

Friday June 30th - Morning session - 12-1pm

Poster #	Title	Presenter Name
1	The influence of molecular design on structure-property relationships of a supramolecular polymer prodrug	Nivedina Sarma

Abstract

Supramolecular self-assemblies of hydrophilic macromolecules functionalized with hydrophobic, structure-directing components have long been used for drug delivery. In these systems, loading of poorly soluble compounds is typically achieved through physical encapsulation during or after formation of the supramolecular assembly, resulting in low encapsulation efficiencies and limited control over release kinetics that are predominately governed by diffusion and carrier degradation. To overcome these limitations, amphiphilic prodrugs that leverage a hydrophobic drug as both the therapeutic and structure-directing component can be used to create supramolecular materials with higher loading and controlled release kinetics when biodegradable or enzymatically cleavable linkers are used. Here, we report the design, synthesis, and characterization of a library of supramolecular polymer prodrugs based on poly(ethylene glycol) (PEG) and the pro-regenerative drug 1,4-dihydrophenanthroline-4-one-3-carboxylic acid (DPCA). Structure-property relationships were elucidated through experimental characterization of prodrug behavior in both the wet- and dry-state, using scattering techniques and electron microscopy, and corroborated by coarse-grained modeling. Molecular architecture and hydrophobic-to-hydrophilic ratio of PEG-DPCA conjugates strongly influenced their physical state in water, ranging from fully soluble to supramolecular assemblies of micelles and nanofibers. Molecular design and supramolecular structure, in turn, were shown to dramatically alter hydrolytic and enzymatic release, bioactivity, and cellular transport of DPCA. In addition to potentially expanding therapeutic options for DPCA through control of supramolecular assemblies, the resulting design principles elaborated here may inform the development of other supramolecular prodrugs based on hydrophobic small molecule compounds.

2 Fundamental study of catechol retardation effects in the application of dental adhesion Denghao Fu

Polymeric materials containing catechol moieties are attractive in many applications including underwater adhesion and coatings, due to the covalent and particularly strong non-covalent interactions available between catechol and diverse interfaces. One promising application of catechol-containing polymers is dental restoration. These biomaterials require strong, long-lasting adhesion between methacrylate-based resins and exposed dentin surfaces, which is challenging in wet oral environments.

Unfortunately, the incorporation of catechol moieties into polymer networks formed via free-radical polymerization leads to some drawbacks. Mainly, catechol moieties are known to be inhibitors (scavengers) of free-radical polymerization, thus inhibiting and retarding the fast reaction. To better understand how incorporation of catechol-functionalized monomers impacts the overall kinetics of photopolymerizations, systematic studies should be done to better understand the relative rates of free radical generation and quenching.

In this study, a catechol-based monomer, catechol methacrylamide (CMAC), was incorporated into a methacrylate-based adhesive resin at loading levels of 0 to 5 wt%. Additionally, four different photoinitiators, including type I photoinitiators 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO) and type II photoinitiators camphorquinone (CQ) and thioxanthone (TX) combined with ethyl 4-(dimethylamino)benzoate (EDAB), were incorporated into the experimental resins to explore the influence of catechol concentration and initiator on resultant kinetics. Photopolymerizations were monitored using real-time FTIR. Results showed that while significant retardation was observed with Type II photoinitiators starting at 1 wt% CMAC concentration, no significant retardation was found with Type I photoinitiators, even at higher catechol loadings (5 wt% CMAC), as long as adequate light intensity and photoinitiator concentration was employed.

These results show that catechol retardance are influenced by the balance between free-radical generation and quenching. The difference in the free-radical generation mechanism between Type I and Type II photoinitiators results in a more significant influence of retardation for the latter. Overall, this fundamental study can give guidance on how to mitigate the retardation effects of catechol moieties during photopolymerization in other applications.

3 Redox-Responsive
Trehalose Nanoparticles
to Stabilize Glucagon

Ellie

Puente

Patients with Type 1 diabetes regularly inject insulin to manage blood glucose levels, but improper insulin injections can lead to severe cases of hypoglycemia. Glucagon is a peptide hormone that converts glycogen into glucose when interacting with glucagon receptors in the liver, raising blood glucose levels. Glucagon is administered as the first emergency treatment for patients experiencing a hypoglycemic event. Due to glucagon's low stability and solubility at neutral pH, its formulation for emergency delivery poses a challenge for patients and non-medical professionals. We have shown previously that trehalose polymers are able to stabilize proteins against various stressors through excipient stabilization and covalent attachment. In this proposal, we will create a responsive trehalose-based nanoparticle delivery formulation that will stabilize glucagon in solution at neutral pH for long periods of time. The stability, activity, and biocompatibility of the glucagon nanoparticles will be studied at various temperatures and environments that mimic biological systems and cold chain transport. Our work will demonstrate the stabilizing abilities of polymeric trehalose-based nanoparticles to stabilize glucagon at neutral pH. The proposed work would provide a chemical pathway to a novel glucagon formulation that is easy to administer and safe for the biological application of treatment for hypoglycemia.

