm. The LCE laminate was heated to 180°C.
POLY 481: Stimuli-responsive hydrogel/elastomer composites via fabric interphases

Amber M. Hubbard, amhubba2@ncsu.edu, Wei Cui, Yiwan Huang, Riku Takahashi, Michael D. Dickey, Jan Genzer, Daniel King, Jian Ping P. Gong. (1) Graduate School of Life Science, Hokkaido University, Sapporo, Japan (2) Chemical and Biomolecular Engineering, NC State University, Raleigh, North Carolina, United States (3) Hokkaido Univ Grad Sch of SCI, Sapporo, Japan

Stimuli-responsive structures find use in many areas of technology, ranging from soft robotics to biomimetic structures. Drawing inspiration from biologic materials a recent interest in polymer composites has centered around the ability to combine hydrophobic (elastomer) and hydrophilic (hydrogel) materials. While previous research has utilized chemical approaches to generate strong adhesion between hydrogels and elastomers, herein a more general methodology is presented. This talk will focus on the production of hydrogel/elastomer composites based on a physical adhesion approach (i.e., a fabric interphase) and the composite application as stimuli-responsive actuators. In our method, a glass fiber fabric is implemented as an interfacial compatibilizer between a polyampholyte hydrogel and an elastomer; this composite structure results in a tearing toughness (143 kJ m⁻²) which vastly exceeds the toughness of either neat soft component. We use this approach to demonstrate stimuli-responsive curvature throughout the entire composite structures when exposed to organic solvents, salt solutions, or vacuum. Notably, we demonstrate cyclic actuation which demonstrates tension intensities ~ 20% that of human skeletal muscle. Experimental results are qualitatively and quantitatively compared with Timoshenko modeling exhibiting excellent agreement. The method presented within this talk merges the benefits of fabric-reinforced composites and hydrogel/elastomer composites to produce robust soft materials with wide applicability. Being able to produce robustly bound hydrogel/elastomer composites with various stimuli-responsive actuation mechanisms and a cyclic nature lends to a wide range of applications, such as artificial muscles, demonstrated here.
The key Materials Science challenge is to achieve energy-dissipation in stiff (load-bearing) materials (modulus, $E > 100$ MPa) that usually do not dissipate much energy when stressed to fracture, and therefore often fail at very low strains. By contrast, natural materials such as the mussel byssal cuticle have a high modulus, similar to structural engineering polymers ($E \approx 800$ MPa), and an impressive 100% elongation-to-failure. Many studies have shown that energy dissipation in synthetic polymers is possible, but most previous reports were limited to soft polymers/hydrogels ($E < 10$ MPa), which lack the strength needed for load-bearing applications. In our recent studies, energy dissipation of stiff polymers ($E > 100$ MPa) have been shown with a high extensibility ($\varepsilon_{\text{max}} \approx 150\%$) (Science 2017, 358, 502-505). However, our previous approach is also limited to polymers that swell in water (moisture sensitive). In contrast to all the prior studies, here we aim to not only translate the biological features into dry/hydrophobic (moisture insensitive) synthetic materials but to incorporate control of structural properties at multiple length scales. We will leverage our established success in microphase separation techniques to replicate the biological microcellular structural properties while at the same time allowing molecular control through sacrificial, reversible chemical interactions.
We report here an overview on the self-assembly in water of amphiphilic block copolymers developed in our laboratory into different nanomedicines, mainly focusing on polymer vesicles, also referred as polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules.

We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles and their development in nanomedicine. Indeed, the field of synthetic polypeptides has seen many significant advances in recent years, including studies on block and hybrid copolypeptides that form vesicles, fibrils, and other structures with potential applications in medicine and materials chemistry. In this context, we developed over the last years synthetic strategies for the design of glycosylated polypeptides and polysaccharide-polypeptide biohybrids with controlled placement of sugar functionality. We were especially interested in designing amphiphilic copolymers able to self-assemble into well-defined micelles and vesicles that can advantageously be loaded with drugs and present a surface with multivalent presentation of bioactive saccharides or oligosaccharides. The ability of these nanoparticles for different biomedical applications, from drug-delivery to inhibitor, will be presented. We especially evidenced the particular benefit of nanoparticles and their multivalency toward the interaction with biological receptors.

Finally, our recent advances in using “biomimicry approaches” to design complex, compartmentalized and functional protocells will be proposed. Such a system constitutes a first step towards the challenge of structural cell mimicry and functionality, and may act in the future as an autonomous artificial cell that can sense and cure in situ any biological deregulation.
Antifreeze (aka ice-binding/structuring) and ice nucleating proteins have many desirable properties for modulating ice growth/formation, but they are often not suitable for application, where scale-up, tuneability, immunogenicity and stability must be considered. We have introduced the concept of using synthetic macromolecules (polymers) to mimic antifreeze proteins and have applied these to challenging problems in cryopreservation. However, the rational design of these is complicated by the gaps in our knowledge of how native proteins function on the molecular scale, and if our polymer mimics even function by the same mechanisms. E.g., just because they have related macroscopic properties, does this mean they interact with ice in the same way? Here I will summarise our progress in developing synthetic mimics of antifreeze proteins, particularly those which can inhibit ice recrystallisation, for application in cryobiology. The role of the chemical functionality will be discussed, and show that specific functional groups are not essential, but rather other structural features, in particular amphipathy, are required. I will also discuss what constitutes ‘active’ – a high enough concentration of anything will slow ice crystal growth, and some emerging macromolecules appear to be potent cryoprotectants but do not interact with ice strongly.
A cooperative research program between the Navy, Army and Air Force research laboratories is developing innovative, sustainable, non-toxic, non-isocyanate polyurethanes (NIPUs) that can be applied via conventional high volume low pressure spray (HVLP) equipment eliminating volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) while maintaining or exceeding critical performance requirements specified in SAE AMS-C-83231. The NIPUs that are being investigated focus on reactions that eliminate isocyanates from polycondensation reactions. The monomer 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyldiphenylbis(carbonate) has been reacted with 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine via a polycondensation reaction from the melt using 10 mole% of initiator (dibutyltin oxide). High molecular weight NIPUs have been obtained with 10%: 90% of polyurea to polyurethane linkages. This ratio was determined by $^{19}$F and $^1$H NMR spectroscopy and EDAX. These NIPUs can be sprayed onto silicon wafers from solution (~30 weight % in acetone) to produce thick films (~200 microns) in one hour. These coatings have a static contact angle between 89-95° and thinner films (~50 microns) exhibit the rose petal effect. These coatings will be examined for their rain erosion properties after spraying using HVLP spray equipment from acetone solutions onto the leading edges of military aircraft wings.
Thermoplastic polymers are of interest as replacements for thermoset matrix materials in continuous fiber reinforced composites because of their reduced cost of processing, longer shelf lives of raw materials, faster processing times, moldability, reduced waste, and ability to be recycled. High performance resins offer high use temperature and excellent mechanical properties in composites, however they present the challenges of high processing temperatures and melt viscosities. It has been demonstrated in a number of low temperature polymers that addition of small amounts of polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals yields enhanced melt flow and ability to change rates of crystallization, without altering thermal and mechanical properties. The degree of rheology modification depends on the structure and dispersion of the POSS in the polymer matrix. We describe the rheological and crystallization performance of POSS blends with PPS and PEEK semi-crystalline polymers and amorphous polysulfones.
POLY 487: *In situ* polymerisation on the carbon fiber surface for enhanced interfacial adhesion

**Luke C. Henderson, luke.henderson@deakin.edu.au, Chantelle L. Arnold. Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia**

Carbon Fibers are typically coated in a 'sizing' as the final stage of manufacture which serves to protect the fibers from mechanical damage during handling and also serves to enhance the adhesion between the fibers and the reinforcing matrix. The optimisation of sizing and resin is typically done empirically or through broad 'compatibility' classifications which are provided by the fiber manufacturer or sizing supplier. The ultimate fate of the sizing in the composite, i.e. whether it remains near the fiber surface or diffuses into the matrix, is largely unknown and difficult to determine. In this work we develop a means to rapidly grow acrylate-derived polymers from the carbon fiber surface which serves as a covalently bound sizing. The process and effect on interfacial adhesion will be presented.
Today’s composite structures are mostly assemblies depending on adhesive and mechanical joining. Although the achievable level of complexity of individual composite parts has improved and, as a result, the part count did reduce, the assembly still is elaborate and costly. By moving away from the use of thermoset composites, the assembly can be made more effective and affordable. Further enhancements in structural efficiency and lowering cost can be achieved by relying more on fusion bonding. We are able to manufacture thermoplastic composite parts using a wide variety of methods which include compression molding, filament winding, pultrusion and many specialized methods combining several principal forming methods. If we could add to this repeatable and scalable joining methods and true additive manufacturing techniques, fastener free assembly could become reality. Progress in 3D printing of thermoplastic composite and in induction welding will be discussed as potential ways forward. 3D printing has shown the large opportunity of thermoplastics and fusion bonding. In principle 3D printed parts are fusion bonded spirals of thermoplastic polymer. Unfortunately pure thermoplastic polymer is not suitable for high performance structures. To obtain acceptable levels of strength and stiffness the polymer needs to be combined with high performance fibers. Progress in overprinting of continuous carbon based polymer will be shown to be a solution for fastener free assembly of detail structural parts. Induction welding is one of the methods to efficiently join thermoplastic composites. Progress in designing, analyzing and manufacturing induction welded parts will be discussed, as well as the need for in-situ monitoring of the critical process variables. Additional concepts to improve affordable manufacturing will be discussed and a view on the main challenges to achieve full fastener free assembly will be presented.
A fundamental challenge in materials science is to create synthetic nanoarchitectures that rival the structural complexity and functions found in nature. A promising bioinspired approach is to synthesize sequence-defined, non-natural polymer chains that fold and assemble into precise protein-like structures. In order to efficiently produce such information-rich polymer sequences, we use the automated solid-phase submonomer synthesis method to generate sequence-defined peptoid polymers up to 50 monomers in length. The method uses readily available primary amine synthons, allowing hundreds of chemically diverse sidechains to be cheaply introduced. Here we show that all known crystalline peptoid assemblies, including lamellar solids, nanosheets, nanotubes, and membranes, all share a fundamental secondary structure motif based on a backbone containing all cis amide bonds. This unexpected universality of peptoid backbone folding offers a unique opportunity to rationally design and engineer these materials to create robust, nanomaterials capable of protein-like functions like specific molecular recognition and catalysis.

Peptoid diblock copolymers assemble into crystalline nanosheets in water. The hydrophobic core is comprised of N-decylglycine units, and the polar domain is comprised of triethlyeneglycol containing monomers. Peptoid lattices generally contain extended chains consisting of all cis-amides.
Peptoids hold a special place in the foldamer field. They are very close mimics of peptides because their main chain is composed of glycine units. But, the peptoids main chain is deprived of N–H donors and chirality, two main features that control peptide folding. Because of these properties and the intrinsic flexibility, experimental 3D structures characterization is a difficult task. Experimentally available 3D information are mainly based on X-ray structures of medium sized molecules. NMR spectroscopy is routinely used for the characterization of the primary sequence and, in few cases, for 3D structure determination. When chirality properties are reintroduce by side chains with asymmetric carbons appended to the nitrogen atom of the backbone, Electronic Circular Dichroism (ECD) allows to determine secondary structures. Classical Molecular Dynamics (MD) simulations combined to the quantum chemical calculations of spectroscopic data can be employed nowadays in order to obtain further insight into the three dimensional structures. The analysis of MD trajectories allows to describe specific structural characteristics. Quantum chemical structures used to reproduce experimental spectroscopic data can highlight unambiguous conformations or intramolecular interactions responsible of the ECD or NMR signatures.

First, we will discuss results based on MD simulations coupled to quantum chemical calculations of $^{13}$C NMR spectra (B3LYP-GIAO) performed on mixed cis-trans $\alpha,\beta$-oligopeptoids. This joint experimental and theoretical study has highlighted specific patterns of intramolecular weak interactions existing in this family of polypeptoids. On a second part, we will focus on the calculations of ECD spectra (TD - B3LYP) that was carried out on a set of chiral $\alpha$-peptoids with tert-butylethyl side chains. This theoretical study, based on the quantitative reproduction of experimental ECD spectra of oligomers of different sizes, revealed a set of specific conformational properties to explain all the spectral characteristics.
I want to make an overview of recent achievements in the field of the synthesis and self-assembly of triphilic poly(2-oxazoline) triblock copolymers. A variety of novel fluorine-containing copolymers was synthesized combining hydrophilic, hydrophobic and fluorophilic moieties into one segmented polymer [1-4]. The presence of the blocks with the different nature in one copolymer structure facilitated self-assembly of the copolymers in water and some organic solvents as observed by dynamic light scattering, cryo-TEM, and small-angle neutron scattering. The nanoparticle morphology is strongly influenced by the order and length of each block and the nature of solvent, leading to nanoparticles with core-shell structure as confirmed by small angle neutron scattering. The supramolecular structures described represent a potential platform for 19F magnetic resonance imaging contrast agents.
POLY 492: Investigating the effect of charge-charge interaction on the solution self-assembly of sequence-defined ionic peptoid block copolymers

Garret L. Sternhagen², Sudipta Gupta², Pu Du², Yueheng Zhang¹, Vijay T. John¹, Gerald J. Schneider², Revati Kumar², Steven W. Rick³, Donghui Zhang², dhzhang@lsu.edu. (1) Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana, United States (2) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (3) Univ of New Orleans, New Orleans, Louisiana, United States

Charge-charge interaction is ubiquitously present in a variety of natural and synthetic soft matters (e.g. protein, DNA, gene delivery carrier, and ion-conducting membrane, etc.). They often play a dominant role in the structure and dynamics of soft matters. Understanding the effect of charge-charge interaction on the structural and dynamic outcome of ion-containing soft matters is important. This presentation will be focused on our recent work on the design, synthesis and investigation of solution self-assembly of sequence-defined ionic peptoid block copolymers in aqueous solution. The position and number of ionizable monomers along the polymer chain were systematically varied during synthesis to allow their effect on the solution structure to be revealed. Our first study has shown that the ionic micellar structure can be precisely controlled by the position and pattern of the ionizable monomers in the sequence-defined polymers. The aggregation number and micellar size can be related to the position of the charged monomer by scaling relationships. Computational simulation of micelllation also provided insights into the balancing act of charge-charge interaction and solvation of the charged monomers that dictate the micellar structure. Results from the study of semi-dilute solution of ionic peptoid block copolymers containing interacting micellar particles will also be discussed.

Figure 1. Representative chemical structure of sequence-defined ionic peptoid block copolymer, sequence library and the cartoon depiction of micellar structures for sequence 1, 3, and 5.
The permanent antimicrobial equipment of surfaces is one key strategy for the provision of improved hygienic living conditions that are favourable in water tanks/pipes, food processing, sanitary equipment, and generally in all areas publicly frequented. The blending/compounding of commodity polymers such that mere surficial contact of microbes is sufficient to provide the targeted antimicrobial effect has gained considerable attention. Two strategies have become prominent: Polycationic polymers are able to repel the calcium layer surrounding numerous microbes, which results in microbial death (Figure 1). Tungstate and molybdate polyanions easily undergo protonation-deprotonation cascades and cause proton-mediated microbial death. Experimental findings involving these strategies will be presented. The microwave-assisted syntheses of poly(2-oxazoline)s and poly(2-oxazine)s from microwave-assisted polymerizations and subsequent polymeranalogous modifications will be presented. The number of cationic functionalities in the polymers can be increased by continued acid-mediated hydrolysis of the side-chain amide bonds. Hydrophobic side-chains are present in, e.g., poly(2-nonyl-2-oxazoline), poly(2-phenyl-2-oxazoline), and poly(2-phenyl-2-oxazine) as well as their congeners. The antimicrobial activity in PP-based compound plates will be discussed with special respect to the balance of cationic and hydrophobic functionalities in the biocidal polymers. The (antimicrobial) activity of compounds containing tungstate and molybdate polyanions will be correlated with zeta-potential measurements, which are caused by the net electrical charge contained within the region bounded by the slipping plane. As such, the zeta potential is often the only available path for the characterization of double-layer properties and can be used for the characterization of the composites.

Figure 1: Mechanism of the interactions among polycationic polymers and microbes.
POLY 494: Poly(2-oxazoline)s as matrix excipient for sustained release formulations

Ali Tigrine¹, ali.tigrine@ugent.be, Aseel Samaro², Valerie Van Hoorne², Victor R de la Rosa¹, Maarten Vergaelen¹, Martin Purino¹, Bryn Monnery¹, Chris Vervaet², Richard Hoogenboom¹. (1) Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium (2) Pharmaceutical Technology, Ghent University, Ghent, Belgium

Formulations containing large doses of highly soluble active pharmaceutical ingredients (APIs) are especially challenging, in particular due to the risk that the drug is released too fast (burst release). The maximum tolerated concentration in the blood can then be exceeded, inducing toxicity and causing side effects. This risk can be ameliorated by applying multiple administrations, however at the expense of a lower patient compliance and incurring in higher healthcare costs. These issues can be solved by using polymeric matrices that ensure sustained release formulations with the intended pharmacokinetics.

Despite the need for sustained release drug formulations, the number of commercialized drug products including a highly dosed and highly soluble API is limited. This is mainly attributed to the lack of suitable polymers that allow to sustain the release of these challenging compounds. Poly(2-oxazoline)s (PAOx) has demonstrated to be an excellent polymer platform to develop such formulations. In addition to their biocompatibility and stealth behavior, PAOx show a high synthetic versatility, allowing to finely tune the hydrophilic/hydrophobic balance of the polymer by varying the side chain composition.

In the present work, the design and synthesis of PAOx of different hydrophilicity will be shown. Well-defined polymers with molecular weights above 50 kDa were synthesized. These polymers were used as matrix excipients for the formulation of a variety of APIs via different routes, including direct compression, hot melt extrusion (HME) and HME coupled with injection molding (HME/IM). PAOx show a high thermal stability, which is of importance for their processability. The release profile of the API could be tuned by variation of the polymer hydrophilic/hydrophobic balance. In our work we demonstrated that drug loads up to 70% API, 30% polymer (w/w) were possible using high molar mass PAOx. The possibility of controlling the dissolution kinetics of APIs using different PAOx blends was also investigated.

In vitro drug release from direct compressed tablets (n = 3) with 70% w/w anhydrous theophylline and 30% w/w poly(2-n-propyl-2-oxazoline) (PnPrOx)
Transmucosal administration offers numerous advantages for drug delivery. These include improved drug bioavailability, possibility of targeting particular organs, ease of dosage form application and avoidance of painful injections. Hydrophilic polymers have been widely used in the design of dosage forms for transmucosal drug delivery. Poly(2-oxazolines) is a class of functional polymers that are highly promising for biomedical and pharmaceutical applications. Over the recent years, our research group studied the use of polyoxazolines in the design of dosage forms for mucosal administration. Thiolated silica nanoparticles decorated with short-chain (5 kDa) poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) were found to exhibit enhanced ability to diffuse through gastric mucus. Decoration of thiolated silica nanoparticles with 5 kDa poly(2-ethyl-2-oxazoline) also resulted in a significant reduction of their mucoadhesive properties with respect to ex vivo rat intestinal tissues. Ability of poly(2-ethyl-2-oxazoline) to form hydrogen-bonded complexes with Carbopols® was utilised for the design of mucoadhesive tablets for buccal and gastrointestinal drug delivery. Tablets made of pure poly(2-ethyl-2-oxazoline) exhibited weaker adhesion to porcine buccal mucosa compared to Carbopols®. Their complexation or physical mixing with Carbopols® improves their mucoadhesive properties. The complexation between these polymers also has a profound effect on the swelling and drug release behaviour of tablets. Polymeric films were also designed by blending chitosan with poly(2-ethyl-2-oxazoline). In both in vitro and in vivo experiments, these films were found to be promising as mucoadhesive dosage forms for ocular drug delivery.
Our research laboratories have successfully demonstrated the synthesis of semi-fluorinated aryl ether polymers which include perfluorocyclobutyl (PFCB) aryl ether polymers prepared via radical-mediated thermal cyclodimerization of trifluorovinyl ethers (TFVE). \(^1\)\(^2\)PFCBs have been widely explored for high performance passive-optics, electro-optics, polymer light-emitting diodes, space survivability, polymeric fuel cell membranes, high use temperature fluorosilicones, and liquid-crystalline polymers. We have also demonstrated the nucleophilic addition of bisphenols to TFVEs affording fluoro-arylene vinylene ether (FAVE) polymers. \(^3\) Perfluorocycloalkenylnyl (PFCA) aryl ether homopolymers and copolymers were prepared in one step via nucleophilic addition/elimination of bisphenols and perfluorocycloalkenes. \(^4\) Current efforts in our group are focused on TFVE functionalization of curved-surface polyaromatic hydrocarbons e.g. acenaphthenequinone, corannulene or buckybowl-type substrates. The solution and solid state characterization including optical, thermal, and electronic properties of these new materials is presented.
(Meth)acrylate copolymers are one of the important polymers for industrial use. Copolymerization of (meth)acrylates and polymer reaction of (meth)acrylate homopolymers are used to obtain the copolymers. Each procedure has advantage and disadvantage. We paid attention the latter procedure because there is a possibility to obtain the copolymers having specific monomer composition, monomer sequence, and stereotacticity. But, transesterifications of ester group on poly(meth)acrylates side chain proceed under particular conditions generally.

We have reported synthesis of aliphatic polycarbonate by irreversible polycondensation of diphenyl carbonate with diols catalyzed by dilithium tetra-tert-butylzincate (TBZL). The exchange reaction with phenol obtained as byproduct did not occur under these conditions because of low activity of phenol, while that with diols did.

In this work, modifications of the polymer side chain by transesterification of ester group on poly[phenyl (meth)acrylate] [PPh(M)A] and alcohols using TBZL were developed. First, PPh(M)A having different MW and MWD was obtained by anionic polymerization using TBZL and by RAFT polymerization to use for the transesterification. The PPhMA was reacted with excess methanol in toluene or THF in the presence of catalytic amount of TBZL. PPhMA-MMA copolymer was obtained in this reaction conditions. MMA ratio was increased by extending the reaction time, and not affected by reaction solvent and MW of PPhMA. From these results, transesterifications of ester group on PPh(M)A side chain with alcohols other than methanol were also carried out. This reaction provides a process for the synthesis of specific (meth)acrylate copolymers.
The development of novel polymerization techniques has provided great opportunities to access well-defined polymers. For example, the merging of photoredox catalysis and radical polymerizations afford excellent temporal and spatial control over the chain growth under mild conditions. However, most of the current photosystems are based on electron transfer (ET) events between the excited state photocatalysts (PCs) and initiators, but few examples utilize energy transfer (EnT) to initiate/control the polymerization. Here, we demonstrate two protocols of radical polymerizations of vinylcyclopropanes, proceeding through either electron or energy transfer to control the backbone structure of the obtained polymers after an exclusive ring-opening process.
Organocatalyzed atom-transfer radical polymerization (O-ATRP) is a controlled radical polymerization mediated by organic photoredox catalysts. Typically, O-ATRP systems have required very high catalyst loading (1000 ppm) in order to achieve high control the polymerization. A library of N,N-diaryl dihydrophenazine catalysts possessing electron-poor, extended conjugation, and electron-rich core substitutions were explored for O-ATRP. Because of the new photophysical properties imparted by the substitutions, these catalysts efficiently operated efficiently at very low catalyst loading (5-50 ppm). Polymers were synthesized with excellent molecular weight control, initiator efficiency near unity, low dispersity, and high fidelity of the chain-end.
POLY 500: Design and synthesis of functional polyethers using the N-Al adduct catalysts

Jennifer Imbrogno, jennifer.imbrogno@utexas.edu, Nathaniel A. Lynd. Chemical Engineering, UT Austin, Austin, Texas, United States

Polyethers, derived from epoxides, are important for a range of applications including pharmaceutical formulations and membranes for carbon capture. Access to new polyether materials could advance these applications and also address other areas of growing technological challenge. Building off the previous success of mono(µ-alkoxo)bis(alkylaluminum) (MOB) initiator/catalysts which displayed rapid kinetics for epoxide polymerizations, it is now possible to independently control molecular weight and end group functionality by decoupling the initiation and catalysis functionalities of the MOB species. This new class of catalysts consist of a simple Lewis pair between an alkylamine and alkylaluminum. X-ray diffraction crystallography was used to determine the structure of the catalysts and associated initiators. End group control was verified with electrospray ionization mass spectrometry. The rate of polymerization was tuned by catalyst identity and concentration. Kinetic studies of the polymerization of allyl glycidyl ether monomer suggested that the rate was strongly dependent on catalyst concentration. A transition from 0th-order to 1st-order kinetics in monomer was observed with increasing catalyst concentration. With a new understanding of N-Al catalyzed polymerization kinetics, a simple and versatile tool for new polyether materials design has been developed.
Polyethers are a well-established class of polymers in permanent good standing due to their good thermal/chemical stability and versatile syntheses. They are used in a wide range of applications that go from industrial manufacturing to nanomedicine. This polymer family is usually limited to polyethers based on low chain aliphatic polyethers that can be obtained by the ring-opening polymerization of the corresponding cyclic ethers. In this work we report the production of medium-to-long chain aliphatic polyethers by a bulk polycondensation method using a simple and recyclable protic ionic liquid organocatalysts (H⁺-ILs). H⁺-ILs organocatalysts were easily prepared by forming stoichiometric and non-stoichiometric complexes of methanesulfonic acid (MSA) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The non-stoichiometric 3:1 MSA:TBD complex showed superior thermal stability and catalytic activity, and it was used for the bulk synthesis of a wide range of aliphatic polyethers with a number of methylene units ranging from 6 to 12 units. We envisage the potential of this economic & sustainable synthesis strategy as a green approach to produce unique polyethers.
Organocatalyzed atom transfer radical polymerization (O-ATRP) employs organic photoredox catalysts and alkyl halide initiators to synthesize well-defined polymers of target molecular weights and low dispersity. In this work, core modified phenoxazines are used as photoredox catalysts for O-ATRP. These molecules were found to exhibit superior catalytic performance in O-ATRP compared to their parent compounds for the synthesis of poly(methyl methacrylate) using white-light irradiation. In addition, it was shown that the O-ATRP of methyl methacrylate can be performed in the presence of minimal air when using this class of catalysts.
A variety of complex materials have been created via ADMET polymerization, including various types of branched polyethylenes, and polyolefins functionalized with hydroxyls, carboxolics, phosphonics, halogens, to name a few. Many of these materials are synthesized in a precise manner in which functional groups are placed in exact locations along polymer backbones. Precision results from the selective ADMET reaction of symmetrical α,ω-diene monomers (Figure 1) using tolerant and robust catalysts. Effective control of polymerization conditions eliminates unintentional side reactions and defects, yielding precision materials. We now report the expansion of ADMET’s versatility, using microwave irradiation, a technique synonymous with control.

ADMET Polymerization and subsequent alkene saturation providing a precision polyolefin
Organocatalyzed atom transfer radical polymerization (O-ATRP) is a method that employs organic photoredox catalysts (PCs) for the synthesis of polymers with targeted molecular weights, narrow molecular weight distributions, and defined architectures. The utilization of an organic PC in this method is beneficial, as it allows for precise spatiotemporal control over polymer growth while reducing our dependence on less sustainable precious-metal based PCs. Despite advantages associated with this method, its monomer scope remains largely unexplored and is primarily limited to methacrylate monomers, especially when phenoxazine and dihydrophenazine-based PCs are used. To address this limitation, PCs in these families have been applied for the O-ATRP of acrylonitrile with the goal of producing well-defined poly(acrylonitrile) and gaining more insight into the reactivity of these PCs.
POLY 505: Radical ring-opening copolymerization of cyclic ketene acetals with vinyl monomers

Catherine LEFAY, catherine.lefay@univ-amu.fr. Aix-Marseille Université, Marseille, France

The ring-opening polymerization of cyclic ketene acetals (CKA) by free radical or controlled radical mechanisms (rROP) attracts considerable research interest since it presents an alternative route for the synthesis of aliphatic polyesters. These monomers can indeed undergo radical addition on their C=C double bond that subsequently leads to propagation by ring opening.

The CKA/vinyl monomer rROP appears as an elegant method to elaborate partially or fully degradable copolymers depending on the proportion of ester functions incorporated in the copolymer backbone. Although this approach seems promising, important limitations still remain. The unfavorable reactivity ratios of CKAs with traditional vinyl monomers like (meth)acrylics or styrenics ($r_{\text{CKA}} < r_{\text{vinyl}}$) indeed leads to considerable discrepancy between the incorporated fraction of CKA in the copolymer and its initial fraction in the monomer feed.

The particular reactivity of CKAs was originally explained by the strong nucleophilicity of the double bond. To promote radical addition onto nucleophilic olefins, electrophilic radicals are usually required. Surprisingly, vinyl acetate, whose propagating radical is nucleophilic, appears experimentally to be the best comonomer for a good incorporation in the polymer chain.

Thanks to DFT Calculations, we are now able to understand the reactivity of the CKA and common vinyl monomer and in particular, we found first that vinyl ether appears the most favorable vinyl monomer to copolymerize with CKA to get random architectures whereas trifluoromethyl vinyl acetate (CF$_3$VAc) should provide alternating copolymers. These structures were confirmed experimentally with reactivity ratios of 0.73 and 1.61 for the couple MDO/VE and values close to 0 for the couple MDO/CF$_3$VAc (MDO for 2-methylene-1,3-dioxepane).

The good understanding of the reactivity of CKA monomers that allow for the tunable incorporation of main-chain functionalities in the copolymer would open up exciting perspectives in the field of degradable materials for bio-related applications.
Radical photopolymerization (RPP) is widely recognized and rapidly growing as an important green technology relative to conventional thermal polymerization because of its potential to reduce energy consumption and waste, while increasing productivity. The spatial and temporal controls afforded by on-demand light initiation are highly desirable in applications such as photolithography and 3-D printing, yet restrict the general use of RPP in many polymeric material applications due to efficient termination of polymerization upon irradiation discontinuation. Any low/moderate conversion regions within an undercured polymer contribute to compromised properties that cannot be rectified without additional irradiation. This limitation imposed by the rapid termination behavior severely limits implementation of RPP in potential applications that involve curing of dimensionally thick or expansive samples as well as in light-attenuating situations such as with composites, adhesives, pigmented materials or exposing irregular surfaces. Herein, we demonstrated the first example of a solvent-free radical photopolymerization of common (meth)acrylate resins, which enables rapid surface cure and subsequent dark cure to vitrification-limited conversion in initially under-cured regions after brief irradiation. We compared the radical-based dark curing photoinitiator (DCPI) to a conventional type II photoinitiator (CVPI), using a commercially available 365nm LED. For instance, DCPI can dark cure the initial 20% conversion up to 80% without additional light while CVPI remains at 20% conversion. Then, we probed unique dark curing behaviors in bulk resins, providing insights into a hitherto unstudied phenomenon in RPP. We believe that practical DCPIs will be utilized as a next green technology, expanding the use of RPP into applications that were not previously feasible with automatic built-in correction of under-cured regions.
Owing to the global scale establishment of polymer technology in the past few generations, the capability to carry out new polymerization reactions typically affords new applications and processes with far reaching implications. Here, we report a novel polymerization methodology utilizing homogenous gold catalysis (HGC) to facilitate the reaction of an unsaturated substrate with a dialkyne. Through optimization of the catalyst, ligand, solvent, and reaction parameters these polymerizations have been demonstrated to yield high molecular weight products under facile reaction conditions. Additionally, the unique 1,1-alkenyl linkage formed through the process gives rise to novel polymer architectures and connectivities. The high functionality tolerance of HGC allows for incorporation of diverse functionalities into the synthesized polymer system, affording large increases in structural complexity starting from simple substrates. Through an extensive investigation of unsaturated substrates and dialkynes with varying steric bulk, electron density, and substitution patterns, we have demonstrated a modular synthetic approach toward accessing novel polymer architectures derived from unsaturated substrates.

Generalized overview of the gold catalyzed polymerization process
Poly(ethylene oxide)-based polyoxyalkylene block copolymers have been developed and commercialized for more than half century and are still being used in many different fields such as cosmetics, cleaners, lubricants, and medicines. This type of amphiphilic block copolymer is able to self-assemble into nanoscopic structures. Significant effort has been put into the development of a series of nanosized therapeutic products to solubilize hydrophobic drugs, allow their sustained release, improve their pharmacokinetics, and facilitate their access to the site of action. Besides the copolymers with propylene oxide, block copolymers with 1,2-butylene oxide (BO) have received special attention due to their potential to control rheological properties in aqueous systems as associate thickeners and their bioactivity when used as drug delivery carrier. It has been postulated, demonstrated by computer simulation, and proven by experimental measurements that the self-assembly behavior of block copolymers can be impacted by their dispersities, such as the molecular weight dispersity of each block and of the chain, the compositional dispersity, and the dispersity of the block sequence, etc. The characterization of polyoxyalkylene block copolymers has been explored using many approaches; however, the quantification of different species in the reaction mixture is still unclear.

As polyoxyalkylene block copolymers are often synthesized by the anionic ring-opening polymerization of alkylene oxides, one has to take into account all the possible side reactions leading to the formation of homopolymers. In the presence of water, polyalkylene glycol may be formed and results in tri-block formation during the di-block copolymer preparation (see Figure below). This presentation will discuss our analytical approaches to identify the different species in the reaction mixture, and then to quantify the homopolymers and tri-block copolymers in polyoxyalkylene di-block copolymers.

SECxLC for identification of different species in reaction mixture
Pluronic block copolymers are nonionic polymeric surfactants, typically composed of PEO-PPO-PEO triblock copolymers. Pluronics are produced on a commercial scale for use in a wide range of applications of nanotechnology and biotechnology. While the Pluronic block copolymers offer the advantages of being readily available in a large quantity, they contain different levels of low MW polymeric “impurities” (Figure 1) that would interfere with the self-assembly of PEO-PPO-PEO macromolecular surfactants. In particular, the polymeric impurities in Pluronics have been known not to participate in the micellization of the triblock copolymers in water even at temperatures above critical micellization temperature.

Two major advances will be highlighted in studying Pluronic block copolymers. First, we have developed a large scale (e.g. multi-gram scale) purification technique by taking advantages of competitive adsorption between low MW polymeric impurities and triblock copolymers in the silica slurry upon tuning the solvent quality. Adsorption-based HPLC confirmed that the content of the polymeric impurities could be less than 2 wt. % by using silica slurry purification method, while the as-received Pluronic samples can contain about 20 wt. % impurities. Second, we have investigated the impact of the polymeric impurities on the micellar packing and solution phase behavior of Pluronic F108 and F127 samples. Small angle x-ray scattering (SAXS) and rheology experiments on as-received and purified Pluronics are compared to reveal how the presence of non-micellizable impurities in as-received Pluronics would interfere with the micellar packing, temperature-induced gelation and ordered structure formation of PEO-PPO-PEO triblock copolymers in water.

Fig. 1. SEC profiles of Pluronics before and after the polymeric impurity removal. The solid and dotted lines represent the profiles of as-received and purified Pluronics, respectively.
Block copolymers have been a subject of intensive research in the last few decades due to their formation of ordered nanophases that can be used as templates for various applications in nanotechnology. Block copolymers are also used in structural materials such as thermoplastic elastomers or high impact polymers. They are usually prepared by controlled polymerization methods such as anionic polymerization or controlled radical polymerization to produce a well-defined block structure in the polymer chains.

For the molecular characterization of block copolymers, size exclusion chromatography (SEC) has been used routinely, but it often fails to elucidate the details of molecular dispersity due to their size dependent separation and large band broadening. Other chromatographic methods can do a better job in the characterization of block copolymers. For examples, liquid chromatography at the critical condition (LCCC) successfully characterized individual block in block copolymers. Interaction chromatography (IC) is effective to fractionate homopolymer byproducts from the block copolymers and able to fractionate individual blocks into narrower fractions. In this talk, our works on detailed molecular characterization of block copolymers will be presented.
Molecular exchange processes are important equilibration and transport mechanisms in both synthetic and biological self-assembled systems such as micelles, vesicles and membranes. Still these processes are not entirely understood, in particular the effect of crystallinity and the interplay between cooperative melting processes and chain exchange. In regular block copolymer micelles insight to the exact mechanism of molecular exchange is obscured by polydispersity which leads to extremely broad distribution of relaxation times. Here we focus on a set of simple polymer micelles formed by binary mixtures of poly(ethylene oxide)-mono-n-alkyl-ethers (Cn-PEO5) which allows the melting point to be tuned over a wide range. We show that while the melting transition is cooperative in the confined 4-5 nm micellar core, the exchange process is widely decoupled and unimeric in nature. As confirmed by calorimetry (DSC), the total activation energy for ejecting a molecule out of the micellar core below the melting point is the sum of enthalpy of fusion, and the corresponding activation energy in the melt state. This suggests that while the global melting/crystallization mechanism is cooperative, a 'local, single-chain melting process' preludes the molecular diffusion out of the micelle during chain exchange.
In recent studies we have expanded our work producing cationic PISA-latexes for strong adhesion to anionic surfaces, using RAFT-mediated surfactant-free emulsion polymerization with self-assembly (PISA) of block copolymers. Starting with two types of macroRAFT-agents, either 2-(Dimethylamino)ethyl methacrylate (DMAEMA) or N-[3-(Dimethylamino)propyl] methacrylamide (DMAPMA), latexes are tailored to have a hydrophilic, cationic corona with a hydrophobic core of either poly(n-butyl acrylate) (PBA), poly(methyl methacrylate) (PMMA) or poly(n-butyl methacrylate) (PBMA). Varying the degree of polymerization (DPn) of the core-polymer, one can tailor the size of the formed nano-latexes (from 30 up to 200 nm). These cationic latexes show strong adhesion to cellulose surfaces (visualized by quartz crystal microbalance, QCM-D, and scanning electron microscopy, SEM). However, the chain-extension efficiency from the initial macroRAFT-agent, during PISA, was shown to affect the adsorption to a large degree. Shown as a small adsorption but especially low surface coverage, using QCM-D and SEM on both silica and cellulose surfaces. The results for efficiency of PISA during the latex-formation can be further corroborated with SEC and 1H-NMR. The latexes were then successfully cleaned with centrifuge work-up protocols, thus indicating for some latexes as low as 75% of the macroRAFT-agents being chain-extended, showing residual free hydrophilic polymers in the water phase. The combined results clearly show how large impact even a small fraction of such free polymer has on the adsorption, if not removed sufficiently. The fraction of free polymer is seemingly low but still efficient to neutralize charges on a surface also due to the faster diffusion. The presented methods are powerful tools to analyze residual charged or non-charged surface-interacting polymers within such RDRP-system. The methods also allow to characterize when sufficient work-up protocols have been applied.
The number of new antibiotics that reach the market is currently much lower than that of newly developing antibiotic-resistant bacterial strains. This causes serious health problems even in industrialized societies. Thus, the need for antibiotics with changed activity profiles and resistance forming potential is great. A common way to achieve this is derivatization of established antibiotics. We have investigated the antimicrobial behavior of polymer antibiotic conjugates, which has been rarely investigated. Poly(2-oxazoline)s (POx) are biocompatible polymers considered as alternative to Poly(ethylene glycol) (PEG) and therefore promising candidates for the conjugation with antibiotics.

Covalent conjugates of POx with the antibiotic ciprofloxacin (CIP) were found to be antimicrobially active against several nosocomial bacterial strains. Thereby, the activity is controlled by the nature of the linker between CIP and the polymer, the nature of the polymer itself, and the length of the polymer chain. In the some cases, the molar antibacterial activity of the conjugates even exceeds that of pristine CIP. It was further shown that the resistance formation of S. aureus and E. coli against the conjugates is significantly delayed compared the CIP. Conjugates of POx with penicillin G and penicillin V, respectively, were also found to be active. Here, the length of the polymer does not play a significant role, due to the fact that these antibiotics are not required to cross the cell membrane to be active. Further, the penicillin POx conjugates were found to be less susceptible to hydrolysis by the enzyme penicillinase, which makes them active against penicillinase-producing and thus resistant bacterial strains.
Vaccination is a successful strategy for combating disease, both infections and cancers. However, many diseases lack vaccines due to insufficient control of immune responses. Adjuvants provide a route to improve and direct immune responses, but there are few controlled and mechanistic adjuvants. While most known adjuvants like alum generate a Th2 and antibody mediated responses, the number of adjuvants eliciting a robust CD4⁺/Th1 or CD8⁺ response is limited. We are currently investigating if the NLRP3 inflammasome can be targeted for this purpose. The NLRP3 inflammasome plays a role in the inflammatory response to vaccines, in antimicrobial host defense, and in autoimmune diseases. The chemical and structural diversity of inflammasome activators has made it difficult in translating inflammasome activators into controlled adjuvants. No current activator can be tuned to generate a desired degree of activation. Thus, in order to design such immunomodulatory biomaterials, we developed a new tunable polymeric lysosomal rupture probe that leads to significant differences in inflammasome activation owing to minute structural changes due to chemical modification as small as a single amino acid. We demonstrate that each molecule differentially activates the inflammasome based solely on their degree of lysosomal rupture. We have employed the understanding of chemical control in structure-based design of immunomodulatory NLRP3 agonists on a semi-predictive basis. When used as vaccine adjuvants, these polymeric biomaterials elicit a robust cellular response. We are currently investigating the application of these polymers as vaccine adjuvants for a Q-fever disease model and in development of tumor vaccines. Thus, these polymers provide an effective chemical platform for designing novel vaccine adjuvants.
POLY 515: Intracellular delivery via noncharged sequence-defined cell-penetrating polymer conjugates

Ngoc N. Phan¹, np377@cornell.edu, Christopher A. Alabi². (1) Chemical & Biomolecular Engineering, Cornell University, Ithaca, New York, United States (2) Chemical Engineering, Cornell, Ithaca, New York, United States

The discovery of cell-penetrating peptides (CPPs) over three decades ago uncovered a novel method for transporting a variety of cargoes into cells. Although promising, CPPs have several drawbacks that hinder their use for in vivo therapeutic applications such as rapid metabolic degradation by proteases, immunological response, undesired interactions with extracellular matrix components, and nephrotoxicity. Recently, the Alabi group developed an approach for the rapid assembly of sequence-defined oligothioetheramides (oligoTEAs). OligoTEAs have three distinct advantages over native peptides, including i) abiotic design to reduce proteolytic degradation and immune response, ii) backbone and pendant group access to tune interactions, and iii) diverse monomers for massive compositional space.

To overcome the drawbacks of cationic cell-penetrating peptides, we have designed and synthesized a new class of noncharged cell-penetrating oligoTEAs (CPOTs) that undergo extensive and rapid cellular entry across different cell lines with low cytotoxicity. CPOTs outperform a widely used CPP, the R9 peptide. This new class of highly efficient noncharged macromolecular transporters are distinct from their cationic counterparts and show strong promise for the intracellular delivery of therapeutics. This talk will focus on the sequence controlled assembly of this new class of cell-penetrating agents, their uptake efficiency across a variety of cell lines, and their ability to deliver hydrophilic molecules into cells. Notably, I will discuss the assembly of a reducible CPOT-vancomycin conjugate and its efficient transport into host cells towards the treatment of an intracellular pathogen, Listeria monocytogenes. CPOT-vancomycin conjugates were efficient at clearing intracellular Listeria monocytogenes within macrophages in less than six hours, thus showing promise as viable macromolecular therapeutics.
POLY 516: Slow-release and extended shelf-life of coordination polymer encapsulated vaccines

Jeremiah J. Gassensmith, gassensmith@utdallas.edu. Chemistry and Biochemistry, University of Texas at Dallas, Allen, Texas, United States

Many vaccines use a weakened or engineered form of the pathogenic virus to generate an immunogenic response, which helps prepare the immune system for a real infection from that virus. Being proteinaceous therapeutics, however, these vaccines denature when exposed to elevated temperatures or organic solvents. Recently, we published a communication showing how the surfaces of VLPs could nucleate the growth of a crystalline porous coordination polymer (PCP) called zeolitic imidazolate framework-8 (ZIF-8), which could stabilize tobacco mosaic virus (TMV) against harsh conditions and the virus could retain its shape even after the ZIF-8 shell was removed by EDTA. Many questions, however, persisted including i) what effect did the nucleation and growth of ZIF-8 have on the surface of the virus, ii) if the viral nanoparticle RNA was likewise protected against degradation, and iii) how this technology could be translated to *in vivo* use.

I will present work that answers these questions: To address i) TMV or encapsulated TMV (TZ-Thick) was stressed under various conditions and measured by ELISA. The results indicated that the ZIF-8 shell improves the surface stability of TMV compared to the unencapsulated virus when boiled in water for 20 min by 2390% and when left in methanol, 6 M guanidinium chloride, or ethyl acetate overnight by 172.4 %, 1850 %, and 97.5%, respectively. To address ii) we infected *Nicotiana benthamiana* (n = 6 pots) with TZ-Thick or after exfoliating TZ-Thick and after 10 days the leaves were harvested for measurements by ELISA. Plants infected with TZ-Thick showed an ELISA response at 66.6% and exfoliated TZ-Thick at 72.2%, indicating that the RNA is protected against degradation—KP buffer (0 %) and TMV (100 %) were used as controls. To begin addressing iii), Cy5 labeled TMV (Cy5-TMV) was encapsulated (Cy5-TZ-Thick) and injected subcutaneously into mice to evaluate the dispersal over time. Cy5-TZ-Thick remained fluorescent 7 days longer than Cy5-TMV owing to the slow dissolution of ZIF-8, which we believe will expose antigen presenting cells to the virus longer and should lead to a stronger immunogenic response.
POLY 517: Zwitterion-modified dendrimer-entrapped gold nanoparticles loaded with gadolinium for enhanced CT/MR imaging of lung cancer metastasis

Jinyuan Liu1, Zhijuan Xiong1, Jiulong Zhang2, Chen Peng3, Mingwu Shen1, Xiangyang Shi3, xyshius@yahoo.com. (1) Bioengineering, Donghua University, Shanghai, China (2) Department of Radiology, Shanghai Public Health Clinical Center, Fudan University, Shanghai, China (3) Cancer Center, Shanghai Tenth People’s Hospital, Tongji University School of Medicine, Shanghai, China

To improve the accuracy and sensitivity of early diagnosis of diseases, it’s essential to make full use of the strengths of all kinds of imaging modalities. One ideal solution is to combine two or more imaging elements in one platform for dual mode or multimode imaging applications. In addition, nanoparticles (NPs) often suffer quick clearance by reticuloendothelial system (RES) once they are injected to the body. Therefore, it’s critical to render the NPs with good antifouling properties. Herein, we describe the synthesis of three antifouling agents modified generation 5 (G5) polyamidoamine (PAMAM) dendrimers entrapped with gold nanoparticles (Au DENPs). Through protein resistance, macrophage cellular uptake and pharmacokinetics assays, we show that Au DENPs modified with 1,3-propane sultone (1,3-PS) exhibit the best antifouling property. We then prepared G5 PAMAM dendrimer platform modified with Gd (III) chelator DOTA, targeting agent arginine-glycine-aspartic acid (RGD) peptide, 1,3-PS and used them as templates to synthesize Au DENPs, followed by Gd (III) chelation. In particular, the formed multifunctional Au DENPs displayed enhanced X-ray attenuation property, high r1 relaxivity (13.3 mM s⁻¹), good cytocompatibility, targeting specificity, and enabled effective dual mode CT/MR imaging of a lung cancer metastasis model in vivo. The developed multifunctional zwitterion-functionalized Au DENPs may be potentially used as an efficient nanoprobe for enhanced dual-modal CT/MR imaging of other cancer types.

Schematic illustration of the synthesis of zwitterion-modified dendrimer-entrapped gold nanoparticles loaded with gadolinium for CT/MR imaging applications
POLY 518: Cyclic peptide / polymer conjugates for therapeutic applications

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

We describe the synthesis, characterisation and therapeutic applications of bioconjugate based on cyclic peptides covalently attached to well-controlled polymeric chains. The conjugates assemble into short nanotubes (20 to 200nm) through the stacking of the cyclic peptide motives, with functionality imparted by the polymeric chains. The resulting constructs show remarkable properties in terms of cell penetration, and in vivo biodistribution.
Therapeutic strategies involving human monoclonal antibodies (mAbs) are becoming increasingly prevalent. However, solutions of mAbs possess unusually high viscosity, caused by their self-assembly into clusters. This is a bottleneck for industry's ability to scale-up manufacturing and imposes product formats that require healthcare professionals to administer the mAb, both of which increase cost. At present, the cost of mAb therapies can reach several thousands of dollars per year, which is prohibitive to their use – irrespective of how well they treat disease. There is thus an immediate and urgent need to address the manufacturing challenges posed by high viscosity, and this presentation showcases bioconjugate approaches to do so. First, a bioconjugate ‘scavenger’ will be presented to achieve the affinity purification of mAbs from cell culture supernatant. Remarkably, the properties of the polymer component within the bioconjugate were determinant on controlling protein–protein interactions between the scavenger and the mAb. Secondly, a bioconjugate strategy will be presented to reduce the viscosity of concentrated mAb solutions. A polymer additive that transiently couples to mAbs will be described that very efficiently prevents mAb self-assembly, leading to reduced viscosity.

A monoclonal antibody
Oxytocin, a cyclic nine amino acid neurohypophyseal hormone therapeutic is effectively used in the control of postpartum hemorrhaging (PPH). It has a limited shelf life stability in aqueous solutions at temperatures > 25 °C thus limiting its use in the developing world. This study describes the development of bioconjugation strategies as an effective method for stabilizing solution formulations of this peptide for prolonged storage in the absence of efficient cold chain storage which often proves difficult due to capital investment requirments. The conjugation chemistries investigated herein includes irreversible amine targeted conjugation methods utilizing NHS ester and aldehyde reductive amination chemistry.
POLY 521: Salt permeation mechanisms through charge-patterned mosaic membranes

William A. Phillip, wphillip@nd.edu. Chemical Biomolecular Eng, Yale University, Notre Dame, Indiana, United States

Charge-patterned mosaic membranes, which consist of discrete positively-charged and negatively-charged domains patterned on a template, are capable of transporting dissolved salts more rapidly than neutral molecules of comparable size. For example, when tested in filtration experiments, this class of membrane is able to enrich the salt concentration in the permeate relative to the feed solution. This ability to facilitate the transport of whole salts is a direct result of the chemically-patterned surface. To date, however, few charge mosaics have been fabricated and as a result, their design and proliferation have lagged. Here, using inkjet printing techniques to precisely-pattern membrane chemistries, a series of experiments that helped to elucidate the membrane-solute interactions underlying the transport properties of charge-patterned membranes were executed. Membranes of varied charge (i.e., positively-charged, charge-patterned, and negatively-charged) were fabricated and their salt permeabilities as a function of concentration were quantified in diffusion cell experiments. Salt permeability increased with concentration for the single-charge membranes and decreased with concentration for the charge-patterned membrane. A theoretical framework capable of describing these trends was developed. In particular, it was shown that the structural charge heterogeneity of the patterned membrane surface modifies the local electrostatic potential, and in turn, availability of ions for transport. These insights informed experiments that examined the effects of pattern geometry (e.g., stripes, cubes, and hexagons) and feature size on membrane throughput. The variations in salt transport for this family of membranes could be captured using a single variable, the interfacial packing density, $\sigma$, that quantified the length of junctions between oppositely-charged domains in a unit area. In filtration experiments, the enrichment of symmetric salts (e.g., KCl) increased monotonically with $\sigma$. In contrast, the transport of asymmetric salts (e.g., MgCl$_2$) was independent of $\sigma$. These results will enable further development of charge-patterned membranes.
POLY 522: Influence of relative permittivity properties on ion transport in hydrated polymer membranes

Geoffrey M. Geise, geise@virginia.edu. Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia, United States

Polymer membranes enable technologies that could address critical need for sustainable supplies of water and energy. Advanced membranes, however, are needed to realize fully the potential of these technologies. Much remains unknown about the chemical factors that influence polymer membrane transport properties, and understanding these fundamental structure-property relationships is critical for developing the next generation of polymer membranes.

Transport in non-porous polymer membranes is often described by a solution-diffusion mechanism where both thermodynamic partitioning and diffusion contributions affect transport properties. In desalination membranes, polymers with simultaneously high water permeability and low salt permeability are desirable to prepare selective membranes that can efficiently desalinate water. Therefore, polymers that exclude salt are desirable. In electro-membrane processes, salt exclusion is also needed, as mobile salt (or co-ion) exclusion is critical for attaining favorable permselectivity properties that are critical for efficient operation of electromembrane processes. This study reports an investigation of the influence of polymer chemistry on salt exclusion in polymers for membrane applications.

Microwave dielectric spectroscopy measurements were made on hydrated polymers based on poly(glycidyl methacrylate), pGMA. Relative permittivity properties are linked to ion sorption properties that are critical for desalination applications, but little is known about the influence of polymer chemistry and water sorption on relative permittivity. The pGMA-based materials considered in this study had lower relative permittivity compared to Nafion®, which is a perfluorosulfonic acid polymer considered for fuel cell applications, at comparable water content. This result favors ion exclusion and demonstrates the importance of polymer chemistry in engineering polymers for desalination membrane applications.
Engineered osmosis (EO) involves the contact of two solutions with different chemical potentials of water across a membrane interface to generate a water flux. This difference in chemical potential is obtained by a difference in concentration or/and pressure. EO applications use spacers with large openings to reduce concentration polarization. When pressure is applied in processes such as osmotically-assisted reverse osmosis, pressure-assisted osmosis, and pressure-retarded osmosis (PRO), membranes undergo a mechanical deformation as they are compressed against the spacer. This deformation causes an increased reverse salt (RS) flux as the hydrostatic pressure increases.

We incorporated membrane deformation into boundary layer equations to describe water and RS flux in EO. We deformed a commercial TFC membrane using a tensile testing machine with the goal of correlating the linear membrane strain with water permeance and salt reverse flux obtained via direct-flow permeation. We measured cross-flow PRO water flux and used similar literature data to train the mathematical model for predicting changes in RS flux with increased pressure. Laser measuring microscopy revealed the area on the membrane with increased deformation, and confirmed that the deformation profile follows a parabolic trajectory. We refined our model and correlated our PRO data with the opening size and relative open area of feed spacer.

Results showed that the linear membrane strain reaches values above 15%, which are greater than the reported strain-to-fracture values for these membranes. Water and RS were not statistically different when measured using increasing and decreasing pressure profiles, suggesting that active layer deformation is partially reversible. Best fits were obtained using a model that incorporated diffusion through a film comprising intact polymer, deformed polymer, and occasional fracture sites. Deformations in more than 2% of the membrane area lead to exponential increments in the RS flux as pressure increases. This work introduces membrane deformation as a factor to consider in the design of membranes and modules for engineered osmosis applications.
Clothing provides a microclimate between the body and the external environment, and acts as a barrier for heat and vapor transfer in between. In sweating conditions, in order to maintain the thermal comfort, fabric next to the skin should not only absorb liquid rapidly but also transport it through the fabric promptly to avoid the discomfort of the fabric sticking to the skin. On the other hand, in the raining weather, the fabric next to the environment is desired to prevent the water passing from the environment to the skin, and thus should possess water-resistant or water-proof properties. Therefore, there’s a demand to design a fabric material that has an asymmetric wettability and could directionally transport water from the skin to the environment, but minimize the transport in the reverse direction.

In this project, we worked towards this goal — endowing asymmetric wettability on breathable fabrics to enable directional (differential) water transport properties. We used a combination of superhydrophobic finishing and plasma selective treatment to create gradient wettability channels through the fabric thickness. While these channels were served for directional liquid transport, the untreated larger surface remained superhydrophobic, therefore could still provide thermal comfort and water-resistant properties next to the skin and the environment, respectively. The directional water transport ability was confirmed by a home-made measurement device. Additionally, SEM, TGA, chemical analysis, and contact angle measurements were performed to determine the surface structure and wettability of the fabric after various modification conditions.
One of the most efficient methods for understanding the transport of gases and liquids through polymeric membranes is using computer simulations. In general, the construction of amorphous materials in silico is quite challenging due to the lack of a reference structure (X-ray crystallography) and the nature of unfavorable energy from steric effects as a function of chain length. Currently, the state-of-the-art approach for construction of amorphous polymers is by simulated polymerization. This approach involves energy minimization and molecular dynamics simulations as new bonds form throughout the synthesis process. The power and usefulness of this methodology is its predictive capability and general applicability, demonstrated, in this talk, for a representative group of polymers including the so-called polymers of intrinsic microporosity. Moreover, most studies to date consider the systems as static, which might be an unrealistic assumption especially at high pressures. In particular, phenomena such as swelling, plasticization, and aging are known to affect the properties of polymers in general, and will be discussed in this talk as well. Validation of the methodology is provided by characterization of the simulated structures in excellent agreement with available experimental data produced from our experimental collaborators and others, including densities, wide-angle X-ray scattering, surface areas, pore-size distributions, gas adsorption isotherms, selectivities and permeabilities.
Solvent-filled polymers are an important class of membrane-electrolytes because the imbibed solvent imbues the material with high conductivity while maintaining mechanical stability. Both these attributes are essential for membrane-electrolytes in numerous energy-storage and conversion devices. However, these membranes’ favorable ion-transport properties pose a challenge when multiple ion types are present. Specifically, there are few quantitative material design guides for polymers to balance the movement of certain species that are desirable, such as current-carrying ions, against transport of contaminants, additives, or redox-active species, which decrease device performance. To address this challenge and provide material design insights, this work describes the theory of multi-ion transport in these polymer-electrolyte membranes.

Specifically, we use Stefan-Maxwell-Onsager theory to rigorously describe concentrated-solution transport in the membrane. To connect performance to the molecular-level structure of the polymer, hydrodynamic theory provides constitutive relations for the involved ion/solvent and ion/ and solvent/polymer friction coefficients, with classical porous-media theories scaling tortuosity. Additionally, electrostatic relaxation dictates friction between ions. To account for the contribution of weak electrolytes, the model incorporates ion speciation into species’ transport coefficients.

The model compares favorably to a number of published measured membrane transport properties (e.g. conductivity, transference numbers, electroosmosis, and water transport coefficient) in dilute and concentrated binary and ternary electrolytes. The model isolates the contribution of each type of molecular-scale interaction between species to the measured properties. Moreover, we show how to encode concentrated-solution theory into dilute-solution transport parameters and explore the limitations of both approaches.