4 Magnetoactive Properties of Biocompatible Magnetic Hydrogel Composites: Effects of Magnetic Particulate Type and Magnetic Annealing Jacob Schewe

Magnetic hydrogels are a novel smart material made up of a flexible, tissue-like hydrogel polymer with an incorporated magnetic particulate, producing a biocompatible material capable of mechanical deformation in response to an applied magnetic field (H). In this study, the potential biomedical applications from incorporating magnetically soft and hard additives, magnetite (Fe₃O₄) and strontium ferrite (SrFe₁₂O₁₉) respectively, into a crosslinked Polyvinyl alcohol (PVA) matrix were investigated. The impact of soft and hard magnetic particulate incorporation on the magnetic and magnetoactive properties PVA ferrogel were determined via sample hysteresis analysis and quantification of sample deflection under an applied magnetic field (H). The enhancing effects of magnetic annealing on the magnetic properties of ferrogels was investigated by comparing resulting magnetic and magnetoactive properties of annealed samples with analogous control samples. magnetoactive deflection testing. Mechanical properties are determined via tensile elongation testing. In addition to property characterization, the distribution of the magnetic additives was investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (SEM EDS). SEM EDS analysis revealed an evenly dispersed particulate throughout the hydrogel network at all loading content levels. Mechanical analysis revealed an increase in ferrogel stiffness contingent on an increase in magnetic additive content, regardless of the magnetic properties of the additive. Addition of magnetically hard additives yielded magnetically responsive ferrogels capable of complex motion, characterized by a high magnetic remanence and highly customizable magnetoaction that included a combination of deflection along a transverse magnetic field (H) and twisting around the same field. In contrast, the inclusion of a soft magnetic additive yielded highly magnetoactive ferrogels, characterized exclusively by deflection along a single transverse magnetic field (H). These findings show potential applications in implantable therapeutic biomedical applications such as controlled drug delivery and tissue scaffolding.

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| 5 | Multifunctional Polyesters as Tissue Adhesives to Control Soft Tissue Hemorrhage | Avanti | Pandit | <p>Soft tissue hemorrhage accounts for nearly 90% of preventable death in both military and civilian settings. Traditional methods and commercial products for stopping hemorrhage rely on the use of pressure which is not suitable for soft tissues and can even cause further harm to soft organs such as the liver. Current literature utilizes hydrogels of biocompatible polysaccharides, such as chitosan or hyaluronic acid, functionalized with catechol pendant groups to improve adhesion. Catechol functionalization is inspired by mussel adhesion underwater which utilizes proteins rich in dopamine. While these systems can provide moderate adhesion to dry substrates, they do not adhere to wet or underwater substrates thus they cannot be used in true hemorrhage conditions where the tissue surfaces will be wetted with blood until hemorrhage is stopped and hemostasis is achieved. Past work has shown that polyester coacervates can adhere to substrates that are submerged in water. Polyesters are also biodegradable and have demonstrated flexibility for composition and functionalization. Catechol can be added to impart underwater adhesiveness. Lysine is often used to create covalent bonds between polymers and proteins. And C12 or C15, which are long alkyl chains, can be used to collect and aggregate red blood cells. A polyester functionalized with catechol, lysine, and C12 can adhere strongly to blood-wetted tissues and potentially stop hemorrhage in soft tissue organs. We have already found that our polyesters can adhere to substrates submerged in water and cause blood to clot which encourages us to test our materials in animal liver models. This work will allow us to create a material that can be used to stop hemorrhage in soft tissues which can then be applied to other types of hemorrhage as a safer and less damaging method to stop all hemorrhage and save lives.</p> |
| 6 | Photochemical 3D printing of Bioresorbable Microneedle Arrays for Controlled Transdermal Drug Delivery | Alexander | Bahnick | <p>Microneedle arrays (MNs) have been extensively studied for transdermal drug delivery due to their ease of use and ability to deliver a wide range of therapeutics. However, current fabrication methods hinder throughput and customizability, and the scope of viable materials is limited. Additive manufacturing (3D printing) of microneedle arrays allows for high control over resolution, reproducibility, manufacturing speed, and part customization. Furthermore, poly (propylene fumarate) (PPF) is a synthetic, bioresorbable polymer that has been used previously for 3D-printed, biomedical applications. In this work, PPF-based microneedle arrays were fabricated via Continuous Liquid Interface Production (CLIP), which enabled facile part manufacturing and customization of microneedle size and geometry. Thiol-ene click chemistry yielded crosslinked polymeric materials during the photochemical printing process, resulting in a unique window of tunable mechanical and degradation properties. These 3D-printed MNs successfully penetrated porcine skin ex vivo and demonstrated controlled release of a model drug surrogate in vitro.</p> |