Illustration of the types of frictional interactions between ions in solvent-filled membranes
POLY 527: How membrane chemistry influences transport mechanisms in various separation processes

Abhishek Roy¹, alroy@dow.com, Mark Brayden¹, Marcos Martinez¹, Junqiang Liu¹, Mou Paul¹, Steven Rosenberg², Marty Peery². (1) The Dow Chemical Company, Freeport, Texas, United States (2) Dow Water and Process Solutions, Edina, Minnesota, United States

In the last couple of decades, significant progress has been made in identifying membrane as a potential candidate for several separation applications like the fuel cell, water purification, and various gas separation applications. In all of these applications, a common need and opportunity space are to develop structure-property relationships between membrane chemistry and transport. In H2 driven fuel cells, there has been evidence of membrane morphology playing a significant role in guiding the nature of water and proton transport across the membrane. Ionic block copolymers have shown promise as a potential candidate to improve proton conductivity at lower water content. Similarly, in water purification membranes, designing membranes with specific functional groups have known to impact Donnan Exclusion and solution-diffusion mechanism. Recently, there has been a strong emphasis in designing membranes which can potentially reduce the distillation cost by a partial replacement of distillation columns and thus reducing CAPEX and OPEX expenses. It is believed a strong structure-property relationship is needed to address the challenges associated with this application. The presentation will focus on these topics and will share future perspectives.
POLY 528: Electron tomography reveals details of the internal microstructure of desalination membranes

Tyler Culp², Yuexiao Shen³, Mou Paul⁴, Abhishek Roy⁴, Manish Kumar³, Enrique Gomez¹, edg12@psu.edu. (1) Penn State University, University Park, Pennsylvania, United States (2) Chemical Engineering, The Pennsylvania State University, State College, Pennsylvania, United States (3) Pennsylvania State University, University Park, Pennsylvania, United States (4) The Dow Chemical Company, Pearland, Texas, United States

Many open questions remain regarding the internal structure of thin-film composite RO membranes. In this work, fully aromatic polyamide films that serve as the active layer of state-of-the-art water filtration membranes were investigated using high-angle annular dark-field scanning transmission electron microscopy tomography. Reconstructions of the 3D morphology reveal intricate aspects of the complex microstructure not visible from 2D projections. We find that internal voids of the active layer of compressed commercial membranes account for less than 0.2% of the total polymer volume, contrary to previously reported values that are two orders of magnitude higher. Measurements of the local variation in polyamide density from electron tomography reveal that the polymer density is highest at the permeable surface for the two membranes tested and establish the significance of surface area on RO membrane transport properties. The same type of analyses could provide explanations for different flux variations with surface area for other types of membranes where the density is distributed differently. Thus, 3D reconstructions and quantitative analyses will be crucial to characterize the complex morphology of polymeric membranes used in next-generation water-purification membranes.

Electron tomogram of polyamide film used in RO modules.
Most of the earth’s water is in the oceans and only 3% is fresh water and the leading method for making potable water from seawater is reverse osmosis (RO). The polyamide (PA) barrier layer in commercial RO membrane systems is made through an interfacial polymerization process carried out on the surface of nano-porous polysulfone (PS). Despite the technical importance of the barrier layer (the smallest pore size component in a RO membrane), an understanding of the relationship between molecular level structure and function has yet to emerge. To determine the molecular level structure of the barrier layer, we have carried out grazing incidence wide angle x-ray scattering (GIWAXS) studies on BW30 and BWXLE membranes, commercially available products manufactured by DOW Filmtec. For the x-ray measurements, the non-woven fabric is first peeled off and the PS is dissolved with an organic solvent. At the end of the process, the PA film is in contact with a polished silicon wafer with the PA surface facing the wafer. The x-ray measurements were carried out at the CMS beamline at NSLS II (BNL) with varying incidence angles as this provides a measure of the depth dependence of the scattering. The GIWAXS patterns exhibit diffuse scattering features (see figure) characteristic of an amorphous structure with several characteristic length scales. The BWXLE membrane shows the existence of two peaks in q, each with about the same intensity whereas BW30 exhibits a single peak. For both samples, the anisotropy shows the existence of preferential surface induced alignment. Further, the dependence of the scattering profiles on the incident angle suggests that the molecular structure is depth dependent. The effects of using different solvents to dissolve the PS on the x-ray results will be discussed. On the basis of the scattering results, we present a structural model of the packing of the aromatic motifs. Further, we will discuss these results in the context of their permeance properties and published physical characteristics.
Bone is an interpenetrating composite material consisting of collagen fibrils and nanocrystalline hydroxyapatite. The combination of organic and inorganic components in a tightly controlled hierarchical structure results in outstanding mechanical properties and is essential for both the structural function of bone and its dynamic role in a variety of biochemical processes within the body. A similar nanostructure can be achieved in acellular constructs using a polymer-induced liquid-precursor (PILP) process to modulate the deposition of calcium phosphate within and around collagen fibrils. PILP droplets form as the polyanionic process-directing agent sequesters calcium and phosphate ions/clusters from solution into hydrated ion enriched droplets; these droplets then infiltrate the collagen matrix and deposit an amorphous mineral phase within the collagen fibrils, which then crystallizes to form tiny intrafibrillar platelets of hydroxyapatite aligned with the collagen fibrils. A variety of polyanions can serve as PILP process-directing agents, including simple polyamino acids such as polyaspartic acid (pASP), and natural acidic proteins such as osteopontin (OPN), a non-collagenous protein found in bone. This study focuses on the effects of PILP process-directing agents on the mineralization process and osteoclast activation. For binary combinations of artificial pASP and natural OPN (from bovine milk), the OPN-rich mixtures result in faster mineralization kinetics and more abundant resorption structures (actin rings) but fewer tartrate-resistant acid phosphatase (TRAP)-positive cells than pASP. The dose-dependent response may be a valuable tool for tailoring in vivo resorption and remodeling of biomimetic bone substitutes.
Donor cells and tissue are vital components of modern medicine. However, once removed from the body, the lifetime of cells and tissue is severely limited. For example, red blood cells can be kept for a maximum of 42 days, platelets for 8 days, and donor organs for just a matter of hours. In principle, cryopreservation can be used to enable the prolonged storage of cells and tissue. However, current methods of cryopreservation use large volumes of organic solvents which negatively impact the viability of cells post-thawing and can cause unwanted side effects when transplanted into patients. A key cause of cell death is ice growth as well as membrane damage due to the low temperatures, and any additives which can modulate this could be hugely beneficial for applications relating to cell/tissue storage.

Here I will present our work using biomimetic approaches to improve cryopreservation of mammalian cells, inspired by how polar fish survive in freezing ocean environments. I will discuss recent progress we have made in the polymer-enhanced cryopreservation of cells in both suspension and mono-layer formats. This will include the design principles of polymer cryoprotectants as well as investigations into their mechanism of action, beyond just inhibiting ice growth.

Cryopreservation of mammalian cells in both suspension and monolayer culture is improved by the addition of polymer cryoprotectants, compared to traditional methods using organic solvents.
Mucins play diverse and crucial roles in the body. These functions range from lubrication of articular joints and the eye, to protection of stomach endothelium, to modulation of oral and gut microflora populations. Despite their diversity, these functions commonly stem from modifications in a general structure shared by all mucins: a blocky polypeptide backbone comprised of terminal moieties for binding surfaces or crosslinking and a characteristic glycosylated bottlebrush.

Inspired by this adaptable structure, we have created a mucin analogue platform which engenders key structural features preserved among native mucins. We have emulated the mucinous bottlebrush with a lysine-rich elastin-like polypeptide backbone, which provides primary amines for conjugation of synthetic polymer “bristles.” Binding modules target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct.

To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mucin analogues to osteoarthritis and kidney stone disease, conditions infamous for profound morbidity and high prevalence. We will demonstrate that collagen-targeted mucin analogues adsorb to model surfaces and prevent protein fouling. This recapitulates the function of lubricin, a mucin downregulated in osteoarthritis. Similarly, we will show that we can target mineral surfaces relevant in kidney stone disease by exchanging the binding module of our analogue mucins. We will show that these altered analogues also inhibit protein-fouling, which is implicated in stone growth. In this platform technology, we have been inspired by the diverse functions of native mucins. By harnessing the general structure which gives rise to these properties, we hope not only to replicate the in vivo function of mucins, but also to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings, such as inhibiting the growth of kidney stones.
POLY 533: Fast synthesis of biodegradable elastomers with tunable mechanical and surface properties via thiol-ene click chemistry for skeletal muscle regeneration

Mohamed Alaa Mohamed1,2, mm446@buffalo.edu, Aref Shahini1, Julia Caserto1, Ahmed El-Sokkary2, Magda Akl2, Stelios Andreadis1, Chong Cheng1. (1) Department of Chemical and Biological Engineering, The State University of New York at Buffalo, Buffalo, New York, United States (2) Chemistry Department, College of Science, Mansoura University, Mansoura, Dakahliya, Egypt

Skeletal muscle tissue engineering is a promising strategy aiming at restoration of injured muscle tissue functions and compensation of volumetric loss of tissues. Here, we report facile synthesis of novel series of optically transparent elastomers with tunable mechanical properties, surface wettability, and degradability via thiol-ene click chemistry (Figure 1). A novel glycerol-based monomer with thiol-reactive olefin functionalities, glycerol tripentenoate (GTP), was synthesized, and subsequently crosslinked with a series of di- and tri-thiols, including 1,6-hexanediithiol (HDT), 1,4-butanediol bis(3-mercaptopropionate) (BDBMP), trimethylpropane tris(3-mercaptopropionate) (TMPTMP), and ethoxylated trimethylolpropane tri(3-mercaptopropionate) (ETTMP 700) to generate crosslinked networks of varying surface hydrophilicity. To tune mechanical properties of networks, 4-pentenyl 4-pentenoate (PP) monomer with two clickable olefin groups was further synthesized, and then copolymerized with GTP and BDBMP to generate crosslinked GTP-co-PP-co-BDBMP network; varying the molar ratio of [ene]GTP/[ene]PP in the feed resulted in crosslinked networks of varying mechanical and swelling characteristics. Mechanical studies revealed Young’s modulus spanning from 0.07 MPa to 11.3 MPa and elongation range of 15.2 – 445%. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed decomposition temperature range of 320 – 430 °C, and Tg values between -21 and -51 °C. Proliferation and myogenic differentiation of primary mouse myoblast cells on GTP-co-HDT, GTP-co-BDBMP, GTP-co-TMPTMP, and GTP-co-ETTMP elastomers revealed their biocompatibility and myogenic differentiation ability with obvious formation of contractile myotubes. Overall, these biodegradable elastomers are promising for potential applications in skeletal muscle tissue engineering.

Figure 1: Schematic illustration of development of the biodegradable elastomers.
POLY 534: Development of a polymer-based delivery system for the treatment of *Clostridium difficile* using a Galili-antigen analogue

**Brady Hall**\(^1,2\), grnltre5@gmail.com, Colleen Malley\(^2\), Michael D. Schulz\(^2,1\). (1) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

*Clostridium difficile* (C. *diff.*) bacteria is a species of anaerobic intestinal bacterium responsible for causing *Clostridium difficile infection* (CDI). Regulated by competing gut flora, C. *diff.* often exists asymptotically in the intestines. However, C. *diff.* overgrowth occurs when antimicrobial treatments eliminate the normal, competing bacteria. Furthermore, toxins produced by the C. *diff.* bacteria then cause symptoms associated with CDI. Current therapies for CDI are largely ineffective; antibiotic approaches, for example, in addition to facilitating C. *diff.* antibiotic resistance, presumably disrupt the gut flora that provide colonization resistance against CDI. Toxins produced by C. *diff.* bacteria are known to bind to a naturally occurring oligosaccharide. We aim to prepare an oligosaccharide which can be appended to a polymer via post polymerization modification. Herein we propose a strategy to prepare and characterize a polymer sequestrant that is capable of eliminating toxins produced by C. *diff.*
POLY 535: Biomimetic graft-copolymers for restoring the lubrication properties of damaged cartilage

Giulia Morgese², Lucca Trachsel¹, Marcy Zenobi-Wong³, Edmondo Maria Benetti¹, edmondo.benetti@mat.ethz.ch. (1) Materials, ETH Zurich, Zurich, Switzerland (2) Technical University of Eindhoven, Eindhoven, Netherlands (3) Health Sciences and Technology, ETH Zürich, Zurich, Switzerland

Within the articular joints of mammals, boundary lubricants featuring highly branched biomacromolecules provide very low coefficients of friction at the cartilage surface, and ensure no wear over decades. During degenerative diseases of the joint, such as osteoarthritis (OA), a progressive depletion of these macromolecules within the synovial fluid accompanies an irreversible tissue degradation, and the concurrent damage of the cartilage.

Mimicking the structural and functional properties of natural biolubricants, we have designed graft-copolymers capable of binding to the degraded tissue during the early stages of OA, protect it from the surrounding environment, and re-establish its lubrication properties. These feature functional polymer “backbones”, which selectively anchors to the damaged tissue, and poly(2-alkyl-2-oxazoline) (PAOXA) side chains, which form a biopassive a lubricious brush interface. Fine modulation of the molar mass, density and topology of the PAOXAs enable to adjust the physicochemical and tribological properties of the treated cartilage. All these attractive properties, combined with their high biocompatibility, make PAOXA-based graft-copolymers promising candidates for halting or slowing down cartilage degeneration during OA.
Nucleobase containing polymers are a class of materials that employ the hydrogen bonding motifs found in natural DNA for programmed material assembly. Synthesis of such polymers often lack sequence specificity limiting the degree of assembly for the material. Click nucleic acids (CNAs) have overcome this challenge of sequence definition through the use click chemistry conjugation reactions. CNAs use iterative addition or substitution reactions to construct sequence defined building blocks, which can be subsequently polymerized by efficient thiol-ene click reaction. Unfortunately, current designs of CNAs utilize chemistries that exhibits sluggish kinetics, such as the thiol-acrylamide and thiol-halogen reactions, in the iterative synthesis of sequence specific building blocks. We have recently developed a new class of CNAs using vinyl sulfonamides (VS-CNAs) as a thiol-Michael ‘click’ acceptor in the synthesis of sequence defined building blocks. Thiol-Michael reactions involving vinyl sulfonamides proceed rapidly to full conversion at ambient condition and produce little to no side-products. Furthermore, the high selectivity of the thiol-vinyl sulfonamide conjugation allows for material recycling lowering the cost of production. Finally, we have developed facile synthetic strategies to synthesize all four nucleobase monomers for the construction of sequence defined building blocks for the assembly of materials on the gram scale.
Complex DNA nanostructures were created with an isothermal self-assembly method called hybridization chain reaction (HCR). HCR is a supramolecular polymerization of DNA that proceeds as a cascade of strand displacement reactions. Two DNA monomers are kinetically trapped in hairpins until the addition of an initiator strand opens the hairpin of one monomer through a strand displacement reaction. The unhybridized end then opens the hairpin of the other monomer through a strand displacement reaction. This cascade of strand displacement reactions continues, producing a supramolecular DNA polymer.

We have demonstrated that HCR produces supramolecular polymers of DNA through a living polymerization mechanism. Synthesizing DNA polymers by HCR yields supramolecular polymers with low dispersity whose molecular weight is controlled by the monomer to initiator stoichiometric ratio, consistent with a living polymerization mechanism. Additionally, HCR polymerization can be continued by the addition of further monomer, demonstrating its living nature by the absence of termination and chain transfer reactions. Identification of the living character of HCR presents new opportunities in macromolecular assembly of structural DNA nanotechnology.

Utilizing the demonstrated living nature, complex nanostructures are created via HCR. Supramolecular star polymers are created by modifying a DNA star to initiate HCR from each arm. Asymmetric star polymers are created by independently controlling the growth of each arm. Bottlebrush structures are created by modifying the monomer to include an additional overhang that initiates a secondary HCR polymerization. The creation of these complex nanostructures is demonstrated by gel electrophoresis and atomic force microscopy. Independent control over bottlebrush mainchain and sidechain lengths allows for the easy creation of bottlebrushes with controlled aspect ratios, which has potential applications as a model bottlebrush system.

Schemes of complex nanostructure assembly by hybridization chain reaction.
POLY 538: Biomimetic glycopolymer models for determination of interaction modes with amyloid β peptides

Ashleigh N. Bristol, ashleigh.bristol@eagles.usm.edu, Pradipta K. Das, Sarah E. Morgan. Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Biomimetic glycopolymer models that match the same stereochemistry as those found in GM1 ganglioside (which is known to exacerbate Aβ aggregation and is implicated in Alzheimer's disease) were synthesized via RAFT polymerization. Previous studies in our laboratories used these glycopolymer models, containing either glucose or galactose pendent saccharide groups, to evaluate the effect of saccharide clusters on the Aβ assembly process in solution and found for high molecular weight glycopolymers the specific stereochemistry drastically influenced Aβ aggregation. Literature has shown the stereochemistry of the C4 atom hydroxyl influences the type of hydrogen bonding (intramolecular vs. intermolecular) available within the glucose or galactose group; therefore the type of hydrogen bonding within the pendent saccharide group of each glycopolymer may explain the differences in Aβ aggregation in the presence of glucose- and galactose-containing glycopolymers. Light scattering studies indicate not only conformational differences between the neat glucose- and galactose-containing glycopolymers in solution, but also different binding characteristics when blended with amyloid beta. FTIR and NMR studies indicate differences in hydrogen bonding patterns for the two systems.
[FeFe]-hydrogenases are a class of enzymes that are composed of a metal-complex active site (H-cluster) surrounded by a protein scaffold. This enzyme, found in anaerobic bacteria, uses earth abundant metals in the active site and generates molecular hydrogen at very fast rates in aqueous media, with a low overpotential requirement. Extensive research has been done on mimicking the active site of this enzyme to generate a carbon-free energy carrier (i.e., H$_2$) by using water as a feedstock. However, most of the enzyme mimics suffer from low catalytic activity, limited lifetime, low oxygen stability and insufficient water solubility, all of which point out the importance of the outer coordination sphere around the active site. Atom transfer radical polymerization (ATRP) has been used to generate well-defined metallopolymers containing a [FeFe]-H$_2$ase active site mimic from a [FeFe] containing metalloinitiator. By changing the pendant functionalities on the polymeric arms, we demonstrate the ability of tuning desired properties of the resulting metallopolymers, such as water solubility, catalytic activity and resistance to oxygen. We find that [FeFe]-grafted metallopolymers perform electrocatalytic hydrogen production in neutral water at rates faster than hydrogenases and unlike the hydrogenases, these systems are insensitive to oxygen during catalysis. We will discuss our most recent efforts on the synthesis and applications of different metallo(co)polymers for electrocatalytic hydrogen evolution reactions. [Figure1]
Glycosaminoglycans are physiologically active and consist of alternating copolymer structure. Although some glycopolymers have been synthesized as mimics of such polysaccharides via controlled polymerization, sequence control of repeating units in glycopolymers are still beyond our reach. Alternating copolymers are the most basic sequence-controlled polymers. Also, it has already been recognized that copolymerization of an electron-rich and an electron-deficient vinyl monomer can afford alternating copolymers via radical polymerization. By developing this method, the author has synthesized of well-defined alternating copolymers by RAFT copolymerization of an OH-functionalized vinyl ether (VE) and a maleimide (MI) derivative. In this study, the author newly designed VEs and MIs having pendant unprotected carbohydrate moieties by click reaction between alkyne-substituted VE or MI and glycosyl azides. Here, maltosyl and lactosyl azide were obtained by Shoda’s activation of unprotected sugars using 2-chloro-1,3-dimethylimidazolinium chloride. The author firstly performed the copolymerization of maltose-substituted VE (Mal-VE) and ethyl maleimide (EtMI) by 2-benzyl-sulfanyl thiocarbonyl sulfonyl ethanol (BTSE) and VA-044 in water/CH3CN (4/3, v/v) at 60°C ([Mal-VE]₀/[EtMI]₀ = 50/50). GPC and NMR analyses revealed that formation of the copolymers [Poly(Mal-VE-co-EtMI)] with unimodal GPC traces and MWDs < 1.5. Moreover, \( M_n \) of the copolymers proportionally increased as the conversion increased. These suggest the copolymerization proceeded in a controlled manner. Due to the homopolymerizability of EtMI, the copolymers contain a small excess amount of EtMI units (composition, Mal-VE/EtMI = 42/58). MALDI-TOFMS data indicates the most parts of the copolymer possess alternating structure but contains a very small amount of consecutive sequence of EtMI. The author has also demonstrated the synthesis of periodic glycopolymers by RAFT copolymerization of lactose-substituted VE (Lac-VE) and maltose-substituted MI (Mal-MI) under a similar polymerization conditions. Specific interactions between the periodic glycopolymers and lectins were also investigated.
Proteoglycans are important brush-like biomacromolecules that are quite challenging to mimic them synthetically. We present the modular synthesis of proteoglycan-mimicking protein–bottlebrush hybrids using copper-catalyzed azide–alkyne cycloaddition. We exploit the recently discovered imidazole-1-sulfonyl azide (ISA) in a diazotransfer reaction to introduce an N-terminal azide onto an elastin-like polypeptides (ELP) model proteins. Next, we use a click reaction to couple the azido-ELP to an alkyne-terminated amine-rich polymer, which is later modified with a second diazotransfer step for an azide-rich scaffold. Finally, we used a second click reaction to graft alkyne-terminated poly(oligoethylene glycol methacrylate) (POEGMA) bristles to the azide-rich backbone to produce the final protein–bottlebrush hybrid. We demonstrate the effectiveness of this synthetic path at each step through careful characterization with 1H NMR, FTIR, GPC, and diagnostic test reactions on SDS-PAGE. Final reaction products could be consistently obtained for a variety of different molecular weight backbones with final total grafting efficiencies around 70%. The high-yielding reactions employed in this highly modular approach allow for the synthesis of protein–bottlebrush hybrids with different proteins and brush polymers. Additionally, the mild reaction conditions used have the potential to avoid damage to proteins during synthesis.
Aromatic polyimides are important high-performance, engineering polymers. They are especially known for their superior (but passive) mechanical properties and high-temperature capabilities as well as their utility in aerospace, automotive and electronic applications. An adaptive (active) material system responds temporally and spatially, e.g. changing its bulk geometry or morphing, in response to the change(s) in its surrounding and in a controllable manner. Stimuli-responsiveness requires multiscale structural chemistry that spans from molecular design and synthesis to morphological (e.g. free-volume) control. We have found that amorphous PIs with high $T_g$ and modulus are very versatile as a common platform (see Figure below) to investigate the stimuli-responsive properties at the molecular and morphological levels because of the synthetic flexibility in introducing responsive functionalities, for example, to light or moisture as well as the opportunity to incorporate origami engineering (folding) concept into the poly(amic acid)/polyimide processing chemistry for various 2D-3D objects via insertion of “thermally-induced, assisted-unfolding and stress-free self-folding” programming into their conventional film/membrane fabrication scheme. In this talk, I’ll provide an overview to highlight our collaborative efforts in tailoring polyimide chemistry by incorporating adaptively important functions related to high-temperature shape-memory effect, photo-mechanical behavior, and water-gradient actuation into polyimide structures.
Currently, there are limitations in launch capability regarding requisite payload volume and mass for long duration extra-terrestrial missions. In-space additive manufacturing may provide a solution to this challenge and is applicable for articles ranging from large system and subsystem architectures to small consumables and replacement articles. For small articles, additive manufacturing is becoming more feasible through advances in instrumentation and novel manufacturing strategies capable of generating complex shapes. Many approaches, however, utilize feedstock materials that, once consumed, must be replenished before additional architectures can be generated. Thus, although promising, a major challenge with additive manufacturing is the required starting materials to support on-demand article generation. This presentation describes research toward reversibly assembling materials that can revert to the starting material state for subsequent fabrication. Polyimides were synthesized with thermally reversible Diels-Alder reaction functionalities, furan or maleimide moieties. These materials were characterized utilizing typical spectroscopic, thermal, and mechanical techniques. Amine hardener-enriched epoxy microparticles were synthesized for use as a mechanically robust substrate. Integration of these technologies into a single system and application toward generation of secondary structures on a launch vehicle as a means of in-situ resource utilization will be described.
POLY 544: New approaches to scaling the production of liquid crystal elastomers

Tyler Guin\textsuperscript{1,3}, tylercguin@gmail.com, Logan Kearney\textsuperscript{1}, Holly Humphrey\textsuperscript{1}, Eric Burgeson\textsuperscript{1}, Ngoc A. Nguyen\textsuperscript{2}, Christopher Bowland\textsuperscript{1}, Amit K. Naskar\textsuperscript{1}. (1) Physical Sciences Directorate, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (3) Air Force Research Laboratory, Dayton, Ohio, United States

Liquid crystalline elastomers (LCEs) are soft, anisotropic materials that exhibit large shape transformations when subjected to various stimuli. Here, we demonstrate a method to scale the production of LCEs by many orders of magnitude, while still maintaining the extreme shape transformation and unique mechanical behavior of the material. This increase in scale is enabled by a room-temperature polymerizable composition that is readily oriented by simple shear. Additionally, some initial results of incorporating nanomaterials into these LCEs will be presented. Small loadings of nanoparticles result in enhanced mechanical properties, electrical sensitivity, and anisotropic optical properties.

Figure 1. A 7 cm x 30 cm strip of liquid crystalline elastomer, cut from a larger sample, demonstrating the excellent handibility, durability, and size. This marks a significant increase in scale from prior work.
ABSTRACT:
Shape memory polymers (SMPs) are smart materials that can revert back to permanent shape upon exposure to external stimuli (e.g. heat, light, and moisture). Due to their unique properties such as tunable shape memory temperatures, high shape recovery ratio, and excellent biocompatibility, SMPs are widely applied to areas ranging from biomedical devices to aerospace engineering. Moreover, the shape memory properties of SMPs depend largely on their glass transition ($T_g$), melting temperatures, and viscoelastic properties. In addition, the creep phenomenon under constant stress and temperature is the most common behavior observed in the SMPs that continuously deform the performance of the materials. In the study outlined here, the influences of $T_g$ behavior, viscoelastic properties, and creep-recovery of polymers in the presence of ionic liquids (ILs) are examined. Composites obtained through this process have been characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry to evaluate homogeneity and other associated properties. The viscoelastic component and creep behavior of these composites were examined using dynamic mechanical analyses. Interestingly, these moduli and creep-recovery were found to be dependent on the viscous properties of the ILs and on electrostatic interactions. In this talk, we will emphasize studies of the process of synthesis and characterization, as well as resultant change in the properties for each composites.
With fossil fuels running low, the need for new lightweight polymeric materials with the ability to perform both structural and functional tasks is increasing rapidly. In this contribution we will report on the synthesis and properties of new lyotropic and thermotropic high-performance liquid crystal polymer chemistries and how they can be used to design new functional materials. We will show that sulfonated all-aromatic liquid crystal polymers (LCPs) are interesting candidates for preparing new classes of nanocomposites and molecular composites for Li-ion battery applications.[1] The synthesis of novel thermotropic main-chain liquid crystal (AB)$_n$-multiblock copolyesterimides has enabled us to design a new family of single component high-temperature shape memory polymers. Such polymers enable engineers to design novel light-weight structures in which the structural component can be combined with a functional component. LC (AB)$_n$-multiblock copolyesterimide films show excellent dual-SM behavior at 170 °C and after crosslinking, tunable high-temperature (>250 °C) triple SM and one-way reversible SM behavior could be demonstrated.[2,3]
A new healing chemistry exhibiting stability at extreme temperatures and holding mechanical properties as well as mechanical stability comparable to widely used engineering plastics is reported. This self-healable thermosetting polymer is synthesized using commodity reactants (toluene-2,4-diisocyanate and diglycidyl ether of bisphenol F) through the formation of an isocyanurate-oxazolidone network which exhibits a high service temperature as shown by their glass transition temperature of 270 °C and decomposition temperature of 365 °C. We demonstrate that this network polymer is repeatedly self-healable in the presence of a macroscopic crack, yielding considerable recovery of the polymer's strength after thermal annealing. This self-healing behavior is derived from a high density of mechano-responsive isocyanurate rings which are introduced as cross-links in the polymer network. After mechanically initiated bond scission, the transformation to oxazolidone rings from isocyanurate rings is thermally initiated at the crack surfaces, resulting in the healing of the cracks. We developed a new class of intrinsically self-healable polymers withstanding high temperatures, which will greatly impact the application of thermosetting polymers in structural laminates in the aerospace industry.
POLY 548: Conjugation and release of drugs from poly(2-oxazoline) hydrogels

Tim Dargaville, t.dargaville@qut.edu.au, Jongryul Park, Nathalie Bock, Melody de Laat, Richard Hoogenboom. (1) Institute of Health and Biomedical Innovation, Queensland University of Technology, Kelvin Grove, Queensland, Australia (2) Ghent University, Terneuzen, Netherlands

Several recent examples in the literature have highlighted the potential of poly(2-oxazoline)s (PAOx) in polymer-drug conjugate applications. PAOx has a distinct advantage in that comparatively high drug loadings can be achieved because of the possibilities of functionalizing the repeat unit side chains. Compare this to other polymers, such as polyethylene glycol, which can only be loaded at the end groups. Like other soluble drug delivery systems, however, PAOx-drug conjugates may suffer from low drug delivery efficiencies if it is cleared from the body before all the drug has been cleaved. To address this we hypothesize that crosslinking PAOx-drug conjugates may allow for implantable drug delivery devices with good efficiencies and sustained drug release for days to weeks.

A homologous series of poly(2-oxazoline) copolymers was synthesized from 2-methyl, 2-ethyl, 2-propyl or 2-butyl-oxazoline copolymerized with the alkene-containing monomer 2-decenyl-2-oxazoline. A proportion of the alkene handles were then used to conjugate a small molecule drug via a hydrolytically cleavable group followed by photo-crosslinking of the polymer-drug conjugates by thiol-ene coupling of the remaining alkenes with a small molecule dithiol. In vitro drug release experiments showed that the drug release profile could be varied depending on the length of the alkyl side-chain demonstrating the versatility of these polymers.

Figure 1. The ability to change the hydrophilicity-hydrophobicity of a series of networks by varying the length of the alkyl group on the 2-oxazoline monomers is demonstrated. Drug conjugation after polymer synthesis followed by photo-gelation of the remaining alkene groups led to networks with capacity to release the drug in a sustained fashion.
POLY 549: Anionic ring-opening polymerization of activated aziridines to produce linear polyethylenimine

Paul Rupar, paul.rupar@gmail.com, Louis Reisman, Canisius P. Mbarushimana, Elizabeth A. Rowe. Chemistry, University of Alabama, Tuscaloosa, Alabama, United States

While the polymerization of 2-oxazolines has provided a strong platform for the synthesis of linear polyethylenimine (LPEI), there is room for improvement. The polymerization of 2-oxazolines suffers from decreased control at high molecular weights as well as difficulties removing 100% of the acyl protecting groups to yield LPEI. Recently, we have produced LPEI through a controlled, living anionic ring-opening polymerization of sulfonylaziridines.\textsuperscript{1,2} This finding improves upon the previous route, which utilizes 2-oxazolines, by allowing for increased control at high degrees of polymerization as well as narrower molecular weight distributions.
POLY 550: Mimicking nucleopore by track-etched polycarbonate membranes modified by poly(2-alkyloxazoline)

Philippe Guegan¹, philippe.guegan@upmc.fr, Dihia Benaoudia¹,², Pauline Kolbeck³, Sha Li⁴, Véronique Bennevault¹, Jérôme Mathé⁴, Fabien Montel³, Jean Christophe Lacroix². (1) Laboratoire de Chimie des Polymères, Sorbonne Université, Paris, France (2) ITODYS, Paris, France (3) Laboratoire de Physique, Ecole Normale Supérieure de Lyon, Lyon, France (4) LAMBE, Université d'Evry Val d'Essonne, Evry, France

The nuclear pore complex (NPC) is a large multifunctional protein complex with an eight-fold symmetrical torus-like structure spanning the double lipid bilayer of the nuclei of eukaryotic cells. Mimicking the NPC function is quite a challenge but open new perspectives in the filtration area. The NPC features have been reproduced by grafting native nucleoporines (Nups) inside track-etched polycarbonate membranes. The chemistry is quite challenging, and difficult to scale up, but the resulted nanopores were selective and function in a similar manner than the NPC. Still, analysis of the function of the Nup-decorated nanopores did not provide any microscopic information's upon the filtration process. We suggest replacing the Nups used in the previous work by poly(2-alkyloxazoline) chains to reproduce the high selectivity of NPC. Poly(2-methyloxazoline) (PMeOx) and poly(2-isopropyloxazoline) (PiPOx) with an aminophenyl chain-end were successfully synthesized by cationic ring opening polymerization, with various molar. Then electrografting, using by the diazonium electrografting process, of the PMeOx or PiPOx, was conducted to obtain well-defined polymer brushes at the entrance of the nanopores, that were characterized by AFM, XPS and zero-mode waveguide technique (ZWT). The translocation process of DNA studied by ZWT was analyzed using a suction model characterizing the interaction of the translocating macromolecule and the wall of the pore, and the local organization of the polymer chains inside the nanopore. On the other hand, electric detection evidenced the diffusion of ions as a function of the nature of the grafted polymers in the nanopore. The polymer brush weakly and reversibly crosslinks inside the nanopore and thus forms a sieve-like gel. The LCST of PiPOx unables a commutation of the nanopores from a selective filtration to a quasi-free diffusion of nanoparticles inside the nanopores.

DNA translocation through the poly(2-isopropyloxazoline-decorated nucleopore as a function of temperature analyzed by the Zero Mode Wave Guide Technique
Polyoxazolines (POx) are well known thermoresponsive polymers, which exhibits a reversible and rapid hydrophilic-hydrophobic interconversion through the lower critical solution temperature (LCST). Narrow molecular weight distributions of POx can be achieved by cationic living polymerization of oxazoline monomer. More importantly, we can easily introduce various functional groups to the both initiation and termination ends through the living polymerization process. We can utilize functional initiators to introduce specific functional groups at initiation end. Alternatively, termination end can be easily modified by treating with functional nucleophile to the living cationic terminal. Using those properties, recently, we have designed redox-active POx that exhibited color and thermal transition temperature changes by redox potential application. Moreover, we have fabricated network polymers using the redox-active POxs to achieve redox- and thermo-responsive shape change of polymers. The details of POx-based polymers will be discussed in the symposium.
POLY 552: From polymer to application: solvent electrospinning of poly(2-oxazoline)s

Ella Schoolaert1, Richard Hoogenboom2, Karen De Clerck1, karen.declerck@ugent.be. (1) Centre for Textile Science and Engineering (CTSE), Department of Materials, Textiles and Chemical Engineering (MaTCh), Ghent University, Ghent, Belgium (2) Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Ghent, Belgium

The unique combination of structural variability, ease of functionalization, thermoresponsiveness and biocompatibility has recently led to an increasing interest in an emerging class of polymers: poly(2-oxazoline)s. This pseudopeptide has not passed by the attention of the growing field of solvent electrospinning in which nanofibers with diameters below 500 nm are produced. Thanks to their thin fiber diameter and high porosity, nanofibers are characterized by a large specific surface area being a desired property in varying applications including biomedicine, sensors and filtration. In solvent electrospinning a strong electrical field draws a polymer solution into nanofibers which are deposited as a flexible, stand-alone, easy-to-handle membrane. Poly(2-oxazoline)s are of particular interest to this process as the polymers are soluble in more environmental friendly solvents, e.g., water and/or ethanol, compared to the commonly applied hydrophobic polymers needing deleterious solvent systems to be solubilized, a critical parameter in solvent electrospinning. Two types of well-defined poly(2-oxazoline)s, i.e., poly(2-ethyl-2-oxazoline) (PEtOx) and poly(2-n-propyl-2-oxazoline) (PnPPrOx), have been successfully electrospun from aqueous solvent systems into uniform, bead-free nanofibers with interesting characteristics such as the rose-petal effect. This research paves the way towards electrospinning of other poly(2-oxazoline) polymers and investigation of their yet undiscovered properties. PEtOx and PnPPrOx nanofibers are very sensitive to moist, particularly below the lower critical solution temperature (LCST), which might be inconvenient for some applications. Therefore, crosslinking strategies have been proposed for both polymers. PEtOx nanofibers were chemically crosslinked by selenol or benzophenone functionalization. PnPPrOx was physically crosslinked upon addition of tannic acid. The fast and straightforward poly(2-oxazoline) nanofiber production combined with the possibility of crosslinking allows for application of these materials in for example sensor applications where a dye is either physically or chemically linked to the poly(2-oxazoline) nanofibers.
Molecularly imprinted polymers (MIPs) are synthetic polymers obtained during polymerization of a mixture composed of functional monomers, cross-linkers, and template molecules. As a result, they possess antibody-like affinity towards the molecules that were used as templates during the imprinting process due to the presence of cavities that are selective towards these molecules in terms of size, shape and location of functional groups.

Poly(2-oxazoline)s represent a group of polymers which are obtained by cationic ring-opening polymerization of 2-oxazolines. In recent years, they have received much attention due to their biocompatibility, stealth behavior and high synthetic versatility. However, the limitations of cationic ring-opening polymerization of 2-oxazolines, particularly necessity to avoid presence of any nucleophilic groups, makes it challenging to imprint poly(2-oxazoline)s during the polymerization.

In the present work, we synthesized molecularly imprinted poly(2-oxazoline)s by crosslinking of short poly(2-oxazoline) prepolymers possessing methyl ester groups in their side chains using a direct amidation reaction. The applied cross-linker, diethylenetriamine, simultaneously acted as a cross-linker and functional monomer to interact with the template molecules. The maximum amount of template that could be adsorbed by the imprinted polymer was one order of magnitude higher than for an analogous non-imprinted polymer. The kinetics of the adsorption process was found to follow the pseudo-first-order kinetic model while the release kinetics of indometacin (a nonsteroidal anti-inflammatory drug) generally followed Higuchi model, providing proof-of-concept for potential future drug delivery applications.

Scheme of synthesis of poly(2-oxazoline) molecularly imprinted with indometacin and its proposed structure
Likely due to the lesser degrees of control exhibited, there has been significantly less work done on the polymerization of 2-oxazines to produce linear poly(trimenthyleneimine) (LPTMI) compared to the polymerization of 2-oxazolines to produce linear polyethylenimine (LPEI). LPTMI, which has an additional methylene spacer compared to LPEI, can also be utilized in non-viral gene-transfection. Recently, we have produced LPTMI through a controlled, living anionic ring-opening polymerization of sulfonylazetidines. After post-polymerization removal of the sulfonyl groups, this finding yields polymers with high degrees of control over both the target molecular weight and dispersity, which are essential in applications of non-viral gene-transfection.
Two classes of highly reducing organic photoredox catalysts, N,N' diaryl phenazines and N-aryl phenoxazines, have been utilized to mediate organocatalyzed atom transfer radical polymerization (O-ATRP) for the production of well-defined polymers using visible light. These catalyst families provide a platform on which catalytically relevant properties including redox potentials and absorption profiles can be finely tuned enabling the design of O-ATRP catalysts that exhibit greater control over the polymerization. To this end, we have developed a catalyst system able to synthesize acrylic polymers with predictable molecular weights and dispersities less than 1.10.
POLY 556: poly(N-Acetylguanidine)s as reactive handle or reactive intermediate for post-polymerization modification of pendant ester groups

Joachim Van Guyse, joachim.vanguyse@ugent.be, Xiaowen Xu, Richard Hoogenboom. Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

Post-polymerization modification reactions of pendant esters generally utilize activated ester substrates and the modification of unactivated esters is avoided, partially due to the well-established activated ester alternatives and the challenging nature of direct PPMR of unactivated esters. Within this work, we present a method for the direct modification of pendant polymeric esters by utilizing either acetylguanidines as a reactive handle for modification or as a reactive intermediate towards functional polymer structures from unactivated pendant esters. More specifically, a kinetic screening of reactions involving the use of N-acetylguanidine intermediates, i.e. amidation and transesterification, was performed with respect to the nature of the substrate and of the reactants. Finally, the utilisation of N-acetylguanidines for further post-polymerisation modification reactions is demonstrated, allowing heterocycle synthesis on the polymer.
In this presentation, new results will be described that highlight the utility of the terminal alkyne to manipulate polymers using metathesis polymerization. Unlike olefins, terminal alkynes undergo rapid addition reactions with Grubbs-type ruthenium alkylidenes that can direct the carbenoid to a new site of reaction. Following this general paradigm, the simple functional group can be leveraged to prepare functional initiators in situ, effect stoichiometric polymer-polymer coupling, and synthesize degradable polymers. This enables new classes of metathesis polymers to be prepared from renewable feedstocks and also presents opportunities to create well-defined hyperbranched polymers in a one-pot process. Recent progress towards these targets will be presented, along with an outlook for future potential in the area.
Cross-linked polydicyclopentadiene (PDCPD) is a light-weight material of superior mechanical strength. The cross-linked network is a result of ring-opening metathesis polymerization (ROMP) of the highly reactive C=C double bond of norbornene ring system in addition to the ring opening cross metathesis (ROCM) of the less reactive C=C double bond of the cyclopentene ring. We have demonstrated that under certain conditions, a 3rd generation Grubbs-type catalyst can be used to exclusively synthesize linear PDCPD, in particular when very low catalyst loadings were used to a degree that molecular weights were close those of a controlled polymerization. Some branching of the linear polymer as a result of ROCM was observed particularly at higher catalyst loadings. We developed two methods to terminate the ROMP reaction, 1) with PPh₃ which retains the Ru-alkylidene end group of the polymer and 2) ethyl vinyl ether which detaches the Ru-alkylidene from the polymer. The thermal properties of the isolated linear PDCPD materials were investigated and the materials containing Ru-alkylidene end groups exhibited later onset temperatures for decomposition. The addition of bromine resulted in a linear material in which the C=C double bonds of the linear PDCPD is partially brominated. Varying degrees of bromination affected the thermal properties of these materials which exhibited higher energies and onset temperatures of an endothermic dehydrobromination process with higher amounts of covalently bonded bromine in the polymer.

Synthesis of linear polydicyclopentadiene (LDCPD) via living ROMP containing a reactive Ru-alkylidene end group.
Highly tailorable polymers via the aza-Michael polymerization of hydrazides

Dillon Love¹, dilo7362@colorado.edu, Dylan Domaille², Benjamin Fairbanks³, Kangmin Kim⁴, Olivia Williams¹, Christopher Bowman⁵. (1) Chemical and Biological Engineering, University of Colorado, Boulder, Colorado, United States (2) Chemistry, Colorado School of Mines, Golden, Colorado, United States (3) University of Colorado, Boulder, Colorado, United States (4) University of Colorado Boulder, Boulder, Colorado, United States (5) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

Aza-Michael reactions, the conjugate addition of a N-nucleophile to an electron-deficient alkene, has been extensively used for pharmaceutical and natural product synthesis. To a lesser extent, aza-Michael polymerizations are utilized for preparing high-molecular-weight, linear step-growth polymers from diamine monomers, as well as polymers with greater topological complexity. Here in, we report the synthesis of the first high-mw linear polymers (up to 30 kDa) via the bis-addition of a primary N-nucleophile (hydrazide, R(CO)(NH)NH₂) with divinyl sulfone and other difunctional Michael-acceptors. The diverse range of hydrazides commercially available and capable of undergoing this polymerization facilitates the introduction of functional side-groups that allow for the tailoring of the polymer's physical properties and ability to be post-synthetically functionalized. In this report, we investigate the nature of the hydrazide nucleophile through reaction kinetics and density functional theory calculations to understand the reaction efficiency compared to 1° amines that only form oligomers under the same conditions. Further, we demonstrate the robust nature of this polymerization to construct copolymer ranging from periodic copolymers, alternating short-block copolymers, graft copolymers, using the ability to incorporate multiple orthogonal functional sites into a single polymer chain.
Design of alternative routes to today's commercial plastics are being sought to achieve numerous goals, including more well-defined structures and architectures, intricate functionality and/or more sustainable products from renewable resources. In this presentation focus is on designing functional green biobased polyamides (PAs) and polyurethanes (PURs) utilizing ring-opening reactions as a driving force in their synthesis, while achieving the targeted structure-property relationships. The PURs are debated and several methodologies to achieve isocyanate free PUR have been proposed and developed. One such methodology is the ring-opening of carbonates with diamines, which can be tailored to afford materials with high or low urethane density mimicking the PURs on the market today. By adopting the same fundamental chemistry, that is aminolysis, we synthesized biobased and isocyanate free PUR gels and demonstrated their function as antibacterial gels. Ring-opening aminolysis was also utilized to form strong metal adsorbers for waste water treatment, via the reaction of amines of different structures with a biobased sugar derived lactone. A synthesis route to fiber forming linear polyamides was also developed, utilizing comparably mild reaction conditions and ring-opening aminolysis condensation of a biobased dilactone with a variety of diamines as the reaction pathway. Well-defined and purely amide functional PAs were synthesized with fiber forming ability and thermal properties matching their oil-based analogues.
POLY 561: Polycyclic aromatic core—enchained perfluorocyclobutyl (PFCB) aryl ether polymers derived from phenanthrenequinone

Behzad Farajidizaji$^{1,2}$, bf708@msstate.edu, Ganesh Narayanan$^{1,2}$, Ketki Shelar$^{1,2}$, Karl Mukeba$^{1,2}$, Andrzej Sygula$^{1,2}$, Charles U. Pittman$^{1,2}$, Dennis W. Smith$^{1,2}$. (1) Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, United States (2) Marvin B. Dow Advanced Composites Institute, Mississippi State University, Starkville, Mississippi, United States

Two intermediate bisphenols, M1 and M2, were obtained by reacting 9,10-phenanthrenequinone with excess phenol under acidic conditions. Monomers M1 and M2 were then further reacted with 1,2-dibromotetrafluoroethane in dimethylsulfoxide under basic conditions (cesium carbonate) yielding Br-trifluorovinylether (Br-TFVE) bearing monomers, M3 and M4, respectively. Subsequent dehalogenation with zinc afforded the corresponding trifluorovinylether-bearing monomers, M5 and M6. The chemical structures of M1, M2, M3, and M4 and TFVE-bearing monomers (M5 and M6) were characterized fully by FTIR, $^{13}$C-, $^1$H-, and $^{19}$F-NMR, and single crystal XRD analyses. TFVE-bearing monomers, M5 and M6, underwent thermal cyclopolymerization at 180 °C (in diphenyl ether solution or bulk) to form new perfluorocyclobutyl (PFCB) aryl ether homopolymers P5 and P6 in moderate to good molecular weights as observed by gel permeation chromatographic analyses. In addition, both P5 and P6 exhibited high glass transition temperatures ($T_g$) (> 200 °C) as well as high thermal stabilities (5% Td > 450 °C) in nitrogen and ambient atmospheres, by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. This work, highlights the development of PFCB polymers with enchained PAH moieties making these polymers suitable for application in optics, opto-electronics, and dielectric materials where high thermal stabilities and $T_g$s are desired.
Charged telechelic poly(ether imide)s (PEIs) terminated with sodium, calcium, and zinc sulfonates were prepared by reacting dianhydride-terminated PEI (PEI-DA) oligomers with the respective sulfanilate salts. The thermal, tensile, and rheological properties of the charged PEIs were compared to the non-charged analogs including PEI-DA and phenyl-terminated PEIs (PEI-Ph), as well as high-molecular-weight (high-MW) commercial PEIs. All charged and non-charged PEIs were melt-processable and thermally stable up to ~490 C. After incorporating the charged end groups, the glass transition temperatures of the PEIs increased significantly. Among all PEIs with the charged end groups, zinc sulfonated PEI (PEI-SAA-Zn) exhibited the best melt stability and processability. PEI-SAA-Zn exhibited a pivot temperature in the range of ~301–324 C depending on the molecular weight. The viscosities of PEI-SAA-Zn oligomers decreased with temperature. The decreasing rate was more rapid above the pivot temperatures than below the pivot temperatures. Surprisingly, melt-pressed PEI-SAA-Zn with a low molecular weight of 12 kDa showed the best tensile strength, and the tensile properties were comparable to the state-of-the-art high-MW commercial PEIs. The findings herein provide insight into the design of high-performance polymers with enhanced mechanical and rheological properties.
POLY 563: Living anionic polymerization of aziridines tolerates water and gives fast access to amphiphilic multi-block copolymers

*Tassilo Gleede*, t.gleede@gmail.com, Thomas Kuckhoff, Elisabeth Rieger, Manfred Wagner, Frederik Wurm. Max Planck Institut für Polymerforschung, Mainz, Germany

The synthesis of well-defined polyamines remains a challenge in polymer science. Poly(ethylene imine) (PEI) and derivatives are normally produced via cationic polymerization of poly(2-oxazoline)s. Gene delivery applications for instance require accurate control over polymer architecture and weights. Living anionic polymerization (LAP), the superior method for well-defined polymers, is an ideal platform to prepare PEI architectures from activated aziridines with high structural control.

A major paradigm of LAP is the demanding synthesis, as high purity of reagents and solvents are essential to produce well-defined high molar mass polymers. Traces of water will terminate carbanionic or initiate oxyanionic polymerizations. This poster presents the living anionic polymerization of aziridines, which remain living with high control over molar mass and dispersity although in the presence of protic “impurities” such as water and alcohols.

A second paradigm in LAP is that statistical copolymerization produces gradient copolymers or no copolymers (if the monomer reactivities are too different). Again, LAP of activated aziridines breaks this paradigm as the statistical copolymerization with ethylene oxide leads to perfect diblock copolymers with basically no tapering. Various polymer structures such as multiblock polymers with linear or branched architecture are accessible, which can act as non-ionic surfactants.

Furthermore, mild desulfonylation of polysulfonamides can be performed to access well-defined linear PEIs which are usually exclusively synthesized by cationic ring-opening polymerization of oxazolines.

We believe that the LAP of aziridines in combination with other anionically polymerizable monomers and its efficient desulfonation process will provide straightforward access to novel polyamides and –amines with interesting properties for a great number of applications.

*Figure 1:* A; SEC traces (RI signal) of chain extension of P(TsMAz and P(TsMAz-b-TsMAz), with 90 equivalent excess of ethanol. B; Mean composition (F) of the polymer chains versus total conversion. Top: Monomer distribution of a 50:50 block copolymer based on the reactivity ratios of MsMAz (pink) and EO (blue); bottom: TsMAz (orange) and EO.
Twisted amides are a special class of molecules that have distorted, non-planar amide bonds due to the geometric constraints imposed by a bicyclic framework. As a result of this twist, the amide nitrogen becomes very nucleophilic and the carbonyl group becomes more electrophilic. While these reactive molecules have long been studied in physical organic chemistry, their potential as monomers for ring-opening polymerization has remained unexplored. Here, we demonstrate the potential of twisted amides to polymerize through a new mechanism for controlled, living polymerization termed “halide rebound polymerization.” Initiated by simple alkyl halides, the polymerization of twisted amides is a unique case of covalent electrophilic polymerization that produces polymers with living chain ends that are stable to ambient conditions. This permits the isolation of the polymer followed by chain extension to produce block polymers. The resulting polymers are thermally stable and have high glass transition temperatures. By modifying the twisted amide structure, the rates of polymerization can be tuned and predicted through computational analysis.
A longstanding challenge in polymer science is the ability to rapidly build functional materials under milder conditions and with more straightforward protocols. The covalent coupling of complex macromolecules, in particular, is a modern challenge in both chemistry and biology. The development of efficient and chemoselective polymer coupling and functionalization methods has become increasingly important for designing new advanced materials and interfacing with biochemical systems. Despite the common use of ring opening metathesis polymerization (ROMP) in materials science, rapid and quantitative methods for termination of the active alkylidene chain ends with functional molecules remains difficult. This work presents a new design to terminate ROMP polymers that is highly efficient through the use of enyne molecules, and enables direct conjugation of ROMP to both small molecules and synthetic macromolecules. The alkyne serves as a directing group to guide a ruthenium alkylidene to an otherwise unreactive styrenic olefin. This directed cross metathesis leaves the metal center in an inert, chelated state that stabilizes the byproduct. Importantly, this method has been shown to go beyond small molecule couplings and can also be used to directly construct block copolymers.

POLY 565: Relay conjugation and chain-end functionalization of ROMP

Liangbing Fu\textsuperscript{1}, Ifu35@gatech.edu, TIANQI ZHANG\textsuperscript{2}, Will Gutekunst\textsuperscript{3}. (1) School o Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (2) School of chemistry and biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (3) Georgia Tech, Atlanta, Georgia, United States

![Diagram of polymer conjugation and functionalization](image)
Isosorbide (IS) continues to gain large interest as a sustainable, biomass-based, chemical precursor for the creation of sustainable polymers. It is produced through a double dehydration and cyclization of D-sorbitol, which has recently been identified by the Department of Energy as a top 10 platform chemical from bioderived from carbohydrates. The chiral, rigid diol structure of IS has warranted many investigations for its use in condensation polymerizations, such as polycarbonates or polyethylene terephthalate (PET) analogs. However, considerably less attention has been placed towards the use of IS in chain growth polymerization strategies where optimal control over molar mass, dispersity, and advanced architectures are possible. This work will discuss our recent advances in the use of IS as a chemical precursor to produce a variety of new monomers susceptible to chain growth polymerization strategies. Emphasis will be placed on the efficacy of polymerizing or copolymerizing these monomers and the fundamental properties that the rigid chiral structure imparts to the resulting materials.
Polydispersity is an intrinsic feature of all synthetic polymers. In many cases, polydispersity could be beneficial to the physical properties of polymeric materials. For block copolymers, previous experimental and theoretical studies have showed that polydispersity could have significant effects on their phase behaviour. Besides shifting the phase boundaries of block copolymers, polydispersity could be used to regulate the emergence and stability of ordered phases. For the case of diblock copolymers, self-consistent field theory studies have demonstrated that polydispersity of the polymers could enlarge the stability region of the complex spherical packing phases such as the Frank-Kasper sigma phase. Furthermore, polydispersity with designed length distributions could stabilize ordered phases that are metastable for the neat block copolymers. Specifically, theoretical studies have demonstrated that polydisperse diblock copolymers in the form of binary blends of AB diblock copolymers could stabilize the Laves (C14 and C15) and the double diamond phases. In my presentation, I will summarize our recent theoretical progresses on this fascinating topic and discuss possible future research directions.
POLY 568: Effects of polydispersity on microphase separation in thin films of diblock copolymers: Theories, simulations, and experiments

Rajeev Kumar, kumarr@ornl.gov. Oak Ridge National Lab, Oak Ridge, Tennessee, United States

Despite the ubiquity of intentional or unintentional polydispersity in chain lengths of diblock copolymers, its effects on microphase separation in thin films have eluded a clear understanding. In this talk, we will present our ongoing efforts in understanding effects of polydispersity on morphology in thin films by combining field theory-based simulations and neutron reflectivity experiments. In particular, films containing either lamellar or cylinder forming diblock copolymers with one nearly monodisperse and the other highly polydisperse block will be discussed. Also, structure determination of nanostructured composites obtained by blending the diblock copolymers with spherical nanoparticles will be discussed. Polydispersity induced stabilization of coexisting lamellar and cylindrical morphologies in thin films containing cylinder forming diblock copolymers will be discussed. Origin of such a stabilization lies in the entropic segregation of short and long chains among lamellar and cylindrical domains. Furthermore, our approach to directly use simulations (self-consistent field theory or hybrid-particle field theory-based models) for the analysis of the experimental reflectometry data will be discussed. As an outlook, combining field theory-based simulations and neutron reflectivity experiments provides a pathway for quantitative predictions of the structural properties of polydisperse block copolymer nanocomposite thin films.

Our approach for interpreting microphase separated structure in thin films of diblock copolymers, which combines field theory based simulations and neutron reflectivity experiments.
A series of discrete oligomers have been synthesized with the aim to study the behavior of these discrete blocks in block co-oligomers. Novel synthetic routes to oligodimethylsiloxanes are developed and combined with strategies to prepare a number of A-B and A-B-A block co-oligomers of different lengths, while there so-called mono-disperse analogues are prepared as well. “Where and when does it matter to use discrete block co-oligomers?” and “When is it useful to use just the mono-disperse analogue?” are just a few of the questions that will be discussed in the lecture. Where both blocks are amorphous the differences are small, however, discrete structures enhance crystallinity and then the differences become significantly. Intriguingly fast crystallization processes induced by phase separation are observed leading to fascinating adaptive materials. The assembly processes in thin films and in aqueous solutions will be presented with the aim to arrive at the ultimate perfection in nanotechnology.
Continuous-flow chemistry is emerging as a useful technological approach for precision polymer synthesis. Compared to conventional batch processes, the use of small-diameter tubular reactors with large specific surface areas provides rapid mixing, excellent heat transfer, and a small foot-print. Realizing the benefits of continuous-flow polymer synthesis first requires a fundamental understanding of how fluid dynamic phenomena in tubular micro-reactors influences polymer structure and composition. This is especially relevant in controlled polymerizations where precise control of polymer microstructure, molecular weight, and dispersity is crucial to developing next-generation functional materials.

This presentation will detail a comprehensive study of how laminar flow in tubular micro-reactors influences polymer molecular weight, molecular weight distribution, and composition. Using in-line UV-vis spectroscopy, we demonstrate how tubing diameter, solution viscosity, and residence time influence RTD under conditions relevant for continuous-flow polymerization. We subsequently conducted polymerizations under various conditions and reactor geometries to understand how RTD influenced reaction conversion and polymer molar mass and dispersity. The magnitude of the RTD in laminar flow was found to have strong, statistical correlations with polymerization control. These correlations were demonstrated to be general to wide variety of different reaction conditions, monomers, and polymerization mechanisms. The fundamental understanding of how reactor design influences RTD and, accordingly, polymer structure will prove valuable for future work in the burgeoning field of continuous-flow polymerization. Additionally, our comprehensive studies enabled the rational design of a reactor that minimized the RTD using droplet flow to achieve a polymerization that matched the results observed in a batch reactor and provided the continuous production of a well-defined polymer at a rate of 1.4 kg/day.
The self-assembly of liquid crystals and block copolymers into ordered structures often defines the functional properties of these materials. In discrete end-functionalized oligomers, phase-segregation is combined with the directional interactions well-known in liquid crystalline materials. An end-functionalized discrete siloxane oligomer induces phase-segregation and the peripheral block can have a supramolecular hydrogen bonding character or exhibits crystalline interactions. In this study, discrete siloxane oligomers are decorated with dinitrohydrazone end blocks that show both supramolecular and crystalline interactions. An extensive morphological study elucidates the formation of highly ordered and aligned cylinders, irrespective of the volume fractions of the blocks. The ordered structure can be switched to an isotropic structure within 1 degree Celsius, in less than 15 seconds. The isotropic to ordered transition occurs within the same time span and at nearly the same temperature resulting in a material that is very sensitive for temperature and possesses a fast thermal switch. Finally, a disperse reference compound confirms that the discreteness of the siloxane linker is crucial to obtain these unexpected, highly ordered morphologies and macroscopic properties.
The coupling of proteins and stimuli-responsive polymers is a promising strategy to design new soft materials with unique properties. The incorporation of enzymes into stimuli-responsive microgels provides functional colloidal building blocks for the fabrication of adaptive biocatalysts, biosensors or synthetic biofilms.