7	Effect of Cation- π Interactions on the Relaxation Dynamics of Polyelectrolyte Complex Coacervates	Conner	Chee	<p>Polyelectrolyte complex (PEC) coacervates are a group of materials with applications including drug delivery, underwater adhesives, and tissue engineering. These applications are enabled by the control of the rheological properties of the coacervates, which depends on both their physical environment and their chemical composition. Here, we investigate the effect of cation-π interactions on the relaxation dynamics of PECs by studying the rheology of PECs composed of salts with different cation-π interaction strengths. We first prepare a bulk, salt-free PEC composed of poly(styrene 4-sulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA) and then directly hydrate this PEC to prepare coacervate samples with identical salt and polymer concentrations but different inorganic salts. We find that the viscosity and relaxation times of the coacervates increase as the cation is changed from K⁺ to Na⁺ to Li⁺. This trend is consistent with the known cation-π interaction strengths of the three cations, with K⁺ engaging in the strongest binding with aromatic rings on the PSS. Therefore, this binding is the most effectively out-competing cation-π interaction and in turn reduces the extent of “sticky” interactions between the chains. These findings show that cation-π interactions can play an important role in determining the dynamics of PECs and should be accounted for when interpreting rheological data on these materials.</p>
8	Synergistic Enhancement of Peripheral Nerve Defect Repair using Peptide-Functionalized Aligned Nanofiber Conduits	Yin Mei	Chan	<p>The human peripheral nervous system (PNS) lacks an innate ability to restore itself to complete functionality. Current clinical techniques for peripheral nerve repair, including autologous nerve grafting, face many difficulties such as undesirable reliance on donor nerve availability, sacrifice of donor function, and size and structural compatibility, in critically-sized transection injuries (greater than 3 cm in humans). Consequently, a new methodology allowing for in-situ endogenous repair of the severed nerve would advance patient prognosis compared to autologous grafts. Synthetic nanofibrous scaffolds offer a biodegradable and less invasive alternative to enhance the efficacy and success of such repair processes. In vivo, Schwann cells (SCs) traverse an injury gap, serving as biomolecular and topographical cues for regrowing axons. Axonal regeneration only proceeds to the extent of which SCs traverse within the gap. By applying concentration gradients of peptides known to influence the migration of SCs to nanofiber scaffolds, axonal regeneration can be directionally guided from proximal to distal nerve stump. Using a novel touch-spinning fabrication method, functional poly (caprolactone) (PCL) aligned nanofiber conduits with well-defined diameters (1.65 ± 0.25, 1.18 ± 0.25, and 0.87 ± 0.27 μm) were produced. SCs seeded at 8,000 cells/cm² and incubated for 4 hours on such fibrous scaffolds showed increased mean square displacement (MSD) compared to controls. CYIGSR peptides were synthesized using standard solid-phase synthesis techniques for fiber functionalization and were subsequently covalently bound to the touch-spun nanofibers. Future work will include the tethering of a library of bioactive laminin-derived peptides in specified concentration profiles to the PCL fiber-based conduits as well as the in-depth characterization of the fibers' influence on neuronal cells both in vitro and in vivo.</p>