Several synthesis methods for the encapsulation of enzymes in microgels will be discussed including: a) enzymatic polymerization; b) crosslinking in W/O emulsions and c) diffusion-based loading. The biggest challenge is to achieve the high enzyme loading along with high enzyme activity.

We developed enzyme-mediated aqueous precipitation polymerization method, which results in the encapsulation of the enzymes (Laccase, Glucose oxidase) in growing microgels. Alternatively, reactive copolymers can be used as tailored building blocks for the design of microgels by crosslinking in O/W emulsions. The integration of epoxy, succinimide or pyridylidisulfide groups in copolymer structure allows fast conjugation to lysine or cysteine residues of Cellulase in aqueous droplets at mild conditions. This allows encapsulation of enzymes in macromolecular cages during microgel formation process and flexible regulation of their activity and storage stability.

To ensure the selective and efficient biofunctionalization of microgels surface we developed an enzyme-mediated method. The surface of the microgel containing 5 mol% epoxy groups was modified by grafting of a specific recognition peptide sequence (LPETG) for Sortase A from *Staphylococcus aureus*. Sortase-mediated conjugation of the enhanced Green Fluorescent Protein (eGFP) carrying a N-terminal triglycine tag to LPETG-modified microgels was successfully performed. Conjugation of eGFP to the microgel surface was qualitatively proven by confocal microscopy and by fluorescence intensity measurements. We demonstrated that sortase-mediated coupling reactions are a simple and powerful technique for targeted surface functionalization of stimuli-responsive microgels with different enzymes.
POLY 573: Polymer conjugation to enhance cellulase activity and preserve stability

Thaiesha Wright¹, wrigh101@miamioh.edu, Melissa Lucius¹, Benjamin Schmitz¹, Katherine Makaroff¹, Jamie Stewart¹, Henry Fischesser¹, Jerry Shepherd¹, Jason Berberich², Dominik Konkolewicz³, Richard C. Page³. (1) Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States (2) Chem, Paper, Biomed Eng, 64 Eng Bldg, Miami University, Oxford, Ohio, United States (3) Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

The modification of proteins through polymer conjugation is an effective synthetic mimic of naturally occurring post-translational modification. This area of research has gained much interest of the past forty years due to the ability of these bioconjugates to modulate activity and stability of various proteins while introducing new behaviors such as stimuli responsiveness and reusability. With an increasing demand for energy, several promising options that complement fossil fuels have arisen, specifically cellulosic ethanol. A significant challenge in using cellulose derives from linkages in the cellulose backbone, which cannot be hydrolyzed by yeast and many other fermenting organisms. Therefore, it is imperative to develop stable and efficient cellulase enzymes that can degrade these linkages to produce sugars that are fermentable by yeast and other microbes; as well as the ability of the enzyme to tolerate harsh conditions. Here, we describe the production of bioconjugates between polymers and a thermophilic cellulase, FnCel5a, to create an active cellulase with resistance to heat and chemical denaturation. This enzyme was conjugated with various functional polymers including cationic, anionic, and strongly and weakly hydrogen bonding polymers. The activity of FnCel5a toward a high-molecular-weight carboxymethyl cellulose substrate was enhanced by polymer conjugation and tended to confer comparable tolerance to high concentrations of dimethylformamide, with longer polymers typically enabling higher activity relative to shorter polymers. The new FnCel5a conjugates represent an advance in the production of cellulases that maintain activity at high temperatures or in the presence of denaturing organic solvents.

(A) Synthesis of poly(dimethyl acrylamide) by RAFT polymerization and (B) attachment to thermophilic cellulase enzyme, FnCel5a. (C) Structures of all monomers used in this study.
Peptide-polymer bioconjugates combine oligopeptides with synthetic polymer blocks and can be used for various applications in material sciences. In recent years, bioconjugates were applied as compatibilizers and coatings.\(^1,2\) Biocombinatorial approaches, such as phage display, have been shown to yield strong binding peptides, which exhibit excellent coating properties as peptide-PEO conjugates.\(^3\) Phage display represents a widely exploited strategy to select peptides or proteins that exhibit highly specific affinity to various substrates.\(^4\) Following a phage display experiment, DNA sequencing of binding phage clones is required in order to get the sequence information of the binding peptides. Traditionally, random clone picking followed by Sanger sequencing was applied. However, this method may not necessarily identify the strongest binding clones. Next-generation sequencing made sequencing of whole phage libraries possible, which highly improved the selection of strong binders.\(^5\) Here, we show that the biocombinatorial method of phage display combined with next generation DNA sequencing of whole phage libraries represents a powerful tool for an application in material chemistry. Phage display is used to find specific target binding peptides for polypropylene surfaces (PP). PP binders are of particular interest because thus far gluing or printing on PP is challenging due to its low surface energy. Scripts for sequence data analysis were developed and promising sequences were synthesized as peptide-PEO conjugates. Fluorescence based adsorption experiments on PP surfaces led to the identification of strong binding sequences and a better understanding of the peptide-surface interactions.

**Figure.** The concept of combining phage display with next-generation sequencing for the development of adhesive peptide-polymer conjugates.
In this work we seek to exploit site-specific genetic incorporation of biorthogonal “click” handles or initiating species to generate “grafting-to” and “grafting-from” bioconjugates. This utilizes mutant *Methanococcus jannashii* synthetase/tRNA pairs specific for non-canonical amino acids (ncAAs) of unique functionality, which allows for facile expression of mutant proteins with site-specific handles in *E. coli*. We present here three systems of interest: (1) a robust super-folder green fluorescent protein (sfGFP,) the biologically active, neuronal-targeting protein tetanus toxin fragment C (Hc,) and the human carbohydrate-binding protein, galectin-3 (gal3). Optimal protein-polymer conjugates should have intact biological function of the protein and the processability of the polymer. With this work, we aim to capture these qualities and generate solution-stable protein-polymer conjugates that will serve as preliminary studies for future applications of surface-immobilized gal3-polymer conjugates.
Here we report a robust bioconjugation method using cysteine arylation. This chemistry enables site-specific conjugation at cysteine residues within peptides, proteins, and antibodies. Our two developed approaches use either perfluoroaryl-cysteine $\text{S}_{\text{N}}\text{Ar}$ chemistry or organometallic palladium reagents. This work led to the discovery of a self-labeling four-residue sequence that enables regioselective conjugation at only one cysteine residue within an intact antibody containing natural amino acids. Recently, we discovered a new approach for the site-selective attachment of complex natural products such as vancomycin onto peptides and proteins without the introduction of linkers or chemical handles.
POLY 577: Repurposing enzymes: Investigating the mechanism of horseradish peroxidase as a RAFT-initiase

Dominik Konkolewicz¹, d.konkolewicz@gmail.com, Richard C. Page¹, Jason Berberich², Alex Danielson¹, Caleb Kozuszek¹, Dylan Bailey Van Kuren¹, Joshua Bornstein¹. (1) Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States (2) Chem, Paper, Biomed Eng, 64 Eng Bldg, Miami University, Oxford, Ohio, United States

Reversible addition-fragmentation chain transfer (RAFT) polymerization has emerged as one of the most powerful and useful reversible deactivation polymerization (RDRP) method. One feature of RAFT is that it requires an external radical source to drive the polymerization forward. These radical sources are most commonly conventional radical initiators. Here, we explore an enzymatic approach to generating the radicals needed for RAFT polymerization. Rapid polymerization is possible by enzymatic radical generation using horseradish peroxidase as the enzyme, H₂O₂ as the substrate, acetylacetone as a mediator. The specific model system is trithiocarbonate mediated RAFT polymerization of N,N-dimethylacrylamide, although the polymerization is applicable to other monomers. Polymerization is typically very rapid, reaching over 90% conversion in less than 30 min under optimized conditions. A detailed kinetic study of how each component influences the overall reaction is explored, using both polymerization and enzymatic assays. These results can be used to make well-defined polymers as well as complex materials such as block copolymers and bioconjugates under mild conditions.
Polymer bioconjugation is an important tool to enhance protein stability and activity in non-native environments. Many factors can influence the success of a polymer bioconjugate reaction and subsequent enzyme activity-including ligation site (amino acid residue), polymer attachment method (i.e. grafting-from vs grafting-to), and polymer composition. In this presentation we explore how polymer modification impacts the activity and stability of lipase. Lipase is an enzyme which has found application in industrial and pharmaceutical processes including chiral synthesis and biofuels production. Increasing the stability and activity of lipase in both organic and aqueous media has been an area of focus in the field of bioconjugation. In this presentation we demonstrate how Atom Transfer Radical Polymerization can be utilized to graft polymers from lipase modified with ATRP initiators (attached either to acidic or basic amino acid residues). The grafting of polymers from lipase is demonstrated to enhance the activity, stability, and solubility of lipase in organic and aqueous media. We also found that polymer bioconjugation to lipase increased the substrate scope of lipase for transesterification.
The temporal control of enzymatic activity by external stimuli is a hallmark of life, whereby most often chemical reactions are only transiently switched on as long as the stimulus is present. In order to mimic such control over biocatalysis with artificial nanosystems, we have developed bioinspired block copolymer vesicles that become transiently permeable for enzyme substrates in response to visible light or mechanical forces. To this end, amphiphilic block copolymers were functionalized in their hydrophobic block with Donor-Acceptor Stenhouse Adducts (DASAs) or with nucleobases. The resulting biocatalytic nanoreactors can be switched on by light or by turbulent mixing. They switch back to their inactive state as soon as the external stimulus is withdrawn. Thus, these nanoreactors allow precise temporal control over biocatalysis, which opens up new applications in drug delivery and in molecular systems engineering. Moreover, this work shows that stimuli-responsive polymers can not only be used to tune the activity of enzymes when covalently conjugated to biomolecules, but also when the proteins are non-covalently encapsulated in polymeric nanostructures.
Polymeric membranes for water purification are often fouled by the contaminants, drastically reducing water permeance. To overcome this challenge, a variety of approaches to modifying membrane surface have been explored to enhance antifouling properties. However, most of these approaches may be involved with complex chemical reactions, and thus they are not easily integrated into the industrial membrane production lines. In this work, we demonstrate facile fluorination of UF/MF membranes by direct coating of “non-sticking” Teflon AF1600, an amorphous glassy perfluoropolymer with an excellent film-forming ability and antifouling properties to organic matters. Specifically, commercial membranes with different molecular weight cut-off (MWCO) were coated with solutions containing various content of Teflon AF1600 (0.02 to 0.05 wt.%). As the Teflon AF1600 concentration increased from 0 to 0.05%, the coating layer thickness increased from 0 to 7.0 nm, and the water contact angle increased from 63° to 102°. Bovine serum albumin (BSA) was used as a model foulant, and its adsorption on the membrane surface decreased from 14 µg/cm² to 6 µg/cm² after the coating of 0.02% Teflon AF1600. The effect of the coating on the membrane MWCO and pure water permeance were systematically investigated. The modified UF membranes exhibited less water flux decline (35% reduction) than the unmodified one (50% reduction) for obtaining the same amount of permeated water in the dead-end filtration system. The antifouling properties determined using a constant flux system will also be discussed.
Surfaces that have superhydrophilic characteristics are known to exhibit extreme oil repellency underwater, which is attractive for applications including anti-fogging, water-oil separations, and self-cleaning. However, superhydrophilic surfaces can also be easily fouled and lose their extreme oil repellency, thus limiting their usage in practical applications. In this work, we create a robust superhydrophilic coating by spray coating poly(acrylic acid) (PAA)-grafted SiO$_2$ nanochains (approximately 45 nm wide and 300 nm long) onto silicon wafers, forming a nanoporous coating exhibiting superhydrophilicity (water contact angle in air $\approx 0^\circ$) and underwater superoleophobicity (dichloroethane contact angle $\geq 165^\circ$). The polymer-grafted nanochain assemblies exhibit extremely low contact angle hysteresis ($< 1^\circ$) and small adhesion hysteresis ($\approx -0.05$ mN m$^{-1}$), and thus oil can readily roll off from the surface when the coating is immersed in water. Compared to other superhydrophilic surfaces, we show that both the unique structure of spray-assembled nanochains and the hygroscopic nature of PAA are essential to enable robust anti-oil fouling. Even after the PAA-grafted nanochain coating is purposely fouled by oil, oil can be readily and completely expelled and lifted-off from the coating within 10 seconds when placed under water. Furthermore, the coating is tested on existing membranes and it shows enhancement on oil/water separation in terms of flux and oil rejection. Our approach offers a simple yet versatile method to create a robust superhydrophilic and anti-oil fouling coating via a scalable manufacturing method.
Four fouling mechanisms based on Hermia model (complete pore blocking, intermediate pore blocking, cake filtration, and standard pore blocking) have long been used to describe membrane filtration and fouling in constant transmembrane pressure (TMP) operation of membranes. However, these models have not been reported for constant flux crossflow filtration, despite the frequent use of this mode of membrane operation in practical applications. We report derivation of these fouling mechanisms for constant flux crossflow filtration. Of the four mechanisms, complete pore blocking and standard pore blocking were inapplicable due to contradicting assumptions and relevance, respectively. Constant flux crossflow fouling experiments of dilute latex bead suspensions and soybean oil emulsions were conducted on commercial poly (ether sulfone) flat sheet ultrafiltration membranes to explore their abilities to describe such data. A model combining intermediate pore blocking and cake filtration models appeared to give the best agreement with the experimental data. Below the threshold flux, both the intermediate pore blocking model and the combined model fit the data well. As permeate flux approached and passed the threshold flux, the combined model was required for accurate fits. Based on this observation, a physical interpretation of the threshold flux is proposed: the threshold flux is the flux below which cake buildup is negligible and above which cake filtration becomes the dominant fouling mechanism.
Members of our research team previously demonstrated that cross-linked ionic lyotropic (i.e., surfactant) liquid crystal (LLC) assemblies can be used as a new type of membrane material for molecular size-selective water nanofiltration and desalination. In particular, ordered, 3D-nanoporous, cross-linked LLC networks with a type I bicontinuous cubic (QI) phase can be prepared from an imidazolium bromide-based gemini LLC monomer. Using solution-casting techniques, thin-film composite (TFC) membranes of this QI LLC material can be prepared with uniform-size, 0.96-nm-wide ionic pores that separate dissolved molecular solutes from water via molecular sieving and charge repulsion effects. Herein, we present recent progress in exploring this TFC QI polymer membrane for use in treating hydraulic fracturing flowback water via dead-end filtration, and in treating high salinity saltwater via cross-flow filtration to see how this new membrane system performs under conditions more representative of industrial application. The advantages and disadvantages of the TFC QI membrane relative to several commercial reverse osmosis and nanofiltration membranes compared under the same test conditions will be discussed. Some approaches for modifying the chemical structure of the TFC QI membrane system to improve its separation performance in these two applications will also be presented.
Diffusion of chemicals in polymers and composites can induce a mechanical response, causing material deformation, a decrease in the material modulus, and transition of the material to a more rubbery state. These changes in mechanical state are often related to changes in other properties, particularly in the case of functional polymers and lithium ion batteries. Additionally, current physics-based diffusion models may not account for composition-dependent mechanical properties, which can result in errors in predicting chemical permeation. In this contribution, we explore the changes in mechanical properties of both pure polyurethane and polyurethane-based composites after exposure to different chemicals using force spectroscopy (polymer) and tensile testing (composites). The functional dependence of material properties determined by these experiments are input to an adapted viscoelastic diffusion model accounting for the composition-dependent properties. Experimental chemical breakthrough curves are obtained by the use of modified ATR methods based on time-resolved FTIR spectroscopy previously demonstrated in our lab. This work provides experimental methods in addition to an adapted diffusion model which has practical applications in chemical decontamination and polymer-based separation membranes.
POLY 585: Highly selective organic solvent nanofiltration membranes based on polyepoxies to separate fatty acids and more

Ned B. Bowden, ned-bowden@uiowa.edu, Chad M. Gilmer. Chem Dept W425 Chem Bldg, Univ Iowa, Iowa City, Iowa, United States

We recently developed a series of membranes based on cross-linked epoxy polymers that have high size-selectivities to separate chemicals for applications in organic solvent nanofiltration. The membranes were fabricated by mixing diamines with di- or triepoxides to synthesize highly cross-linked polymers. The polymers were characterized by IR spectroscopy, SEM, and Raman spectroscopy. By changing the choice of diamines and epoxides we were able to selectively tune the separation properties of the membranes. This work represents an important advance to investigate how the molecular structure of the membranes affects the separations. p-Nitrobenzaldehyde and tri(p-tolyl)phosphine differ in molecular weight by a factor of 2x, but by optimizing the monomers used to synthesize the membranes their relative flux was measured to be as high as 250/1. These membranes were applied to the separation of saturated fatty acids and the separation of the key omega-3 fatty acid esters found in fish oil. Both sets of fatty acids had different flux and could be separated. A chemically responsive cross-linked membrane was fabricated from a diamine containing disulfides. The size-selectivity of these membranes was changed by cleaving the disulfide bonds to allow for the separation of a mixture of three chemicals into three purified streams.
Membranes that separate small molecules of similar size in the liquid phase based on their chemical properties would transform chemical manufacturing. Here, we aim to prepare synthetic polymer membranes that mimic key features of biological pores such as ion channels and porins: Constricted nanopores that confine permeation, lined with functional groups that interact with the target during passage. We first focused on membranes capable of charge-based separation through electrostatic interactions. To build these nanostructured layers using scalable techniques, we deposited packed arrays of polymer micelles whose coronas exhibit carboxylic acid groups, formed by a random copolymer of trifluoroethyl methacrylate (TFEMA) and methacrylic acid (MAA) in methanol, onto a porous support membrane. When these micelles are coated onto the surface of a porous support membrane whose pores are smaller than the micelles and then immersed into water, a selective layer of micelles packed together is formed. The gaps between the micelles act as nanochannels functionalized with carboxylic acid groups. The membrane showed charge-based selectivity between organic molecules, effectively rejecting negatively charged solutes while allowing the passage of neutral solutes in two-solute separation tests. Interestingly, selectivity was enhanced when a mixture of solutes was used, due to competition between solutes to enter the very narrow pores. We then functionalized the carboxyl groups with phenol moieties that can preferentially interact with aromatic groups through pi-pi interactions. This has enabled us to impart significant diffusion selectivity of ~10 between two hormones of identical size and charge, differentiated by the presence of an aromatic ring. We believe these approaches will eventually lead to novel membranes that can separate molecules of similar size but different chemical structure.
POLY 587: Equilibrium water uptake and transport in thin polymer films measured via Polarization-Modulated Infrared Reflection Absorption Spectroscopy (PM-IRRAS)

Apoorv Balwani², Hyun Wook Ro³, Eric M. Davis², denis d. bendejacq⁴, Christopher M. Stafford¹, chris.stafford@nist.gov. (1) NIST, Gaithersburg, Maryland, United States (2) Chemical & Biomolecular Engineering, Clemson University, Clemson, South Carolina, United States (3) Insight Team, PPG Industries, Allison Park, Pennsylvania, United States (4) COMPASS, Solvay USA Inc, Bristol, Pennsylvania, United States

We use polarization modulated IR reflection absorption spectroscopy (PM-IRRAS) to study the equilibrium water uptake and transport in thin films of Nafion and guar. PM-IRRAS is advantageous since it can measure the IR spectra of thin films in humid conditions, due to surface selection rules of the polarized IR beam. We collect IR spectra as a function of relative humidity using both H₂O and D₂O – D₂O has the distinct advantage that there are no competing vibrational signatures in the O-D region of the spectra. The different states of water within the thin polymer films is assessed by peak fitting the spectra, and the relative fractions of each component is quantified. Transport of water into and out of the thin polymer films is monitored by humidity jumps and/or switching between H₂O and D₂O.

PM-IRRAS technique for studying water absorption into thin polymer films.
Understanding the transport properties of water and salt ions in confined geometries of block copolymers is crucial for water purification including others nanotechnology and biotechnology. Here, we investigate the local diffusivities along with supporting structural properties of water and salt (\(\text{Na}^+\) and \(\text{Cl}^-\)) ions in the different regions from the pore with varieties of sizes made by morphologies of linear triblock copolymers such as lamella, cylinder, and gyroid using dissipative particle dynamics (DPD) mesoscale simulations. Besides, we extend our study to investigate the water and salt permeability through the membranes. Our results suggest that diffusivities of water and salt ions in the different region of pores are different than in the bulk phases. Under the confined conditions, the mobility of water and salt ions are perturbed by the additional interaction forces that arise from the blocks that have preferable water selectivity, which ultimately reduces the local molecular diffusion. Further, the geometries of block copolymers with different sizes of pore also influence the structural and dynamical properties of water and salt ions.
This work will show that epoxy/amine crosslinked polymers can be formulated such that the water barrier properties, solubility and diffusivity of water, are tunable. The addition of hydrophobic segments to epoxy/amine networks were exploited to tune the barrier properties of epoxy/amine crosslinked polymers. Two methods for hydrophobic segment addition were pursued: pendant hydrophobic segment addition and introduction of hydrophobic segments within the polymer backbone. Thus, several sets of epoxy/amine polymers were created using structurally diverse amine curing agents and diglycidyl ether of bisphenol A (DGEBA) as the model epoxy. A set of mono-amido-amines (AMAM<sub>n</sub>s) was synthesized to evaluate the effect of pendant aliphatic chain length on the barrier properties of epoxy/amine polymers. A series of difurane diamines was prepared to further evaluate how the location of hydrophobic segments added pendant to the epoxy/amine network affects barrier properties. An aliphatic amine chain extender was also blended with the dicyclobiaphatic diamine PACM to evaluate the influence of hydrophobic segments within the epoxy/amine network on barrier properties. It was found that that the solubility of water is dominated by enthalpic interactions between water and the polymer network. The atomic concentration of oxygen, [O], and not aliphatic content, was shown to be the dominating parameter in determining the solubility of water in epoxy/amine crosslinked polymers. As [O] decreases, the solubility of water decreases. However, it was also found that as [O] decreases, the diffusivity of water increases. So [O] generally has counteracting effects on the permeability of water. Interestingly, in a special case, it was found that reduction of both water solubility and diffusivity can be attained via the introduction of hydrophobic segments within the polymer backbone.
POLY 590: Biologically-inspired supramolecular systems: architecture and mechanics

LaShanda Korley¹,², lkorley@udel.edu, Chase B. Thompson¹. (1) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States (2) Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States

Supramolecular interactions may hold the key to the development of elastomers with a tailored elastic response and improved mechanics, such as observed in the muscle protein titin. Biological systems illustrate the power of non-covalent interactions to mediate assembly phenomena, responsiveness, and mechanical enhancement. We have developed supramolecular elastomers and interpenetrating network systems that probe the interplay of non-covalent and covalent interactions in structural organization and mechanical response. In this research, concepts of interfacial control of self-assembly, composition, and dynamics as it relates to mechanical behavior are examined. Variations in non-covalent interaction strength and network regularity are also highlighted as handles to tune dynamic response and morphology. Most recently, we have utilized metal-ligand coordination chemistry as an avenue for mimicking gradients of hard and soft mechanics to achieve structures capable of absorbing and dissipating large amounts of energy, where the local concentration of coordination crosslinks can be introduced via the application of a competitive ligand down the length of the film. These changes in crosslink density can be used to impart shifts in local mechanics, thus accessing a tunable material platform for controlling self-assembly and interaction localization.
Biopolymers such as polysaccharides, cytoskeletal proteins, and DNAs show helical structures in molecular scale and self-orientation in a larger scale. Those characters are the key to functionality and morphogenesis of various hierarchically structured materials. Sacran is one of the fascinating cyanobacterial polysaccharides which could naturally form the incredibly giant fiber in micrometer to millimeter scale. It is extracted from cyanobacteria, *Aphanothece sacrum*, which has attached our interest due to the extremely high molecular weight (> 1.6 × 10^7 g/mol) and the self-orienting giant micro-fibers (∼1 μm of outer diameter and > 20 μm length) during the drying process that cannot be encountered in any others polysaccharide. The giant fiber is apparently constructed though self-orientation of the rigid polysaccharides and self-assembly to build a rod-like microdomain.

In this study, to clarify the formation mechanism and microgeometry of fibers, the effect of polymer concentrations, evaporation speeds, and ionic concentrations are validated. The samples were prepared by drying sacran solution on a glass substrate at room temperature under control of the initial polymer concentration, evaporation speeds and concentrations of ionic solution (HCl, NaCl, and CaCl₂). By controlling evaporation speeds, it was found that the twisting structure could be formed by folding of the snaking structure (Fig.1). The fiber form showed significantly different, depending on the drying speed.

To clarify the ionic effect on the assembly and disassembly of the microfibers, in HCl or NaCl solutions, the microfibers were disassembled state as small fragments. In contrast, the microfiber maintained the structure in CaCl₂ solution because Ca^{2+} is capable to bind with the carboxylate groups as a crosslinker. This clarification of the microstructure will help not only understanding of geometric self-assembly of polysaccharides but also developments of biomimetic applications such as artificial muscle, biomimetic template and, micro-spring materials.

Morphological changed of microfiber from snaking form to twisting form (all scale bars = 10 μm).
Porous materials are attractive for a large variety of applications with their high surface and can be designed by the “breath figure” BF method, for obtaining honeycomb HC-structured porous films.\textsuperscript{1,2} In addition, we have demonstrated that copolymers self-assembly CSA can provide a second level of structure on the nano-scale in the wall between pores,\textsuperscript{3} leading to hierarchically structured bio-inspired materials.\textsuperscript{4-10} To go further, a HC film displaying three scales of hierarchy was produced for the first time with two micro- and nano-porosities levels formed by the BF process, giving a bio-inspired diatom exoskeleton, with a third structuration induced by the CSA between the pores (Figure 1). The presence of reactive nano-domains at the film surface allowed successive chemical modifications by click chemistry, which induces a Cassie-Baxter to Wenzel transition,\textsuperscript{10} leading to a hierarchically structured reactive platform by simple click chemistry.\textsuperscript{11}

![Microscopy images of honeycomb films produced by the BF method and schematic representation of the hierarchically structured honeycomb film with three levels of hierarchy](image_url)
Nature can produce very complex assemblies of biological entities or biologically active modules at the nanometer scale. For instance, ensembles of enzymes are organized in well-defined clusters to perform domino-like multi-step transformations and viruses present very peculiar surface patterns, which regulate their interactions with living matter. Synthetically mimicking these natural systems requires to develop extremely precise chemical patterning methods.

Chemical patterning in the sub-50 nm range is a challenge which has so far only been achieved by a few methods, e.g., dip-pen nanolithography, scanning near-field photolithography. Despite being sophisticated, these techniques can present some disadvantages in terms of costs and throughput due to their top-down nature. Our aim is to organize molecules on synthetic surfaces by making use of block copolymer (BCP) self-assembly in the solid state.

Our methodology relies on the introduction of a low percentage of reactive groups into well-known self-assembling hydrophobic block copolymers. We select from the toolbox of modular ligation methods for anchorage of single molecules in close proximity. We develop these nanostructured materials in the form of thin films obtained by spin-coating and in some cases annealing, as well as nanoparticles produced from self-organized precipitation.

We will present our results on the synthesis and the self-assembly behavior of these reactive block copolymers derivatives and introduce our first attempts at modifying their surfaces.
Melanin is a ubiquitous pigment found in plants, animals, fungi, and other organisms. It serves a host of functions such as photoprotection, free-radical quenching, structural color, thermoregulation, and metal ion chelation, among others. In humans, melanin provides pigmentation to the skin and is integral to its protection from UV radiation. Melanin occurs naturally as a polymeric nanoparticle packaged into organelles called melanosomes. These melanosomes are transferred from melanocytes to keratinocytes where they enter the cells and form perinuclear caps that shield the nucleus from UV radiation. Previously we have shown that our synthetic polydopamine melanin mimics can enter human adult epidermal keratinocytes (HEKa cells), form these same perinuclear caps (also known as microparasols), and protect the cells from DNA damage and reactive oxygen species (ROS) upon UV irradiation. Our current work expands the synthetic range of melanin mimics to create a library of nanoparticles with exotic shapes and chemistries, both found in nature and not found in nature. The ensuing particles are capable of penetration into neonatal human epidermal keratinocytes (NHEK cells), forming perinuclear caps, and protecting the cells from reactive oxygen species upon UV or X-ray irradiation. In addition, there is a dose-dependent, visual “tanning” effect of treatment on the cells. We believe these materials can be formulated for topical delivery to serve several purposes such as a biodegradable/biocompatible sunscreen, self-tanning cream, radioprotective agent, and cosmeceutical/therapeutic for hypopigmentation disorders such as vitiligo and albinism.
POLY 595: Sustainable packaging inspired by cellulose and chitin

James C. Meredith, carson.meredith@chbe.gatech.edu. Chemical & Biomolecular Engineering, Georgia Tech, Marietta, Georgia, United States

The problems posed by plastics to disposal in landfills and their accumulation in oceans are widely recognized. Yet, plastics are useful materials that provide vital functions in transportation (lightweight vehicles), packaging (preserving food much longer than historically possible) and medicine (stents, IVs, drug delivery). One solution is the development of more sustainable compostable or recyclable plastics derived from renewable resources. Such materials could enable circular manufacturing, use and disposal that avoids environmental accumulation, just as many naturally-synthesized materials do. Cellulose and chitin are the first- and second-most abundant naturally-occurring biopolymers, respectively, with annual natural production estimated to be 1011-1012 tons per year (cellulose) and 1010 - 1012 tons per year (chitin). Cellulose is sourced from plants and chitin is produced by crustaceans, insects and fungi. In their native nanofibrillar format, these are semicrystalline materials that provide barrier and mechanical properties that suggest usage in packaging materials. This talk will highlight our recent work in developing plant- and food-waste as enabling materials for food packaging. The talk will emphasize high-performance cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs), and recent work in isolating, modifying and coating them as sustainable O2 barrier materials for food and pharmaceutical packaging, along with possibilities for flexible organic electronic and electrochromic devices.
POLY 596: Self-assembled benzene tri-carboxamide hydrogels for tissue engineering

Matthew B. Baker, m.baker@maastrichtuniversity.nl. MERLN, Maastricht University, Maastricht, Netherlands

Supramolecular and non-covalent interactions provide many opportunities to create responsive, self-healing, and dynamic biomaterials. In some cases, these materials can be constructed to form fibrous self-assembled structures, akin to the fibrous proteins found in a cell’s extracellular matrix (ECM). In this talk, I will cover some of the recent advances in the use of 1,3,5-benzenetricarboxamides self-assembled hydrogels as hydrogels for cell encapsulation and tissue engineering. From a fundamental point of view, we have studied the structural and behavioral effect of small mutations on a family of 1,3,5-benzenetricarboxamide (BTA) supramolecular polymers and shown the ability to biofunctionalize hydrogels from these polymers via a host-guest approach. Furthermore, by modular mixing of hydrogelators we can control the mechanical properties of the resultant self-assembled hydrogels and tune the environment in which cells are encapsulated. These materials show significant promise as a fibrous dynamic platform for tissue engineering, showing the ability to support chondrocyte and neural cultures in 3D. Due to their biomimetic self-assembly and modularity of mechanical properties, these materials represent an interesting new class of biomaterials to study the effect of viscoelastic environments for tissue engineering applications.
Hydrogels, which are composed of three-dimensional networks of synthetic and/or natural polymers, are able to absorb significant amount of water and have been extensively used in various biomedical applications. Sacran, which is a cyanobacterial polysaccharide extracted from *Aphanothece sacrum* biomaterials, has a super-high molecular weight over 20 Mg/mol much higher than those of conventional polysaccharides. Sacran contains 11% of sulfate group and 22% of carboxyl group to sugar residues, and then behave as a polyanion having a deep potential well along polymer chains. Sacran has a function of liquid crystals in very thin aqueous solution around 0.2 wt% and a super-absorbent property of 6000 times of pure water and 2000 time of saline. Here we found that the physical hydrogel of sacran can be prepared from the water-cast film by thermal cross-linking. Practically sacran solution with a concentration of 0.5% was dried at 60 °C for 12 h to create the thin film (about 50 mm), and the film was annealed at 70-140 °C to form anisotropic hydrogels having layer structures in water (left picture). Then the hydrogels were predominantly swollen to the direction of thickness. This phenomenon was observed only in high-molecular weight sacran but not in other polysaccharides. The swollen degree of the gels was controlled by the cross-linking temperature, to adjust the swollen degree of the hydrogels from 10 to 400 times. Now we are developing this material for wound dressing. The structural characteristics were applied for specific tissue engineering study. L929 mouse fibroblasts were used to confirm no toxicity and were finely oriented on the hydrogel side face where layer edges made a striped morphology on its surface, while the flat top faces of the hydrogels did not induce any specific cell orientation (right illustration). Further sacran solution was used as a dressing agent having an efficient wound-healing activity and we accumulated case-studies for various patients.
To establish a super-engineering plastic concurrently with a sustainable green society, bio-based polyimide (PI), is an attractive candidate for fabrication of high-performance polymeric materials due to its mechanical durability, thermal stability and chemical compatibility. In this study, we are focusing on 4-aminophenylalanine (4-APhe), a bio-derived aromatic amino acid derived from glucose fermentation, to generate a novel bio-derived monomer for the synthesis of bio-based high performance polymer. Through the molecular design, the established monomer composes of three important parts: diamine, aromatic and 2,5-diketopiperazine (2,5-DKP). Diamines are reactive to synthesis polymers such as PI. Aromatic help improve the performance and overcome the drawbacks of biomass utilization.

Here, we developed bio-based PIs from various dianhydrides with a novel bioavailable aromatic amines, which were dimerized from 4-APhe. These PIs showed high thermal resistance with 427 °C as a highest T10 values. Using the developed synthesis route template, other amino acids such as lysine could be cross coupled with 4-APhe to provide diverse monomers for various polymer generations. Composing of 2,5-DKP units in the polymer structure, this could induce particulation via self-assembly through H-bonding formation. Polyamic acid (PAA) particles, the precursor of PI particles, were basically prepared by reprecipitation with the inclusion of surfactants. The physical properties of PAA particles and PI particles such as shape, size and size distribution were studied.

In this work, the effect of dispersed solvents on PAA and PI particles size and shape was also investigated. Using 20% acetone in water as a dispersed solvent, PAA particles showed virus-like shape while in the absence of acetone the particles in spherical shape were obtained with narrow size distribution.

SEM images of PAA-BTDA particles (a1, b1) and PI-BTDA particles chemically imidized from PAA-BTDA particles (a2, b2). Particles (a1, a2) and (b1, b2) dispersed in H2O and 20% Acetone/H2O, respectively.
Thomas Edison once stated that "I have not failed. I've just found 10,000 ways that won't work." The trial-and-error approach to materials development was the standard for many years, particularly with aerospace-grade composite structural materials. Material formulations were incrementally adjusted, specimens fabricated, and tests performed; and the process is repeated until the material structural requirements were met. The time, material costs, and man-power costs associated with this Edisonian approach are prohibitive roadblocks to new material development.

Fortunately, computational methods have been developed to greatly facilitate the material development process. Using multiscale simulations, materials can be designed at multiple length scales (atomic, microscopic, bulk) and the resulting properties can be efficiently and accurately predicted. Thus, material designs can be optimized via computational modeling before the expense prototyping and testing phases begin. This presentation will outline the Materials Genome Initiative and some recent efforts to develop multiscale modeling techniques for specific polymer-based materials.
POLY 600: Property predictions and analysis for aerospace polymers using molecular simulation

Andrea Browning¹, andrea.browning@schrodinger.com, Jeffrey Sanders¹, Mathew Halls¹, Jacob Gavartin², Caroline Krauter². (1) Schrödinger Inc, New York City, New York, United States (2) Schrödinger Gmbh, Mannheim, Germany

Polymers have become the primary matrix material for aerospace composites. With thermoplastic and thermosets available, these materials provide stability and flexibility needed for a variety of uses. Understanding how these materials provide their desirable combination of properties as well as predict the properties for new polymers are important to their continued long term use. Molecular level simulations provide a key capability in achieving this increased knowledge.

Simulation of aerospace polymer materials has been a major topic of research for decades. With the optimization of the modeling process with flexible crosslinking for network formation, polymer specific builders and automated property workflows, molecular simulation can be integrated into material development process. Molecular has the additional benefit of providing a window into the behavior of polymers that can be probed with structural analysis techniques to provide understanding in how features of the polymer relate to the properties of interest.

This talk will review how simulations can be used to model aerospace thermosets and thermoplastic. Analysis of structural features such as hydrogen bonding, free volume, and density profiles will be discussed. With simulations to quickly simulate polymer matrix materials for multiple properties as well as understand structural changes with chemistry, links between chemistry and properties can be made to enable more rapid development of new chemistries as well as trouble-shoot existing materials.
As the need for manufacturing rate and volume increases, we are pushed to rethink traditional processing methods for thermoset composite materials. Long cure times in high pressure autoclaves pose a challenge, and the need for shorter and lower pressure cure cycles has been identified. These changes in processing conditions can greatly impact the development of material properties of curing thermoset resins. However, simulation tools that allow us to predict the impact of process changes on the evolution of thermoset resin properties during cure do not exist. In this talk we will present efforts to quantify the cure path dependency of epoxy thermoset resin properties and morphology and new methods for simulating resin cure through atomistic and coarse-grained molecular dynamics.
Polymer matrix composites (PMCs) are widely used in many automotive, marine, and aerospace applications. Predicting the damage and failure of such systems is of crucial interest for their reliable performance. In this work, a coarse-grained MD model has been developed to characterize the evolution of free volume density (voids) in DGEBA polymers under loading and its subsequently plastic deformation (e.g. hardening and failure). A detailed atomic monomer is coarsened to create the tailored plastic behavior. Cross-linked polymer networks are created under different curing conditions, including temperature, and cross-linker functionality using a dynamic cross-linking algorithm. The effect of chain size, and degree of cross-linking are also investigated. The free volumes are measured as a function of strain by fitting the largest ellipsoids between neighboring chains in the network. From these simulations we develop a direct correlation between the evolution of plastic deformation and the free volume density. The results of these simulations are then upscaled into a finite element simulations to model the damage and failure of PMCs.
POLY 603: Molecular dynamics simulations of MoS$_2$-dispersed epoxy nanocomposites

Rajiv J. Berry$^1$, rajivpatch@gmail.com, Ian Barrett$^1$, Gary S. Kedziora$^2$, James Moller$^{1,3}$, Triet Nguyen-Beck$^{1,4}$, Nellie Pestian$^1$, John Ryan$^1$, Dhriti Nepal$^5$. (1) Materials & Manufacturing Directorate, Air Force Research Lab, WPAFB, Ohio, United States (2) Engility Corp, Air Force Research Laboratory, WPAFB, Ohio, United States (3) MEE Department, Miami University, Oxford, Ohio, United States (4) Universal Technology Corporation, Beavercreek, Ohio, United States (5) Materials and Manufacturing Directorate, Air Force Research Lab, Beavercreek, Ohio, United States

Polymer-based matrix composites (PMC), a class of structural materials consisting of thermoset and/or thermoplastic matrix resins reinforced by fillers, are among the front runners for aerospace applications. Rational design of PMCs requires understanding and characterization of these materials at the atomistic scale. This project represents our ongoing studies on simulating epoxy nanocomposites using molecular dynamics. In particular, we investigate the thermo-mechanical properties of nanocomposites consisting of DGEBA epoxy resin, DDS hardener, dispersed MoS$_2$ and residual solvent (NMP, acetonitrile, water). Moving forward, we aim to gain an understanding of the nanoscale toughening mechanism in these composites in order to tailor novel PMCs for improved structural performance.

Amorphous cell containing DGEBA resin, DDS hardener and MoS$_2$ bilayer
The Materials Genome Initiative (MGI) was designed to radically change the culture of materials research and enable accelerated development of new materials by coupling computational and experimental tools. The realization of this vision requires major advances in both computational and experimental tools based on an understanding of the physics of these materials. Some examples of efforts to use computationally guided materials development for aerospace applications will be discussed. These include the application of modeling and simulation to guide processing parameters for nanocomposites, using process modeling to improve the quality of additively manufactured components, employing machine learning to optimize advanced manufacturing methods, and employing systems analysis to provide guidance on high impact systems benefits of new materials. Challenges and approaches developed to reap early benefits of coupling computational modeling with experimentation will be presented. The examples will be used to highlight facets of this approach that range from the atomistic scale to the macroscale and identify some gaps in existing knowledge that provide fertile ground for research.
The rapid heating of carbon-fiber reinforced polymer matrix composites leads to complex thermo-physical interactions which not only are dependent on the thermal properties of the constituents and microstructure but are also dependent on the thermal transport between the fiber and resin interfaces. Thus, it necessitates a need to better understand the behavior of carbon fiber/matrix interfaces from the perspective of thermal transport. Using atomistic molecular dynamics simulations, the thermal conductance across the interface between a near-surface region of carbon fiber and bismaleimide (BMI) matrix is estimated as a function of the several interface and bulk features of the carbon fiber. The surface of the carbon fiber is modeled as sheets of graphitic carbon with (a) varying degrees of surface functionality, (b) varying defect concentrations in the surface-carbon model (pure graphitic vs. partly graphitic), (c) varying orientation of graphitic planes at the interface, (d) varying degree of interface passivation (dangling vs saturated bonds), (e) varying degrees of surface roughness, and (f) incorporating high conductive fillers (carbon nanotubes) at the interface. Thereafter, thermal energy exchange is investigated in terms of interface thermal conductance across the carbon fiber and the matrix. It is observed that modifications in the studied parameters (a–f) lead to significant modulation of thermal conductance across the interface and, thus, showcases the role of interface tailoring and surface-carbon morphology toward thermal energy exchange. More importantly, the results provide key bounds and a realistic degree of variation to the interface thermal conductance values at fiber/matrix interfaces as a function of different surface-carbon features.
POLY 606: Poly(cyclic imino ether)s beyond 2-oxazolines

Richard Hoogenboom, richard.hoogenboom@ugent.be. Ghent University, Ghent, Belgium

The living cationic ring-opening polymerization of 2-oxazolines (see Figure) 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. 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.

Recent developments from our research group that broaden the scope of poly(2-oxazoline)s will be discussed in this lecture, focusing on the (co)polymerization of larger cyclic imino ethers, such as 2-oxazines and 2-oxazepines. It was unexpectedly found that copolymerization of 2-oxazolines with 2-oxazines yields gradient copolymers in which the 2-oxazine is incorporated faster. In contrast, during homopolymerization the 2-oxazolines polymerize faster than the 2-oxazines. This difference between the homopolymerizations and copolymerizations will be discussed based on the combination both electronic and steric effects. Finally, the synthesis and homopolymerization of 2-phenyl-2-oxazepine will be discussed revealing significantly slower homopolymerization than the corresponding 2-phenyl-2-oxazoline and 2-phenyl-2-oxazine.
Thermoresponsive block copolymers with lower critical solution temperature (LCST) remain molecularly soluble at laboratory temperature as unimers and upon heating to body temperature they form nanoassemblies. Such nanoparticles may be used as drug or other bioactive cargo carriers (drug delivery systems), for diagnosis and cell tracking (cancer, inflammation, pancreatic islets) or combination of both (theranostics). Our concept is based on amphiphilic copolymers containing two blocks - hydrophilic poly[N-(2-hydroxypropyl)methacrylamide] (PHPMA) or poly(2-methyl-2-oxazoline) (PMeOx) block, respectively, and thermoresponsive poly[N-(2,2-difluoroethyl)acrylamide] (PDFEA) block, forming nanogels after heating of their aqueous solutions. Due to fluorinated chain, these polymers are visible at $^{19}$F MRI, promising noninvasive method for diagnosis. These nanogels are ideal-sized for passive accumulation in solid tumor tissue or special types of inflammation (due to angiogenesis) and therefore, they may serve as contrast agents for diagnosis of these diseases. In second part of our approach, we modified these copolymers with ferrocene moieties, which introduce redox switch sensitivity to reactive oxygen species (ROS), overproduction of which is typical for inflamed and solid tumor tissues. Oxidation leads to degradation of micelle and cargo release; this system is then sustainable as new theranostic system for the treatment of such diseases.
Crystalline nanosheets formed by self-assembly of amphiphilic polypeptoid molecules in water were imaged on atomic length scales using electron microscopy. Imaging soft materials with atomic resolution using electron microscopy is challenging because soft materials are unstable when exposed to electron beam. Low-dose cryogenic electron microscopy micrographs were obtained from frozen hydrated crystalline polypeptoid nanosheets. A combination of crystallographic and single particle methods, developed for cryo-electron microscopy of biological macromolecules, was used to obtain high resolution images of the crystals. Individual crystals contain grains that are mirror images of each other with concomitant grain boundaries.
POLY 609: End-functional poly(2-ethyl-2-oxazoline)s as versatile building blocks to combine CROP and RAFT

Christine Weber\textsuperscript{1,2}, christine.weber@uni-jena.de, Anne-Kristin Trützschler\textsuperscript{1,2}, Martin Sahn\textsuperscript{1,2}, Ulrich S. Schubert\textsuperscript{1,2}. (1) Laboratory for Organic and Macromolecular Chem, Friedrich-Schiller-University Jena, Jena, Germany (2) Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany

The direct termination of the polyoxazolinium chain end represents a straightforward opportunity to introduce a range of functional moieties as ω-end groups of poly(2-ethyl-2-oxazoline) (PEtOx). The use of methacrylic acid results in macromonomers, enabling the combination of PEtOx’s properties with those of polymethacrylates, resulting in graft copolymers. As an example, the grafting of polymethacrylates containing a primary amine functionality with PEtOx side chains significantly reduced cytotoxicity of the non-viral gene carriers, maintaining the transfection efficiency\textsuperscript{[1]} The termination of the cationic ring-opening polymerization with a carboxylic acid functionalized trithiocarbonate enabled access to mono- as well as bifunctional PEtOx macro-chain transfer agents\textsuperscript{[2-3]} Subsequent reversible addition fragmentation chain transfer polymerization of N-isopropylacrylamide (NiPam) and triethylene glycol acrylate (eTEGA) yielded a library of di- and triblock copolymers composed of two different segments featuring lower critical solution temperature behavior in water. Detailed studies by turbidimetry, dynamic light scattering and NMR spectroscopy revealed that the block length plays a significant role for thermo-induced micellization for all four block copolymer types.
POLY 610: Fluorine containing poly-2-oxazolines as contrast agents for 19F MRI: Quest for the structure

Leonid Kaberov¹, kaberovleonid@gmail.com, Zhansaya Sadakbayeva¹, Anastasiia Murmiliuk⁴, Ewa Pavlova¹, Jiri Brus¹, Richard Hoogenboom², Sergey Filippov³. (1) Institute of Macromolecular Chemistry AS CR, Prague, Czechia (2) Ghent University, Terneuzen, Netherlands (3) John A. Paulson School Of Engineering And Applied Sciences, Harvard University, Cambridge, Massachusetts, United States (4) Charles University, Prague, Czechia

2-Oxazolines are known to be popular building blocks for the controlled synthesis of self-assembling polymer systems. Due to the structure similar to poly(amino acids) and peptides, this polymers exhibit a good biocompatibility and immunogenicity. By variation of the monomer structure one can obtain hydrophilic, hydrophobic or stimuli-responsive polymers or blocks. The most widely studied thermoresponsive poly(2-oxazolines) are poly(2-n-propyl-2-oxazoline) (T_{cloud}~25 °C) and poly(2-iso-propyl-2-oxazoline) (T_{cloud}~35 °C). The cloud point temperature of resulting polymer can be tuned by polymer chain length as well as by copolymerization with other 2-oxazolines.

Here we present the synthesis and characterization of novel 2-oxazoline copolymers with hydrophilic, fluorophilic, and thermoresponsive fragments. All polymers were synthesized by Cationic Ring-Opening Polymerization (CROP). In absence of moister and other nucleophilic impurities, the CROP proceeds in a living mode allowing us to control precisely the blocks ratio and, thus, obtain well-defined polymers.

The solution behaviour of all copolymers was studied by a series of physico-chemical methods such as dynamic light scattering, small angle X-ray scattering, transmission electron microscopy, etc.. The presence of hydrophobic fluorinated block contributed to self-assembly of all copolymers in aqueous milieu, whereas the presence of 2-n-propyl-2-oxazoline block made these systems responsive to heating (Figure 1).

The obtained fluorine containing poly-2-oxazolines represent a potential platform for utilization as 19F magnetic resonance imaging contrast agents.

Figure 1. TEM photo of EtOx₅₀-b-nPrOx₅₁-b-CF₃EtOx₁₀ micelles and dependence of block copolymer aqueous solution transmittance on temperature.
POLY 611: Antimicrobial telechelic partially hydrolyzed poly(2-oxazoline)s with two modes of action

**Lena Benski**, lena.benski@tu-dortmund.de, Montasser Hijazi, Fatima Arfeen, Christian Krumm, Joerg C. Tiller. Bio and Chemical Engineering, TU Dortmund, Dortmund, Germany

After the development of antimicrobial agents, bacterial infections have become a minor problem in industrial societies. However, the rise of immune and multi resistant bacterial strains demands new and more effective biocides. Polymer-based antimicrobial agents are a promising alternative to low molecular antimicrobial agents. Telechelic poly(2-oxazoline)s with quaternary ammonium end groups have shown very good antimicrobial activities against Gram-positive bacterial strains, but lack in activity against Gram-negative strains.

We could combine the characteristics of biocidal telechelic polymers and antimicrobial hydrophilic polycationic polymers in one macromolecule by partially hydrolyzing the backbone of a telechelic biocidal poly(2-oxazoline) to poly(ethylene imine) (PEI). The resulting polymers are active against Gram-positive *Staphylococcus aureus* as well as Gram-negative *Escherichia coli*. The contribution of the polycationic PEI backbone was determined by measuring the antimicrobial activity in the presence of calcium ions, which deactivates this polymer. While the presence of calcium ions deactivates PEIs with octyl and decyl quaternary end groups against *E. coli* similarly to linear PEI, this effect is less pronounced for PEIs with longer alkyl chain end groups. This indicates that both, the polycationic backbone and the end groups act synergistically. Similar results were found for *S. aureus*. Furthermore, variation of the length of the polymer backbone revealed, that the antimicrobial activity of telechelic PEIs with lower molecular weights is dominated by the quaternary end groups, while the polycationic backbone dominates the mode of action for PEIs with at least 80 repeating units.
Poly(2-isopropyl-2-oxazoline) (PIPOZ), a thermo-responsive polymer, and poly(lactide) (PLA), a hydrophobic polyester, are miscible (F. Pooch et al, Polym. Chem. 2018, 9, 1848-1856). In cold aqueous dispersions, diblock copolymers of PIPOZ and PLA, self-assemble into colloidally-stable nanoparticles. The inner morphology of the particles is controlled by two opposing interactions: (i) the separation of the hydrophobic PLA block from the hydrophilic PIPOZ block and (ii) the van-der-Waals forces-driven complexation of the PIPOX and PLA monomer units. On the basis of light and neutron scattering data, supported by proton nuclear magnetic resonance spectroscopy, we show how this duel of antagonistic forces is governed by the PLA stereo-chemistry and the molecular weights of the two blocks.
We describe the synthesis, characterisation and applications of a range of multiblock copolymer architectures obtained from RAFT polymerisation. Multiblock copolymers of type (AB)n are shown to self assemble both in bulk and in solution, revealing unique nanostructures based on the size and number of blocks. In addition, more advanced segmented structures such as multiblock copolymer molecular brushes were also synthesised and studied.
POLY 614: Crystallizable comb block polyolefins with broad polydispersity in molecular weight and composition

Patrick Brant, pat.brant@exxonmobil.com. Exxonmobil Chemical Company, Baytown, Texas, United States

Two series of crystallizable comb block copolyolefins have been prepared and characterized. Each series is made starting from a commercially produced high pressure, free radical-produced backbone: poly(ethylene-co-acrylic acid) (EAA; 11 wt% AA, melt peak 95 °C, MWD 10) and poly(ethylene-co-methylacrylate) (EMA; 21.5 wt% MA, melt peak 80 °C, MWD 8). Both backbones have a broad composition distribution, and both are heavily long chain branched. Atactic and isotactic polypropylene hydroxide macromonomers (aPPOH and iPPOH) have been grafted to these semicrystalline backbones via esterification (EAA) or transestification (EMA). The PPOH macromonomers are prepared by oxidative hydroboration of vinyl terminated aPP and iPP that are made via metallocene catalysis. Number average molecular weights, $M_n$, of the aPPOH are between 1 and 7 kDa and $M_n$ of the iPPOH is between 6 and 24 kDa. In all reactions the PPOH is the limiting reagent and grafts to between 1 and 75% of the AA or MA. Starting materials and products are characterized by $^1$H NMR, DSC, GPC (including 4D in selected cases) WAXS and SAXS. Room temperature atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray scattering measurements reveal finely textured phase segregation of the polypropylene and EAA and EMA domains, which persists in the melt state. Self assembly is typically on the ~50 nm scale (see TEM image). Impact of grafting and phase segregation on the rheological behavior of the products will be shared. Binary and ternary blends of these comb blocks with iPP matrix and with iPP and EMA or EAA have been prepared and their morphologies examined. Some speculation on the utility of comb block architectures such as these will be offered.

TEM of a RuO$_4$ stained EAA-cb-iPP containing 50 wt% iPP
POLY 615: Partitioning of molecules in olefin block copolymer (OBC) morphologies: Effect on the size of ordered domains and the phase diagrams of disordered OBC/random copolymer blends

Jeff Weinhold¹, DWeinhold@dow.com, Phillip D. Hustad². (1) The Dow Chemical Company, Lake Jackson, Texas, United States (2) Dow Electronic Materials, Natick, Massachusetts, United States

All phase separated morphologies of binary blends have some level of intermixing of the components. In monodisperse mixtures, the degree of intermixing is primarily determined by the difference between the blend’s critical temperature and the temperature at which the morphology is evaluated. Intermixing is magnified in blends of polydisperse homopolymers and/or random copolymers since the partitioning between phases will vary with molecular weight. A fraction of the lowest MW chains of each component will tend to partition to the phase rich in the other component, resulting in greater combinatorial entropy without the large increase in enthalpy of similar partitioning of high MW chains. The degree of intermixing increases even further for polydisperse olefin block copolymers (OBC). The length of each block follows a most probable distribution but the blocks within each molecule are uncorrelated. Those properties result in the composition distribution depicted for a diblock with an overall 50/50 composition. A large fraction of the molecules are either rich in hard block or in soft block and those chains will partition very differently than those that are close to 50/50. In mesophase separated OBCs, molecules rich in either block tend to move from the interface to the center of the domain matching the majority block composition. This swelling effect makes the domains large enough to reflect light in the visible spectrum even though the viscosity is still in a range that is appropriate for melt processing. Unique partitioning of molecules of disordered OBCs is also observed in OBC/random copolymer blends. Through comparisons of theory and experiment, the complexity of partitioning in OBC morphologies will be demonstrated.
We consider the influence of sequence polydispersity upon the phase behavior and interfacial characteristics of gradient copolymers. We study the dependence of the spinodals, the phase behavior, and interfacial properties of gradient copolymers as a function of gradient strengths and blockiness of the sequences. We demonstrate that the interplay between compositional polydispersity and the overall blockiness of the sequences can play a significant role in determining the morphologies, phase behavior, and interfacial activity of gradient copolymer systems. In systems wherein the inherent blockiness of the sequences is small, such as in gradient copolymers with weak gradient strengths, the introduction of such polydispersity and blockiness effects leads to substantial changes in the self-assembly behavior and interfacial properties. In contrast, in systems for which the inherent blockiness is already large, such as in gradient copolymers with strong gradient strengths, the effects of sequence correlations upon the self-assembly characteristics and interfacial properties are seen to be much more mitigated. Further, we also study the influence of sequence of compatibilizers on the onset of formation and the width of the bicontinuous microemulsion channel in the ternary phase diagram of homopolymer blended with compatibilizer. We observed that diblock copolymers having bidisperse composition are most efficient (i.e., microemulsion phases occupy the largest area of phase diagram) in forming microemulsions. On the other hand, monodisperse diblock copolymers and diblock copolymers having bidisperse MW distribution form microemulsions with the least amount of compatibilizers. We rationalize our results by explicitly quantifying the interfacial activity and the influence of fluctuation effects in the respective copolymer systems.
Miktoarm star polymers are potentially useful in applications ranging from thermoplastic elastomers to drug delivery. In contrast to star homopolymers and radial copolymers, the mikto architecture demands asymmetry in arm connectivity and molar mass distribution, which creates a significant synthetic challenge. Here, we introduce a new design strategy that simplifies the synthesis of miktoarm star polymers using norbornene-functionalized “macromonomers” and grafting-through copolymerization. Self-assembly in the bulk was studied as a function of molecular composition, arm stoichiometry, and backbone degree of polymerization ($N$). Insights generated from scattering experiments suggest our materials behave as dispersed mikto-star at low $N$ with a transition to brush-like conformations as $N$ increases. The impact of dispersity on the self-assembly behavior at low $N$ was investigated experimentally and simulated using self-consistent field theory. These analyses complement previous reports that describe the characterization of low $N$ homopolymer bottlebrushes using neutron scattering and rheology.
POLY 618: Structure-function-dynamics relationships in next generation protein-polymer conjugates

Stefanie Baker\textsuperscript{1,3}, slbaker@andrew.cmu.edu, Aravinda Munasinghe\textsuperscript{2}, Hironobu Murata\textsuperscript{3}, Krzysztof Matyjaszewski\textsuperscript{4,3}, Ping Lin\textsuperscript{5}, Coray M. Colina\textsuperscript{6,2}, Alan J. Russell\textsuperscript{7}. (1) Department of Biomedical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Department of Chemistry, University of Florida, Gainesville, Florida, United States (3) Center for Polymer-Based Protein Engineering, Carnegie Mellon University, Gainesville, Pennsylvania, United States (4) Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (6) Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States (7) Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Protein-polymer conjugates fuse together the synthetic and biologic worlds and are created in hopes of extending a protein’s natural function. Moving past traditional PEGylation techniques, where a chain of polyethylene glycol (PEG) is reacted with a protein, unique polymers with a range of varying attributes can now be grown-from the surfaces of proteins with controlled densities. This means that many protein-polymer conjugate variants can be synthesized and used to study how the various polymers impact protein function to develop structure-function-dynamic based relationships. Currently, it is impossible to predict the ultimate fate that the covalent attachment of polymers will have on a protein’s activity and long-term stability and this is partially due to a lack of insight into what interactions are occurring at the interface between the protein-polymer. Elucidating these interactions could help explain how different polymer types and molecular weights either increase or decrease activity in both native and non-native environments, including low pH. The scales of these interactions are on the Ångström level and can be difficult to probe experimentally in the laboratory. Computational models of protein-polymer conjugates, however, can be built \textit{in silico} and molecular dynamics simulations can be performed in order to visualize dynamic motions and interactions with atomic resolution.