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| 9 | Polycation Stabilized Electrohydrodynamic Co-Jetted Janus Nanoparticle for Co-Delivery of Hydrophobic Drug. | Albert Chang | Currently, poorly water-soluble drugs account for a major portion of the market-available drugs or potential drug candidates in pharmaceutical research setting. They usually require additional surfactants for solubility while also suffer from poor and high variability in bioavailability, thus limit their effectiveness in providing oral or parenteral administration. One drug delivering strategy involves exploiting hydrogels for its biocompatibility and sustainable delivery. However, existing hydrogel formed by either polymer or protein are usually hydrophilic, thereby having low compatibility and dosing efficiency with hydrophobic drugs. High pressure homogenizer (HPH) is an efficient encapsulating method that allowed the inclusion of hydrophobic molecules into protein structure. In this work, we utilize processing to produce hydrophobic drug encapsulated Janus protein nanoparticle stabilized by polycation. Quantitative and qualitative analysis by scanning electron microscopy (SEM) and structure illumination microscopy (SIM) show and corroborated distinct compartments in JNPs with good monodispersity at sub 200 nm in diameter. The JNPs have positively charged surface and maintained size stability for extended period characterized through dynamic light scattering (DLS). Kinetic studies of drug release show that the JNPs are pH-responsive and display different releasing profile in various settings. Our finding suggests that the polycation-stabilized NAB-JNPs is a platform that can be tailored for co-delivery of hydrophobic drugs. Furthermore, we envision that the positively charged nanoparticles can add additional mucoadhesive properties owing to its positively charged surface for targeting and adhesion that can be elucidated in further in vitro and in vivo studies for insight on therapeutic effects. |
| 10 | New Materials for the Thermally Controlled Delivery of Inhalable Nitric Oxide | Shuxiao Li | Inhaled nitric oxide (iNO), is a FDA-approved therapy that can be used to treat a variety of medical conditions related to pulmonary and cardiovascular systems. Current iNO administration systems source NO(g) from costly and toxic concentrated medical grade NO gas cylinders, limiting administration to wealthy metropolitan hospitals. This project describes efforts to address this limitation through the development of NO-releasing polymers specifically designed for high temperature release (>100 °C). Using thermally cleavable protecting groups to stabilize otherwise labile NO donors, we show that the release temperature can be elevated to enhance bench stability and thermal control. Effects of polymer support on NO release yield and latency are also described. |

11	Stereolithography Photopolymerization Resin for Molding Water- Soluble Cavities	Charles	Rafalko	<p>A novel water-degradable photopolymer resin was developed by combining acrylic polymers with hydrolysable functionalities. Monomers were selected based on water compatibility, mechanical properties, and polymerization speed. The resin was used in vat polymerization (VP) to create water-soluble cavities for molding of soft materials. Unlike other examples of water degradable photopolymers, this material does not require elevated temperatures for degradation making it suitable for a wide range of materials. VP also facilitates the creation of shapes that are challenging to produce with traditional methods. The material was evaluated for mechanical strength and thermal properties, while polymerization was monitored via Fourier transform infrared spectroscopy. Various geometries were fabricated to evaluate the dimensional accuracy and dissolution of the resin in VP. The impacts to strength and water uptake were evaluated with various compositions to determine optimal formulations depending on the desired properties of the photopolymer. The printable photopolymer resin can be used for implanting blood vessel structures in silicone organ models to help pave the way toward vascularization of printed objects.</p>
12	Synthetic protein nanoparticle-encapsulated silicon quantum dots as a biocompatible probe for bioimaging applications	Fjorela	Xhyliu	<p>Synthetic protein nanoparticles (SPNPs) are an attractive approach for nanotherapeutics, as they are biocompatible, biodegradable, can carry both small and large payloads, and have good toxicity profiles. Quantum dots (QDs) make excellent contrast agents in the 'biological window' (near-infrared/NIR regime) but are routinely comprised of toxic metals. Recently, non-toxic silicon quantum dots (SiQDs) have become commercially available but are susceptible to rapid oxidation in aqueous. In this work, we present a SiQD-SPNP platform that couples the benefits of SPNPs to those of SiQDs. Utilizing electrohydrodynamic (EHD) jetting, a human serum albumin (HSA) SPNP was used to fully encapsulate SiQDs. NIR emission profiles indicate that the SiQD-SPNP shields SiQDs from most of the oxidation that occurs in aqueous environments. Electron microscopy confirms SiQD internalization into the SPNP and provides an overall SiQD-SPNP diameter of 158 nm, comparing well to non-SiQD SPNPs (161 nm). Finally, in vitro data displayed no toxicity, while SiQD emission remains effective for the visualization of particle uptake. The SiQD-SPNPs and non-SiQD SPNPs possessed similar uptake (ca. 50-60% of cells). This SiQD-SPNP platform provides the benefits of SiQDs to diagnostic tasks in a substrate that is well known for the facile incorporation of genes and drugs.</p>