Herein, we sought to determine how covalently attached polymers impact the activity and stability of our model protein, α-chymotrypsin, as a function of polymer type and molecular weight (polymer charge and length). We synthesized 15 related protein-polymer conjugate variants and measured changes in Michaelis-Menten activities and pH 1 acid stabilities. We further used molecular dynamics simulations to deepen our understanding of how polymers impact conjugate activities. Finally we propose a new mechanism for how polymers stabilize proteins in acid by modulating protein folding.
Understanding the biomolecule-polymer interface is critical for the development of next-generation biomaterials, protein technologies and drug delivery. Understanding the interactions of the polymer with residues on the protein surface as a function of time will pave the road to the development of new materials. Molecular simulations are a powerful tool to complement and enhanced experimental findings, helping to reveal the fundamental interactions that drive these materials. Many atomistic and coarse-grained models have been independently developed for polymers and proteins. However, only a handful of models have been used at the protein-polymer interface level over different time and length scales to determine the effect of their interactions. In this talk, we will discuss the current state-of-the art of these models, both at the atomistic and meso-scale level, from PEGylated systems to the novel polymer-protein system made by ATRP.
The binding selectivity of proteins is currently unparalleled by synthetic nanomaterials. Bioconjugates coupling peptides to lipids and synthetic polymers have enabled bioactive materials with controlled morphologies and stimuli responsive behavior. We are expanding on these capabilities by focusing on molecular-level control to continue to bridge the gap between the precision binding of biological materials and tunability offered by synthetic polymers.
We use molecular dynamics (MD) simulations to model selected biotechnological problems in collaboration with experimentalists. First, we investigate a disintegration of viruses by virucidal nanoparticles, and show that these processes are very sensitive to the structures of ligands and nanoparticles, due to a highly specific multivalent binding. We also show that functionalized cyclodextrines can perform similar tasks, but they are more likely to be applied as nanomedicines. Then, atomistic MD simulations are used to explain the increased reaction rates of oligo-anionic molecular sliders with their conjugates (bromo-substituted N-methyl-Maleimide) in the presence of poly-cationic tracks. The simulations reveal that molecular sliders not only diffuse, but also loop and hop efficiently along or between several polymer tracks, thereby significantly increasing the meeting and reaction rates with their conjugates, in comparison to the bulk solvent.
POLY 622: Molecular sieving through dendronization of enzymes

Alex Adronov, adronov@mcmaster.ca, Stuart McNelles. Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

The development of rapid and efficient synthetic methodology that enables the preparation of well-defined complex macromolecules is important in expanding their use, especially in biological applications. Dendrimers represent a particularly attractive architecture for the development of macromolecular therapeutic and diagnostic agents due to their precisely defined, uniform structure. However, efficiently attaching high-generation dendrimers to the surface of biological molecules, such as enzymes, poses a significant challenge. To address this challenge, it is necessary to functionalize the dendritic macromolecule with a highly reactive group that can couple to specific surface functionalities of an enzyme. To this end, we have recently prepared a series of bis(2,2-hydroxymethylpropionic acid) dendrons of generation 2 through 8 having a strained cyclooctyne at the core and hydroxyl groups at the periphery. The strained cyclooctyne allows strain-promoted azide-alkyne cycloaddition (SPAAC) chemistry to be performed, while the peripheral hydroxyl groups impart aqueous solubility such that the structure is compatible with biologically-derived co-reactants. These dendrons were subsequently used to decorate the periphery of azide-functionalized α-chymotrypsin. We show that the appended dendrons can shield the active site of the enzyme in a selective manner, where a small molecule substrate (benzoyl-L-tyrosine p-nitroanilide) could easily access the active site and be cleaved, while a macromolecular substrate, such as bovine serum albumin is blocked. We show that the size of the appended dendron has a significant impact on the extent to which substrates are blocked from accessing the enzyme active site. There is a critical dendrimer generation at which efficient sieving can be accomplished with bis-MPA dendrons. This work illustrates the importance of macromolecular architecture and size in the shielding of proteins.

Schematic representation of dendronized chymotrypsin with G7 dendrons. Spheres represent dendrons (to scale), lysines are colored blue, and the enzyme active site is colored red.
As protein-polymer bioconjugates become viewed as increasingly promising avenues for industrial processes and therapeutics, the ability for these bioconjugates to withstand harsh conditions or exhibit increased stability becomes ever more important. Among these applications there exists a common desire to improve the stability of protein-polymer bioconjugates to unfolding by exposure to chemicals or thermal stress. In order to robustly characterize the performance of these bioconjugates, biophysical assays enabling high throughput analysis will aid rapid advancements. Two techniques, differential scanning fluorimetry and intrinsic tryptophan fluorescence, meet these requirements for rapidly obtaining thermodynamic parameters of unfolding that allow for direct comparison of protein-polymer bioconjugates, including the effects of variations in attachment site, polymer identity, and polymer length. These two experiments, which are easily amenable to parallelization, are presented as high-throughput replacements for more traditionally employed circular dichroism experiments and as complements to functional chemical stability or functional thermal stability experiments. Discussion of these assays will include advantages and disadvantages and approaches to data analysis.
POLY 624: PEG-based increases to protein conformational and proteolytic stability

Joshua L. Price, jlprice@chem.byu.edu. Chemistry and Biochemistry, Brigham Young University, Provo, Utah, United States

PEGylation is a widely-used strategy for enhancing the pharmacokinetic properties of protein drugs. The development of chemoselective side-chain modification reactions has enabled researchers to PEGylate proteins with high selectivity at specific locations. However, aside from avoiding active sites and binding interfaces, there are few guidelines for the selection of optimal PEGylation sites. Because conformational stability is intimately related to the ability of a protein to avoid proteolysis, aggregation, and immune responses, it is possible that PEGylating a protein at sites where PEG enhances conformational stability will result in PEG-protein conjugates with enhanced pharmacokinetic properties. This talk will describe our recent efforts to understand and exploit the impact of PEGylation on protein conformational stability and to develop structure-based guidelines for selecting stabilizing PEGylation sites.
Inspired by natural materials, we have designed a series of polymer-peptide polyurethane/ureas to explore the hierarchical arrangement critical to energy absorption and mechanical enhancement. We have developed chain-extended and non-chain extended peptide-polyurea hybrids with tunable secondary structure, modulating extensibility, toughness, and stiffness. The sheet-dominant hybrid materials were typically tougher and more elastic due to intermolecular H-bonding, while the helical-prevalent systems generally exhibited higher modulus. We have also explored the impact of a molecular design strategy that overlays a covalent and physically crosslinked architecture in these hybrids, demonstrating that physical constraints in the network hybrids influences hydrogen bonding and morphology. More recently, tailored physical associations within the soft and hard phases were engineered as a function of peptide content, leading to a rheological response dictated by block ordering and highlighting their potential as structural and injectable hydrogels. New thrust areas in shape memory materials and electrospun scaffolds have also been demonstrated.
Our research is fundamentally driven by the desire to understand how nanostructure impacts the dynamics and macroscopic properties of polymers. One of the materials we focus on is a class of single-component, nanostructured polymeric materials comprised of polymers grafted to nanoparticles. Specifically, we have focused on gold nanoparticles (Au NPs) grafted with polystyrene or poly(ethylene oxide) (PEO), which are of interest for membrane separation. PEO, in particular, is interesting for water and gas separations due to being hydrophilic and selective to CO₂ over other gases. We have developed ligand exchange and self-assembly approaches that result in well-ordered nanoparticle monolayers. These approaches enable detailed investigation of the structure and properties of Au NP monolayers. We found that the spacing between NPs is dictated by the molecular weight of the ligands attached to the particle surfaces and the quality of solvent used during the self-assembly process. Monolayer properties such as electrical conductivity and optical absorption have a strong (exponential) dependence on this spacing. Small molecule flux and mechanical strength are expected to also depend on ligand and grafting properties in monolayers and in multilayers.
Recent research efforts have demonstrated excellent potential of metal-organic framework (MOF)/polymer nanocomposite membranes for water purification. Fundamental studies on the specific roles of MOFs inside polymeric matrix are of great importance for the rational design of high-performance nanocomposite membranes. Still, much remains unclear about the exact influence of MOFs on the water and ion transport properties through MOF/polymer membranes. This is because it has been extremely difficult to characterize the ultrathin and heterogeneous polyamide membranes, the most popular water purification material, complicating reasonable analyses throughout the previous studies on MOF/polymer water purification membranes. Herein, we used crosslinked poly(ethylene glycol) diacrylate (XLPEGDA) as a base polymeric matrix to better understand the water and ion transport properties through MOF/polymer membranes. In contrast to the conventionally used polyamide matrix, XLPEGDA enabled us to precisely characterize the influences of incorporated MOFs on the polymer properties and water/ion transport behavior. Microimaging techniques were also firstly introduced to provide a microscopic view of the permeated water and ion distributions inside the MOF/XLPEGDA membranes. Our results reveal that MOFs could actually act as a highly water-permselective channel with judicious selection of polymeric matrix, emphasizing the importance of not only the interfacial gap between MOF/polymer but optimizing the microstructure of MOFs.
Polyamide thin film membranes are used in water desalination applications. Incorporation of graphene oxide nanoplatelets in the polyamide layer can alter the surface characteristics, enhance the mechanical properties, and can improve the permeability and selectivity of the membranes. Here, we present a modular fabrication method to incorporate nanomaterials in polyamide thin films. In this study, a layer-by-layer (LbL) synthesis technique has been used for embedding graphene oxide nanoplatelets (GONPs) in the polyamide thin films. We have synthesized alternating layers of GONPs and polyamide, and GONPs on top of the polyamide layer. The presence of GONPs in the synthesized membranes has been confirmed by SEM and TEM. Incorporation of GONPs resulted in an increase of surface hydrophilicity, as captured by the change of water contact angle. Water flux and salt rejection properties of synthesized membranes have been investigated by using a dead-end cell. The GONP embedded membranes have been found to enhance the salt rejection while keeping water flux similar compared to the pristine membranes also fabricated through the LbL synthesis technique. Upon exposure to chlorine, GONPs embedded membranes retained salt rejection performance better than the pristine membranes.
POLY 629: High flux nanocellulose-embedded mixed matrix membranes

Jackie Zheng¹, jackie.zheng@stonybrook.edu, Nancy Li¹, Pejman Hadi Myavagh¹,², Benjamin S. Hsiao³. (1) Chemistry, Stony Brook University, New York, New York, United States (2) Center for Clean Water Technology, Stony Brook University, Stony Brook, New York, United States (3) Stony Brook University, Stony Brook, New York, United States

Water is an essential resource for both individual consumption and industrial uses in the rapidly developing world. Water pollution is detrimental to the environment and can cause dramatic health issues. Because of this increasing need for uncontaminated water, many researchers investigate water reuse options. Membrane technology is an inseparable part of contaminated water treatment and has received great attention. Despite the advantages of membranes, the high energy demand of the separation process remains a challenge. Many studies have been carried out to enhance the water permeability of the membranes without sacrificing the retention of the contaminants. For example, different types of nanomaterials, such as carbon nanotubes (CNT) and graphene oxide (GO), were incorporated in the polymer matrix to increase their flux. However, the applicability of such matrices were limited due to the incompatibility of the nanomaterials and polymer matrix and high cost of these nanomaterials. On the other hand, cellulose nanofibers (CNFs) are highly hydrophilic, sustainable, and readily available, with high aspect ratio.

This study involves the fabrication of CNF-embedded nanocomposite membranes using cellulose acetate as the polymer matrix and the CNF as the filler to create nanochannels for preferential water flow. We found that incorporation of CNF into the membrane matrix enhances both its pure water flux and antifouling properties. It was also observed that as the CNF concentration in the membrane matrix increased the zeta potential value decreased and the membrane surface became more negatively-charged. The more negatively-charged surface exerts more electrostatic repulsion between the membrane surface and the contaminants in wastewater and decreases the fouling tendency of the membrane. In addition, data collected shows higher CNF concentration facilitates higher water permeability. To understand the mechanism behind the enhancement in the performance of the membranes, we have characterized the pristine and nanocomposite membranes by several techniques, such as molecular weight cut-off, SEM, FTIR, and contact angle.
Polymer membranes utilize the difference in permeability between molecules and ions to achieve molecular separation. For both gas separation and desalination processes, the transport of permeates through polymeric barrier layer films occurs through a solution diffusion process. Typically, the transport is modelled as one-dimensional, i.e. along the thickness direction of the barrier layer. However, recent evidences suggest that these films are often heterogeneous in terms of structure and composition. The effect of spatial heterogeneity, both in terms of length scale and spatial arrangement, on the transport behavior (especially permeability) remains unclear. Besides homogenous membranes, recent developments in mixed matrix membranes aim to use more permeable additives (e.g. metal organic framework or MOF particles) to enhance the permselectivity of the matrix membranes. In this work, we explore a new type of polymeric membrane with tunable, well-defined, spatially heterogeneous permeability. This is achieved by photopatterning over a two-stage thiol-ene system, which leads to spatially varying rubbery and glassy networks with identical chemistry but different permeability. In this talk, I will discuss the materials formulation; photopatterning with regards to both resolution and spatial arrangements; mechanical, and transport properties of these films. Besides their potential applications in molecular/ion separation, the films are promising in areas of encapsulating nanodevices that require spatially varying permeability.
POLY 631: Molecular structure of aromatic reverse osmosis polyamide barrier layers prepared at the oil/water interface

Qinyi Fu, qinyi.fu@stonybrook.edu, Nisha Verma, Hongyang Ma, Francisco J. Medellin-Rodriguez, Ruipeng Li, Masafumi Fukuto, Benjamin S. Hsiao, Benjamin Ocko. (1) Department of Chemistry, Stony Brook University, Stony Brook, New York, United States (2) Beijing University of Chemical Technology, Beijing, China (3) Universidad Autónoma de San Luis Potosí, San Luis Potosí, SLP, Mexico (4) NSLS II, Brookhaven National Laboratory, Upton, New York, United States

Reverse osmosis has become the leading method of converting seawater into potable water due to its lower energy costs compared to other methods. Despite the technical importance of the barrier layer, an understanding of the relationship between molecular level structure and function has yet to emerge. To determine the molecular level structure of the barrier layer, we have carried out Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) studies on well-defined thin polyamide (PA) layers. These were prepared at the oil/water interface using solutions containing m-phenylenediamine (MPD) and trimesoyl chloride (TMC). The GIWAXS patterns exhibit diffuse scattering features (see left figure) characteristic of an amorphous structure with several characteristic length scales. Further, the anisotropy shows the existence of preferential surface induced alignment. Specifically, the q-dependent scattering profiles depend on the azimuthal angle "chi" (see right figure). Detailed fitting analysis to the scattering profiles shows that they are well-described by the sum of several Lorentzian profiles along with a sloping background term. The characteristic lengths scales, determined from the peak positions of the Lorentzian profiles, correspond to about ~3.8 and ~5 Å molecular spacings. The former is associated with the "pi-pi" packing configuration (parallel packing of aromatic rings) whereas the latter is associated with the “T-shaped” packing configuration (perpendicular stacking of aromatic rings). We show that citric acid post-treatment promotes the T-shaped packing configuration.

(A) GIWAXS scattering patterns, after the Ewald correction, in reciprocal space from the MPD-TMC PA film after citric acid post-treatment. (B) Scattering profiles at 8 different chi angles (see A).
Fresh water is integral to health, food security and economic prosperity. An increasing reliance of communities on water desalination means that we need to better understand water transport and contaminant rejection in these systems.

Commercial desalination membranes exhibit relatively rough surfaces on their active polyamide layer. Recently, a novel preparation via molecular-layer-by-layer spin coating of alternating monomer solutions has been presented by Christopher Stafford, that allows manufacturing thin polymer layers on very flat substrates. We prepare ultrathin (<5 nm thickness) layers of cross-linked aromatic polyamide on wafers topped either with a native oxide layer of with Au or Pt coatings. We present high-resolution X-ray photoelectron spectroscopy of these layers, showing that their functional groups resemble those on commercial desalination membranes. The presence of these groups indicates the suitability of these films as model systems for desalination applications. We can provide qualitative assignments of the different chemical species and quantitative analysis of relative signal intensities. We quantify beam damage that occurs when investigating ultrathin polymer films with synchrotron-based X-ray light.

Using ambient-pressure XPS, we probe the solid/liquid interface in situ with high chemical resolution. We present the interaction of water with the functional groups at the interface and in the film. Ambient pressure XPS can make the protonation of the amide groups directly visible. This study forms the basis of further investigations of the film structure, the diffusion of water, and the exclusion mechanism for water contaminants.
Reverse osmosis (RO) membranes have been a key material for the membrane-based separation process including seawater desalination and water treatment. Many attempts have been made to improve the permselectivity of RO membranes, which thus increase the energy and cost efficiencies of the desalination and water treatment processes. Among many proposed strategies, the post-treatment on the membrane with an organic solvent, so-called solvent activation, has been regarded as one of the effective methods to enhance RO membrane performance. However, solvent activation with the previously used organic solvents resulted in a typical flux-rejection trade-off limitation (enhanced water flux along with decreased salt rejection). Furthermore, there have not been proposed clear mechanisms and reliable criteria of the solvent activation effects. In this study, we demonstrate that a new class of an organic solvent, benzyl alcohol, can effectively activate the RO membrane, which significantly enhance water flux without deteriorating salt rejection, thereby overcoming the critical performance trade-off constraint. The underlying activation mechanism was elucidated by comprehensively characterizing the physicochemical structures, properties and separation performance of the membranes activated with various organic solvents. Importantly, based on the results, we proposed a reliable indicator of the solvent activation effect.
Polyelectrolyte multilayers (PEMUs) are ultrathin films composed of alternating cationic and anionic polyelectrolytes generated through the alternating layer by layer deposition of polycations and polyanions. Research in this area has experienced an increase in popularity because of their potential for biological and technological applications due to the control of surface charge. These biological applications, such as water filtration and cell grafting, involve fully hydrated PEMUs. Studies have manipulated the properties of these materials by changing the buildup conditions, thickness, hydrophobicity, and roughness and many of these properties, such as plasticity and non-fouling character, depend on the water content of the system and the ionic strength of the surrounding media (and thus the system). The focus of this study is to quantify the level of hydration experienced by extrinsic sites in PEMUs composed of cation poly(diallyldimethylammonium) (PDADMA) and anion poly(styrene sulfonate) primarily using attenuated total reflectance infrared spectroscopy. The water content was monitored in relation to the amount of extrinsic polyelectrolyte monomer units, and compared to the water content for intrinsic (1:1 ratio of anionic to cationic polyelectrolyte) sites. PSS and PDADMA together form PEMUs whose physical properties can be manipulated with salt concentration and the strength of the salt. As these salts diffuse through the multilayer, they bring in a specific amount of water with them. The salt concentration and strength determine how much water is being brought into the system. By conducting this experiment through the range of the Hofmeister series, the equilibrium level of hydration can be determined for each salt type.

Depiction of how extrinsic sites are estimated to have a higher water content than intrinsic sites in PEMUs.
Carbon nanomaterials, including carbon nanotubes and graphene have emerged as an attractive candidate for various applications due to its unique structure and properties. Like other materials, however, carbon nanomaterial that possesses desirable bulk properties rarely features the surface characteristics required for certain specific applications. Therefore, surface functionalization is essential, and researchers have devised various covalent and non-covalent chemistries for making graphitic materials with the bulk and surface properties needed for various specific applications. Judicious application of these site-selective reactions to carbon nanomaterials has opened up a large variety of multifunctional applications, including energy conversion and storage devices, flexible optoelectronics, chemical/bio-sensors, dry adhesives, to name a few. In this talk, I will provide some rational concepts for the controlled functionalization of carbon nanomaterials for the multifunctional applications with an emphasis on biomimetic systems, along with an overview on recent progresses in this emerging research area.
POLY 636: Micro-nanofibrillar polycaprolactone scaffolds as translatable osteoconductive grafts: An exploration of osteoblast viability, osteogenic phenotype, and innate antibacterial efficacy

James W. Moxley¹, moxley.j@husky.neu.edu, Paria Ghannadian², Thomas Webster¹. (1) Chemical Engineering Department, Northeastern University, Cambridge, Massachusetts, United States (2) Chemical Engineering, Northeastern University, Cambridge, Massachusetts, United States

The treatment of musculoskeletal defects is currently limited by the tissue-regenerative materials available to orthopedic surgeons: autologous bone grafts have a finite amount of harvestable material within a given patient, while allografts are prone to severe immunological complications and host rejection. In order to effectively circumvent these limitations, there are ongoing efforts to engineer polymeric matrices as functional, biomimetic alternatives. Although a diverse range of composite-scaffolds have been explored, complexities in their design have often resulted in complications for industrial scale-up and clinical translation. This motivated research into the development of unmodified, poly(ε-caprolactone) (PCL) scaffolds as synthetic, biomimetic biomaterials for orthopedic tissue-regeneration. PCL scaffolds were produced through three different fabrication techniques: electrospinning (ES), rotary-jet spinning (RJS), and airbrush (AB). ES and RJS were observed to produce microfibrillar scaffolds, while all AB products were nanofibrous. Upon seeding within the scaffolds, osteoblast viability and phenotype were assessed through a combination of adherence, metabolic activity, proliferation, gene expression, alkaline phosphatase bioactivity, and calcium deposition assays. Although the polymeric scaffolds induced slight reductions in initial osteoblast adhesion and metabolic activity, in comparison to tissue-culture treated controls, seeded cells proliferated and demonstrated the osteogenic phenotype. AB products demonstrated reduced bacterial surface colonization when inoculated with Gram-positive (Staphylococcus aureus) and Gram-negative (Pseudomonas aeruginosa) bacterial strains, in comparison to ES and RJS products, without the inclusion of any small-molecule antibiotics, antimicrobial peptides, or reactive nanomaterials during synthesis.
POLY 637: Laser pulse heating of nanocomposites to create self-cleaning superhydrophobic surfaces

Stephen F. Bartolucci, stephen.f.bartolucci.civ@mail.mil, Joshua A. Maurer. US Army - RDECOM - ARDEC, Watervliet, New York, United States

Superhydrophobic surfaces resulting from micro- and nanostructured hierarchical structures are ubiquitous in biological systems and are known to induce anti-wetting and self-cleaning properties. However, traditional formation of these structures is difficult and requires high-resolution micro- and nanofabrication methods. Here, we demonstrate a facile method for the formation of superhydrophobic self-cleaning surfaces by laser pulse heating of a carbon nanotube-polymer composite. Laser treatment exposes a carbon nanotube network which controls surface wetting properties. Advancing and receding contact angle measurements demonstrate that these surfaces are superhydrophobic. Additionally, surfaces show anti-wetting and self-cleaning properties. The use of simple pulsed laser heating to produce nanotube networks provides a cost-effective method for generation of superhydrophobic materials. The development of low-cost scalable technology for self-cleaning surfaces, such as described here, is critical to next generation materials in wide range of industries from energy and defense to the biomedicine and electronics.
Polyphenol coatings have been demonstrated for functionalizing a range of proteins including IgG and various enzymes on diverse materials. Higher activities than conventional techniques were obtained.
POLY 639: Mussel-inspired polyesters with aliphatic pendant groups demonstrate the importance of hydrophobicity in wet adhesion

Amal Narayanan¹, Sukhmanjot Kaur¹, Ali N. Dhinojwala², Abraham Joy¹, abraham@uakron.edu. (1) Dept of Polymer Science, University of Akron, Akron, Ohio, United States (2) Univ of Akron, Akron, Ohio, United States

Mussel adhesion has fascinated scientists for their ability to adhere to underwater substrates. They do this by the secretion of adhesive proteins underwater in a temporal fashion. The mixture of proteins secreted by mussels are tuned to provide both adhesive and cohesive interactions with the substrate. Synthetic adhesives in comparison are for the most part are compromised in an aqueous environment due to their inability to prevent water penetration into the adhesive interface. We will present our work on the design and evaluation of synthetic polyesters that demonstrate strong underwater adhesion. The polyester is designed to flow at room temperature that enables application without any solvent. Catechol units of the polymer provide adhesive contacts with the substrate. The applied polymer is subsequently cured to a crosslinked polymer providing cohesive interactions. Lapshear measurements show strong adhesion even when the polymer is applied underwater and cured. Our current results indicate that the hydroxyl groups of catechol play a role in adhesion and that a hydrophobic environment is necessary for synthetic adhesives to show good performance in wet environments. We will also describe fundamental studies regarding the nature of the adhesive interface as revealed by sum frequency generation spectroscopy and JKR measurements.
POLY 640: Synthesis of bioinspired polymeric adhesives for precise control of properties via well-defined crosslinking chemistry

Hoyong Chung, hchung@fsu.edu, Irawan Pramudya, Cheoljae Kim. Florida State University, Tallahassee, Florida, United States

Bioinspired chemistry is an important new area of study to expand the functionality of modern synthetic materials. In particular, synthetic polymers are applicable to various science fields using bioinspired chemistries. This talk will discuss a new class of polymers using a bioinspired adhesive concept that uses strong adhesion functionality referred to as catechol groups in 3,4-dihydroxy-L-phenylalanine (DOPA) that is found in many marine organisms’ adhesive proteins, such as those in mussels and polychaete. The new bioinspired adhesive is a glucose-based bioadhesive, poly(2-methacrylamido glucopyranose-co-N-methacryloyl-3,4-dihydroxy-l-phenylalanine-co-8-azidooctyl methacrylate) [poly(MG-co-MDOPA-co-AOM)], that has been synthesized by thermally-initiated free radical polymerization. The new bioadhesive is composed of three modules: a hydrophilic glycopolymer segment, a mussels-inspired catechol segment, and a crosslinking azide segment. Poly(ethylene glycol) (PEG)-based crosslinker, (1R,8S,9s)-Bicyclo[6.1.0]non-4-yn-9-ylmethyl PEG (BCN-PEG) was synthesized separately. Bulk adhesion properties of the terpolymer were enhanced by covalent bond forming crosslinking via strain-promoted azide-alkyne cycloaddition (SPAAC). The control of adhesion was studied under various crosslinker concentrations, crosslinking durations, and crosslinker lengths. Even without crosslinking, the new terpolymer adhesive demonstrated 20-fold higher adhesion strength (115 kPa) compared to a commercial rubber cement (5.8 kPa). The most significant factor to control for adhesion was crosslinker length. Crosslinking with the long crosslinker (PEG repeating units: 134) did not enhance adhesion strength. However, the short crosslinker (repeating units: 43) showed significant improvement in work of adhesion (150% higher than uncrosslinked).
POLY 641: Fully degradable polycarbonate/polypeptide hybrid copolymer bioadhesives for soft tissue repair

James Wilson, jameswilson@rcsi.com, Andreas Heise. Department of Chemistry, Royal College of Surgeons in Ireland, Dublin, Dublin, Ireland

The need for degradable bioadhesives for soft tissue engineering has become an increasing socio-economic problem as a consequence of current techniques often causing iatrogenic tissue damage through cytotoxicity and/or requiring costly secondary surgical removal. In order to combat this issue, a hybrid copolymer network of completely degradable composition has been developed combining polycarbonates and polypeptides. The ring-opening polymerisation (ROP) of cyclic carbonates to produce a mechanically robust, yet flexible crosslinkable network was initially synthesised. Inspired by the ability of molluscs to adhere to wet surfaces, the material underwent one-pot end-group conversion and ROP of catechol-functionalised N-carboxyanhydrides (NCAs) in order to be able to adhere in the wet environment of living tissue. The effect of different molecular masses and degrees of crosslinking for the polycarbonate block was investigated in order to optimise the strength and flexibility of the overall material. Furthermore, the cytotoxicity of the hybrid material was also evaluated to determine cell viability and the degradation of the hybrid material was monitored under accelerated conditions. Through this method, a fully degradable bioadhesive has been realised for surgical implantation, which mimics the properties of the adhered tissue.
Mimicking the adhesive capabilities of nature’s marine organisms offers interesting possibilities. For example, mussels strongly adhere to a variety of surfaces by secreting byssal threads that contain mussel foot proteins (Mfps). Recombinant production of Mfps presents an attractive route for preparing advanced adhesive materials. Out of all known types of Mfps, Mfp5 is of particular interest because it is spatially localized on the distal end of the mussel’s byssal thread plaque, implying its crucial role in surface adhesion, and has the highest density of 3,4-dihydroxyphenylalanine (DOPA) and lysine residues, which enable strong underwater adhesion. In this study, we used synthetic biology strategies to synthesize Mfp5, along with Mfp5 oligomers that contain two or three consecutive, covalently-linked Mfp5 sequences named Mfp5(2) and Mfp5(3). We studied the effect of chain length on Mfp underwater adhesion using both colloidal probe atomic force microscopy and quartz crystal microbalance. Our results demonstrated a clear positive correlation between Mfp5 molecular weight with protein underwater adhesive properties, including the force of adhesion, work of adhesion, protein layer thickness, and recovery distance. With sufficient curing time, the DOPA-modified Mfp5(3) displayed a force of adhesion and work of adhesion higher than those of previously reported Mfp-mimetic adhesive materials. The synthesis approach utilized in this study highlights the power of synthetic biology in preparing protein-based materials that are difficult to synthesize by other approaches. The results can be used as generalizable design principles for future engineering of protein-based underwater adhesives.
POLY 643: Understanding the bioadhesion of chitosan-catechol polymers

Ameya Narkar, Ameya.Narkar@ucf.edu, Kollbe Ahn. Chemistry, University of Central Florida, Orlando, Florida, United States

Over the past decade, different methods have been adopted for conjugating catechol with chitosan backbone and the resulting chitosan-catechol has been well characterized. Additionally, the crosslinking mechanisms of chitosan-catechol polymers have been explored in detail. However, the exact interfacial binding strategy of such crosslinked polymers with various tissue substrates is still not clear. For example, consider the bioadhesion of chitosan-catechol adhesive synthesized using the EDC/NHS carbodiimide chemistry to mucin-rich tissue surfaces. First, mucin is rich in the amino acid, cysteine, which contains carboxyl (-COOH) and amine (-NH₂) sites as well as and thiolate groups (-SH). The chitosan itself has primary amine groups that can interact with the negatively charged carboxylic acid presented by mucin. However, in addition to such electrostatic interactions, chitosan and mucin both contain primary amine groups, and H-bonding between them at physiological pH could also contribute to adhesion and needs to be accounted for while predicting adhesion mechanisms. Second, physiological conditions cause the oxidation of catechol to quinone, which is expected to form irreversible covalent bonds with the amine moieties on the tissue surface through either Michael-type addition or Schiff’s base formation, or interact with thiol groups via Michael addition. However, several reports in literature have depicted varying interaction strategies (i.e., some suggesting only Michael-type addition) and there isn’t a consensus on the adhesion strategy. Finally, even though reports have suggested that chemical crosslinking occurs within the chitosan-catechol polymers, the mechanical properties of such polymers and their eventual effect on interfacial binding remain to be systematically investigated. We plan to conduct a study to fill in these gaps in the understanding of the bulk as well as interfacial binding characteristics of chitosan-catechol polymers.

Accounting for bulk and surface interactions of chitosan-catechol adhesives to tissues
Heavy metal contaminants have profound consequences on both health and the environment. Therefore, effective approaches to mitigating the effects of these toxicants are paramount. Heavy metal contamination from mining operations, energy, and industrial sources may be mitigated with appropriate chelating polymers, both for environmental remediation, and in chelation therapy for metal poisoning. Polymers have several advantages as sequestration materials, including relatively low cost and high affinity for target compounds. As a result, we are investigating a number of polymer-based metal-chelation materials.

We will report on the most recent progress in the design, synthesis, and application of polymers for the selective chelation of various heavy metal ions. The effect of metal chelation on polymer architecture will be discussed. In addition, we have examined the thermodynamics of binding using isothermal titration calorimetry (ITC) in order to gain insight into the specific structure-metal binding relationships of these materials. ITC enables the direct measurement of the binding affinity (Kₐ), enthalpy changes (ΔH), and stoichiometry of the interactions between macromolecules and metal ions in solution. By elucidating the thermodynamic profile of each chelating material, we have gained insight into the polymer’s properties as a metal chelator.
Fluorinated acrylate monomer and inimer were synthesized and copolymerized with $N,N'$-dimethyl acrylamide to obtain linear and branched amphiphilic copolymers. These amphiphilic copolymers formed physical hydrogels with water due to the formation of physical crosslinks by hydrophobic association of the fluorocarbon segments. The density of the copolymers increased, while the $T_g$ and equilibrium water content decreased, with increasing fluorine content in the copolymers. SAXS characterization confirmed that the resulting hydrogels exhibited nanophase separation in dry and swollen forms. The nanodomains in the hydrogels are more phase separated in water-swollen form than in dry form. The viscoelasticity of both linear and branched copolymer hydrogels is subject to strain; at low strain, they exhibited solid-like behavior and at high strain they showed liquid-like behavior. The introduction of a methylene spacer between the fluorinated group and the acrylate backbone increased the relaxation time of the nanodomains at elevated temperature. The inter-domain spacing, $d$, was significantly smaller in the branched copolymer hydrogels. In addition, the branched structures were more stiff than the linear copolymer hydrogels at low fluorine content. However, the tensile properties of the linear and branched copolymer hydrogels were similar.
Charge-transfer complex is responsible for the yellowness in polyimide and polyetherimide (PEI). Herein, we investigated the effects of end group and molecular weight on the yellowness of telechelic PEI. Electron-withdrawing dianhydride end groups reduced the yellowness and increased the transparency of PEI regardless of the molecular weight. Electron-donating phenyl, amine, and phthalic end groups increased the yellowness of PEIs, but the effect depended on the molecular weight. As the molecular weight was increased, the yellowness of PEIs with electron-donating end groups initially decreased due to a decreasing end group density and then increased due to an increasing probability of charge-transfer complex formation. The systematic study reveals the correlations among yellowness, end group, and molecular weight of PEIs. The correlations can be used for designing highly transparent PEIs in applications of flexible displays, solar radiation protectors, and optical wave guides.
POLY 647: Nanoscale resolution of electric-field induced motion in ionic copolymer films

Brad S. Lokitz, lokitzbs@ornl.gov, Jason Dugger, James F. Browning. (1) Sandia National Laboratory, Albuquerque, New Mexico, United States (2) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Understanding the mechanisms of electromechanical response on the nanoscale would greatly benefit the development of electroresponsive polymers for energy storage, actuation, and biomedical applications. In order to better design electroresponsive polymeric systems, the characterization of a material’s response to an electric field in situ with subnanometer resolution is needed. Such a characterization provides a deeper understanding of how nanoscale interactions contribute to the electromechanical response. This talk will highlight the use of in situ neutron reflectometry measurements collected under applied electric fields and complementary coarse grained molecular dynamics simulations to provide nanoscale resolution of polymer and counter-anion motion in thin films. A polymerized ionic liquid based diblock copolymer (PIL-BCP) containing a cationic imidazolium block, a deuterated styrene block, and added ionic liquid, 1-Ethyl-3-methylimidazolium (EMim), was investigated. The relative contributions of each block and the added counter anion on changes to the film’s structure was observed and analyzed. These results emphasize the potential of in situ techniques that can achieve nanoscale resolution for investigating the electromechanical response of polymeric systems in thin film geometries. These findings have exciting applications in the development of energy storage systems as well as the fabrication of actuating devices, where counter ion size and its polarizability can be used to tune electromechanical properties.

Figure 1. Reflectivity data for PIL-BCP with Br (left) or BF4 (right) counter ions with added ionic liquid (EMimBr (Br-IL), EMimBF4 (BFE-IL), EMimBr-d11 (Br-dIL), or EMimBF4-d11 (BF4-dIL)).
We report the design and fabrication of a new class of poly(olefin)-acrylic (POA) latex particles. These hybrid materials are fabricated in two steps, starting from the mechanical dispersion of a bulk poly(olefin) into a particle dispersion, which is then used as a seed for the emulsion polymerization of an acrylic shell. Using this approach, POA particles with diameters from 200-700 nm and core:shell weight ratios up to 50:50 can be obtained. The poly(olefin) core is modular in terms of composition, molecular weight, crystallinity, and glass transition temperature, while control over the physicochemical properties of the shell is equally accessible. We use light scattering and asymmetric flow field-flow fractionation (A4F) to study particle size and grow-out, and SEM and AFM imaging to determine particle morphologies. A customized GPC method together with thermal stability experiments provide evidence for, and enable quantification of, poly(olefin)/acrylic grafting. Finally, we show that POA particles are effective impact modifiers in engineering plastics, enabling low temperature impact performance together with other salient material properties such as melt flow. The results of this investigation provide a framework for the design of POA particles for a wide range of applications.
Polymeric nanocapsules (NCs) are promising nanocarriers for various encapsulation and delivery applications. In this study, crosslinked polymeric NCs were prepared through layer-by-layer (LBL) alternating coating of oppositely charged polyelectrolytes using crystallized miniemulsion nanodroplets as the sacrificial templates (Figure 1). Such templates were obtained from the miniemulsions using acrylate-functionalized cationic surfactants, with n-docosane as the oil phase and water as the continuous phase. Surface of these crystallized nanodroplets was covalently stabilized in order to enhance their colloidal stability. Subsequently, poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), as representative anionic and cationic polyelectrolytes, were LBL coated on crystallized core nanodroplets to give nanostructures with polyelectrolyte shells. Well-defined crosslinked NCs were obtained by crosslinking of the PAA/PAH-based shells using amidation chemistry, followed by the removal of crystallized n-docosane cores through dialysis against tetrahydrofuran (THF). The NCs were characterized by a variety of instrumental analysis techniques. Chemical crosslinking was found to be critical for maintaining structural stability of NCs upon the change of environmental conditions. Encapsulation and release using these NCs as nanocarriers were also studied.
The present work is an effort towards the graft polymerization of acrylonitrile monomer on graphene oxide with aid of gamma radiation using Co-60 irradiator. Simultaneous radiation grafting methodology has been employed to study the effect of grafting on the base material using DMF solvent under inert conditions at room temperature. Effect of varying absorbed dose and monomer concentration were studied and grafting percentage was measured gravimetrically. The results suggested that the degree of graft polymerization increases with an increase in absorbed dose of gamma radiation up to a maximum of 20 Kgy. The grafted products were analyzed by FT-IR, Raman and XRD analysis. The presence of FTIR vibration at 2242 cm⁻¹ characteristic of nitrile group confirmed the grafting of acrylonitrile on graphene oxide base material.
POLY 651: Opportunities for electrochemistry in Reversible Addition-Fragmentation chain-Transfer (RAFT) polymerization systems

Francesca Lorandi, florandi@andrew.cmu.edu, Marco Fantin, Sivaprakash Shanmugam, Yi Wang, Krzysztof Matyjaszewski. (1) Chemistry Department, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Aramco Services Houston Research Center, Houston, Texas, United States

Electrochemical stimuli have been efficiently applied to trigger controlled radical polymerization techniques under mild, environmentally friendly conditions, and to temporally control the processes. Moreover, electrochemical tools allow for characterizing and monitoring polymerization systems. However, the use of electrochemistry in Reversible Addition-Fragmentation Chain-Transfer (RAFT) polymerization has been barely explored. Herein, the redox properties of several RAFT agents were measured by cyclic voltammetry (CV). Their electro-reduction is irreversible: short lived radical anions are formed and rapidly involved in side reactions. As a consequence, the direct electrolysis of RAFT agents in the presence of monomers led to uncontrolled polymerizations. CV showed the consumption of RAFT agents and the accumulation of other species (Fig. 1a). This issue was mitigated by switching from a direct to a mediated electrolysis approach. The characteristics for suitable mediators were identified. Hence, electrochemically mediated RAFT polymerizations of acrylate monomers were performed at room temperature, by reducing catalytic amounts of a selected mediator. CV was also used for in situ monitoring the fate of (macro)RAFT agents during conventional RAFT (Fig. 1b) and Photoinduced Electron Transfer (PET) RAFT polymerizations. Moreover, the irreversible direct electro-reduction of RAFT agents could be turned into advantage to modify the chain ends after polymerizations.

Figure 1. Comparison between CVs of di(1-phenylethyl)trithiocarbonate (DPET) RAFT agent, recorded before and after 8 h of (a) electrolysis, (b) conventional RAFT polymerization initiated by AIBN ([AIBN]/[DPET] = 0.1). Conditions: 50 vol% styrene in DMF + 0.1 M Et4NBF4, T = 80 °C, [styrene]/[DPET] = 200/1. For CVs: glassy carbon disk, scan rate = 0.2 V s⁻¹.
Polyolefins, i.e. mainly polyethylene (PE) and polypropylene (PP) are commercially the most important family of polymers with millions tons produced each year. Although they are interesting inert and non-polar materials, some adhesion on their surfaces or their blending with other polar matrixes are desired. Polyolefins functionalized with maleic anhydride (MA) as polar co-monomer is a commercially available product that exhibit enhanced adhesion to polar materials like polyamide, metals, and glass. They are also used as compatibilizing agents that lead to an improvement of impact properties upon blending with polyamide-6 as an example. These products are classically produced by the melt extrusion of the polyolefin and MA in presence of alkyl peroxides as radical initiators.

We recently developed acyloxyimides as new H-abstracting agent for the melt radical grafting of maleic anhydride (MA) onto polyethylene. The reaction was conducted in the temperature range 190 - 250 °C in a mini-extruder and the hydrogen abstraction ability of N-acyloxyphthalimide (NAP)-, N-acyloxynaphthalimide (NANP)- and N-acyloxysuccinimide (NAS)-based derivatives was demonstrated and compared to reference peroxides. Optimal experimental conditions were defined by varying the initial MA content and the degree of grafting of MA was determined by infra-red spectroscopy. The MA grafting degree was as high as 2.98 wt% when using tBu-NAP as H-abstracting agent at 230°C with only a slight modification of the PE chains structures as proved by rheological experiments while the use of a peroxide (L101) lead to a lower grafting degree (1.9 wt%) and a cross-linking of the polymer chains confirmed by the three – five fold higher complex viscosity.
Crude oil contains sulfur contaminants. During petroleum refinement, S-containing compounds are converted to elemental sulfur (S₈), generating millions of tons of waste. This waste can be repurposed and used as a feedstock to create new materials via inverse vulcanization. The use of molten sulfur and liquid monomers eliminates the need for solvents. Heating S₈ above 159 °C initiates ring-opening, forming radicals that react with difunctional monomers to create polysulfides. Synthetic ease and short reactions times have led to the rapid expansion of the field. However, the types of monomers that can be used are limited by the high temperature requirements. Here, poly(S-divinylbenzene) with varied sulfur contents has been synthesized to act as a prepolymer. Less energy is required to cleave the S-S bonds present in the polysulfides leading to the formation of radicals at much lower temperatures (90 °C). Dynamic sulfur bonds can re-initiate radical formation leading to solvent-free polymer modification. These mild temperatures have been used to initiate polymerization with a family of vinylic and allylic ethers. Modification of the polymer structure was examined by NMR spectroscopy. Materials were further characterized by gel permeation chromatography, and differential scanning calorimetry to examine the impact on the physical properties. The prepolymer sulfur content and poly(S-DVB):monomer ratio was varied to determine the impact on solubility. These new methods expand on inverse vulcanization to create a mild route to polysulfide synthesis.
Isosorbide is an inexpensive sugar derived from glucose that has shown great potential as a sustainable substitute in polymeric materials. However, polymerization methods that allow for complete tunability of isosorbide-based polymers are limited. Therefore, the objective of this work is to create a foundation for these materials via ring-opening polymerization (ROP). To this end, we provide mechanistic insights into the ROP of a trianhydrohexitol derived from isosorbide (1,4:2,5:3,6-trianhydro-D-mannitol, 5). An enzyme-catalyzed, regioselective synthetic approach was used to afford 5 with minimal purification. High-throughput screening was then employed to quickly evaluate ROP catalysts and conditions. Density functional theory calculations provided insights into the interplay of ring-strain enthalpy and free energy of activation for ring opening. Ultimately, ring-opening selectivity was achieved by initiating a Sc(OTf)3-catalyzed polymerization with an epoxide. Moreover, the resultant macromolecular architecture (i.e. generation of linear vs. cyclic polymers) can be tuned by careful selection of the polymerization conditions. Finally, unreacted monomer can be easily recycled.
The grafting-through polymerization of norbornene functionalized polymeric macromonomers via ring opening metathesis polymerization (ROMP) is a highly efficient method to produce brush polymers with controlled molecular weight and grafting density. Both ring opening polymerization of lactone monomers, atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT) of acrylic monomers are powerful methods to produce macromonomers of varied chemical composition. However, these syntheses exhibit several drawbacks including complex multi-step preparations, the use of hazardous reagents, and the requirement for rigorous purification. These challenges are demonstrated by the classic ATRP macromonomer synthetic sequence consisting of polymerization, chain end group modification, and subsequent installation of a ROMP-active chain end group, with purification and isolation necessary after each step. A modular method for accessing a wide variety of acrylic macromonomer chemical compositions in a single reaction is presented. Through the development of this scalable, inexpensive, and well-controlled method, the widespread investigation of new brush polymers with diverse properties can be achieved.
A novel multicyclic cage molecule
{heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{5,9}.0^{10,14}]tetradecane (HCTD)} with a 14-carbon core structure, and allylidene groups in the apical positions, has been synthesized and fully characterized. Heating HCTD from 160-240 °C resulted in facile cross-linking to generate a thermoset material that exhibits 5% weight loss at 485 °C, no observable T_g, and a char yield (in air) of 55% at 600 °C. Due to the intractable nature of the thermoset material, it was difficult to obtain information regarding the polymerization mechanism. To provide further insight, a model compound [7-allylenorbornane (AN)] was synthesized and thermally cured. AN readily polymerized under similar conditions to HCTD, but did not form any detectable dimer. This result suggested that the polymerization of HCTD did not proceed via Diels-Alder cycloaddition, but instead through a radical mechanism. The robust properties of the HCTD-derived thermoset material, coupled with the low temperature, volatile-free cure protocol, suggest that allylidene end-capped molecules represent a new class of thermosetting monomer, capable of achieving thermal properties similar to those of thermosetting polyimides.
Although Grubbs-type ruthenium initiators have been widely used in ring opening metathesis polymerization (ROMP) for complex polymers synthesis, they are greatly limited to the nonfunctional derivatives that are currently commercially available. This work presents a new strategy to directly react and modify these ruthenium initiators through the use of functional enyne molecules. In these systems, a terminal alkyne serves as a directing group that rapidly reacts with the ruthenium carbenoid and promotes ring-closing metathesis onto a neighboring olefin. Using this relay strategy, functional enyne molecules can rapidly and efficiently convert the commercially available Grubbs 3rd catalyst (G3) into a variety of functional initiators in situ at ambient temperature. Through the combination with existing termination methods, this technique enables full control over the functionality at either end of the polymer chain, thereby increasing the versatility of classical ROMP materials.
The Domino reaction, also known as cascade reaction, is a chemical process in which one chemical reaction sets off a chain of other reactions in a thermodynamically downhill process. Domino reactions have been widely used in the synthetic organic chemistry to rapidly increase the structural complexity of the resultant product in high atom economy. While holding a great potential, Domino reactions were not applied to the synthesis of macromolecules. In this lecture, I will discuss our efforts of using the Domino reactions to prepare synthetic polymers with complex main-chain structures and sequences. First, a novel chain-growth, radical cascade-triggered ring-opening polymerization (RCT-ROP) approach for the rapid and controlled polymerization of macrocyclic monomers will be presented. A systematic study correlating various designs of the ring-opening trigger and polymerization control were designed to allow optimized reaction kinetics and polymerization control. The optimized conditions were then employed to prepare multi-block copolymers with predefined block sequences and main-chain degradable functionalities. The discussion will be further extended to using the Domino reaction to control the sequence of synthetic polymers. Monomeric building blocks with defined sequences were polymerized in a chain-growth, controlled polymerization through multiple cascade reactions, while still maintaining good control over polymerization and intact chain-end groups. In summary, the application of the Domino reactions to the polymer science provides new strategies for controlling the synthetic polymer structures and sequences that are inaccessible by previous techniques, laying the foundation for the generation of a series of novel bioactive polymers for the mimicry and study of complex biological systems.
The self-assembly of two-component (A/B) block polymers into classical phases (lamellae, gyroid, hexagonally-packed cylinders, and body-centered cubic spheres) has been extensively studied from both fundamental and applied perspectives. Recently, a class of complex structures known as “Frank–Kasper” phases — previously observed in metals, surfactants, and dendrimers — has also been discovered in linear block polymers. This presentation will probe the effect of polymer architecture on Frank–Kasper phase selection using a complement of new materials design, contemporary synthetic methods, and self-consistent field theory. Block polymer architecture plays a key role in promoting the symmetry breaking that is characteristic of Frank–Kasper phase formation. Our insights connecting molecular and mesoscopic structure lay the groundwork for expanding the utility of block polymers through an improved understanding of unique self-assembly behavior.
Natural rubber (NR) has found numerous applications in various branches of industry but, due to its high unsaturation, it is susceptible to oxidation, shows unsatisfactory resistance to solvents. Chemical modification of NR is essential to overcome some of the above-mentioned deficiencies, and the introduction of fluorine-containing functionalities, despite the potential applications of the obtained materials, has been studied only sparsely. Direct fluorination can be an effective method for the preparation of modified NR with improved physical and chemical characteristics but current fluorination methods require the use of highly toxic fluorinating agents and harsh reaction conditions, and are prone to lead to undesirable side reactions such as crosslinking or polymer degradation. We present an efficient and mild fluorination strategy to modify polyisoprene using hypervalent iodine(III) reagents (e.g., Togni’s reagent) that serve as sources of CF$_3$ groups, and which can react with both activated and inactivated alkenes. The obtained trifluoromethyl-modified polyisoprene can undergo further chemical modifications, which yield fluorinated derivatives, with additional pendant alkyl fluoride or hydroxy groups. All reactions were carried out under mild conditions and the products were characterized by $^1$H, $^{13}$C, and $^{19}$F NMR, as well as IR spectroscopy, GPC, DSC, and TGA. The successful synthesis of fluorine-containing derivatives of polyisoprene opens new avenues to previously inaccessible or difficult to prepare materials.
POLY 661: Determination of the chemical heterogeneity of ternary copolymers

Derek Lohmann¹, dlohmann@pss-polymer.com, Thorsten Hofe², Wolfgang Radke². (1)
PSS USA-Inc, Amherst, Massachusetts, United States (2) PSS GmbH, Mainz, Germany

Due to differences in reactivity, copolymers of a given average composition generally exhibit a chemical composition distribution (CCD). In a polymer sample, the individual copolymer molecules therefore differ in their composition. The extent of chemical heterogeneity depends on monomer reactivity, as well as process parameters. Since the CCD may affect application properties of polymers, its characterization is an integral part in QC as well as in R & D.

Usually the average composition is determined by spectroscopic techniques. These techniques do not yield information on the CCD. To obtain that information, chromatographic separation has to be employed. Gradient chromatography has been shown to be able to separate binary copolymers with respect to composition, allowing gaining quantitative information on CCD.

In the past the vast majority of published investigations were related to the chemical heterogeneity of binary copolymers. However, modern copolymers often comprise of more than two monomers, making determination of CCD even more complicated. This is due to the fact that gradient separations are based on a generic adsorption strength, to which the various monomer units contribute differently.

Thus, even at the same molar mass (or more precisely on the same degree of polymerization), identical gradient retention times can be observed for molecules differing in their copolymer compositions. A molecule of composition AₙBₙCₚ might exhibit the same gradient retention time as a molecule having a composition AₙBₖCᵢ.

Additionally, gradient elution can be coupled to Size Exclusion Chromatography (SEC) for simultaneous determination of the CCD and the molar mass distribution (MMD). The present contribution will show that application of two gradient separations, differing in selectivity with respect to the comonomers may help getting more information on the chemical composition distribution of ternary copolymers. This is true even if the separations are not orthogonal.
Organocatalyzed ATRP (O-ATRP) has been developed using strongly reducing organic photoredox catalysts. For example, N-aryl phenoxazines possess valuable photoredox properties for mediating controlled radical polymerizations using visible light. Most examples of O-ATRP have focused on the synthesis of linear polymers. However, to expand the polymer architectures known to be produced by the phenoxazine catalyst family, this presentation will discuss the synthesis of bottlebrush polymers via a grafting-from approach using O-ATRP.
Solution-processable poly(ether imide)s (PEIs) with ureidopyrimidinone (UPy) end groups were prepared by incorporating monoisocyanato-6-methylisocytosine into amine-terminated PEI oligomers. After functionalization with UPy end groups, PEI with a molecular weight as low as 8 kDa (8k-PEI-UPy) can be solution-cast to form films. Tensile tests revealed that 8k-PEI-UPy had an outstanding Young's modulus higher than those of state-of-the-art high-molecular-weight commercial PEIs. The tensile strength, maximum elongation, and Young's modulus of 8k-PEI-UPy were 87.2 ± 10.8 MPa, 3.10 ± 0.39%, and (3.20 ± 0.14) × 10³ MPa, respectively. The discovery herein significantly advances the chemistry of high-temperature PEI resins. UPy-based supramolecular chemistry is an effective and general strategy to achieve outstanding mechanical properties for PEI oligomers.
POLY 664: Effect of quench depth on crystallization in semicrystalline block copolymer/salt mixture studied by depolarized light scattering

Xiuhong Li¹, whitney S. Loo², Xi Jiang³, Xin Wang¹, Michael D. Galluzzo²,³, Katrina Mongcopa², kim.mongcopa@gmail.com, Andrew Wang², wang.andrew@berkeley.edu, Nitash P. Balsara²,³,⁴, Bruce A. Garetz¹. (1) Chemical and Biomolecular Engineering, NYU Tandon School of Engineering, Brooklyn, New York, United States (2) Department of Chemical and Biomolecular Engineering, University of California-Berkeley, Berkeley, California, United States (3) Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, California, United States (4) Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California, United States

Block copolymer/salt mixtures are promising materials for solid-state lithium battery electrolytes. Ion transport in these materials is strongly dependent on their grain structure. We have observed a confined versus unconfined crystallization in semicrystalline diblock copolymer/salt mixture comprising polystyrene-b-poly(ethylene oxide) and a lithium salt, induced by a shallow and a deep quench, respectively. The shallow quench resulted in crystallization confined within the microphase separated polyethylene oxide (PEO) lamellae, and the grain structure is retained. In contrast, the deep quench led to unconfined crystallization, where the crystallization of PEO does not disturb the microphase separated morphology but does alter the grain structure. Although depolarized light scattering (DPLS), small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were applied using the same thermal processing protocol, the difference between the two modes of crystallization can only be detected by DPLS. This is the first report of unconfined crystallization in semicrystalline block copolymers.

Schematic of confined versus unconfined crystallization in semicrystalline block copolymer/salt mixture.
In this study we look into facile strategy of synthesizing highly functional and robust liquid crystalline brush-like copolymers. Ring-opening metathesis polymerization for norbornene monomers bearing cholesteryl (NBCh9), cyanobiphenyl (NBCB6 or NBCB12) and poly(ethylene glycol) (NBMPEG) was used to obtain narrowly dispersed terpolymers that self-assemble to form cholesteric mesophase (N*). The formation of cholesteric mesophase provides a modular platform for 1D photonic materials with broad range wavelength tunability. Chemical crosslinking was used to obtain robust liquid crystalline elastomers with unique optical properties. The cyanobiphenyl mesogens in the terpolymer led to an increase in the helical pitch of the cholesteric mesophase resulting in a red shift while the inclusion of poly(ethylene glycol) monomer led to a blue shift. Hence, one can tailor the optical properties of these terpolymers by monomer sequence or composition. The uniqueness of these liquid crystalline brush-like copolymers, it’s their ability to be multifunctional, on one side the terpolymers can be used as photonic materials and on the other hand the block copolymers of cholesteryl (NBCh9) and poly(ethylene glycol) (NBMPEG) achieve optimized polymeric micellar delivery system for the solubilization and controlled delivery of cancer drugs such as Doxorubicin. The interesting properties of these polymers makes them unique, multi-responsive and multifunctional for different applications including optical devices, telecommunication, nanocarriers and drug delivery system to mention a few.
Poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL) are known to be biocompatible, biodegradable and bioresorbable polymers with complementary properties. It is possible to fabricate the copolymers with tailored rate of degradation along with superior thermal and mechanical properties when utilizing these polymers in combination. The versatility of these polymers have made them ideal candidates for biomedical applications. With the aim of designing materials with tailored rate of degradation, the current research aims at developing block copolymers based on PCL and PLA for potential biomedical applications. In the current work, triblock and stereo-pentablock copolymers based on PCL and PLA are synthesized by two and three-step ring opening polymerization respectively where PCL is incorporated into the terminal PLA segments in order to enhance the mechanical properties of the resulting copolymer. The molecular weight of the synthesized copolymers is determined by \(^1\)H-NMR spectroscopy and gel permeation chromatography. The melting temperature of stereo-pentablock copolymer is found to be higher than that of triblock copolymers as determined from differential scanning calorimetry. Additionally, the thermal stability of the stereo-pentablock copolymer is found to be higher than that of the triblock copolymer. Tensile strength and modulus are found to enhance on forming stereocomplexation. The synthesized copolymers are subjected to \textit{in vitro} studies to determine their biocompatibility. MTT assay is carried out to determine the cell viability on the synthesized copolymers. Further, the degradation studies are conducted to determine the rate of degradation of the synthesized copolymers. The cell adhesion and proliferation on the synthesized copolymers indicate their biocompatible nature along with the tailored rate of degradation ascertained by \textit{in vitro} studies.