13	Enabling printability and shape fidelity of granular hydrogel bioinks via reversible interparticle interactions	Zaman	Ataie	<p>The ability to 3D bioprint complex, multi-layered tissue constructs with high fidelity is crucial for tissue engineering and regenerative medicine. Granular hydrogels, composed of hydrogel microparticles, offer advantages over bulk hydrogels via enabling the on-demand formation of porous scaffolds with interconnected cell-scale void spaces. However, the printability of granular hydrogels requires tightly packed or jammed microgels, compromising scaffold porosity. This limitation may be overcome by enhancing the interparticle interactions using the reversible self-assembly of colloidal nanoparticles adsorbed to the microgel surface. To overcome this limitation, a colloidal dispersion of heterogeneously charged nanoplatelets was hybridized with GelMA microgel suspension, yielding the nanoengineered granular bioink (NGB). The NGB attained high extrudability, printability, shape fidelity, and well-preserved interconnected porosity. Available porosity of 3D printed NGB enabled the immediate transport of large macromolecules, and fibroblast cells were able to rapidly penetrate deep into the scaffold, whereas cell penetration was limited in the tightly packed and bulk counterparts. In conclusion, the NGB overcomes the trade-off between printability/shape fidelity and interconnected porosity, which may open new opportunities in tissue engineering and regeneration, intraoperative 3D bioprinting, and on-demand 3D printing of organs-on-a-chip platforms.</p>
14	Biomacromolecular granular hydrogel scaffolds for assessing the effect of cellular iron content on glioblastoma cell migration	Sina	Kheirabadi	<p>Glioblastoma is a lethal brain cancer that infiltrates healthy brain tissues, making complete surgical removal almost impossible and posing significant therapeutic challenges. The effect of cellular iron on glioblastoma cell migration remains inadequately understood. Granular hydrogel scaffolds (GHS) made up of chemically assembled macromolecular microparticles (microgels) provide a unique platform to investigate cell migration in response to different stimuli. GHS provides interconnected cell-scale void spaces, ameliorating oxygen and nutrient transport and facilitating nutrient gradient generation to promote cell migration within the scaffold. This study sought to develop GHS using gelatin methacryloyl (GelMA) photocrosslinkable microgels, a protein-based biomaterial that partially resembles the extracellular matrix (ECM). Microgels with optimized rheological and mechanical characteristics were fabricated and assembled to mimic the tumor microenvironment properties. The effect of iron on cell migration in three dimensions was assessed using fluorescently labeled T98G and LN229 human glioblastoma cell lines, seeded topically on GHS and subjected to varying concentrations of ferric ammonium citrate (FAC). Results showed that iron treatment significantly reduced the average migration length of both cell lines compared with untreated groups. In conclusion, biomacromolecular GHS is a suitable platform for understanding the role of cellular iron in glioblastoma pathogenesis and developing new therapeutic approaches.</p>

15	Parylene-C-Based Microfluidic Direct Sampling Probes for Chronic In Vivo Neurochemistry Studies	Thomas	White	<p>Direct neurochemical sampling probes have yielded vital insights into the dynamics of brain chemistry when coupled with robust analytical methods. However, spatial and to their bulky cross sections which can exceed 200 μm in diameter. The rigid materials typically employed to construct them increase the likelihood of triggering immune long term fraction collection. Glial scars can form around implanted probes within the surrounding parenchyma and act as a barrier to analyte diffusion during chronic stu sampling neural probes, which are currently under development, fabricated from Parylene-C. Polymers such as Parylene-C possess smaller Young's Moduli (2-5 GPa) c silicon (200 GPa) and are biocompatible. The probes were fabricated at the University of Michigan's Lurie Nanofabrication Facility. The total probe length is 8 mm. The pr sections and channel dimensions of 10 μm x 40 μm. Column buckling studies were carried out in both MATLAB and COMSOL Multiphysics to help guide the design proc a 3 mm shank length would offer sufficient resiliency to exceed the 1.0 mN threshold for penetration into brain tissue. Shank base widths between 180 μm up to 1041 μm potential impact on deflection and insertion force. Simulations yielded deflection values which ranged between 0.91 nm and 1.3 nm. Buckling strengths were within the ra developed a complete fabrication process which yielded finished probes. The probes are ready for tests of functionality and analyte recovery. Viable probes of this type co even new forms of studies relevant to in vivo neuroscience.</p>
16	Biomacromolecular Granular Hydrogel Scaffolds for Wound Healing	Arian	Jaberi	<p>Wound healing rate and quality have been significantly improved with scaffold-based therapies. To further enhance these therapies, granular hydrogel scaffolds (GHS) have been developed via assembling hydrogel microparticle (HMP) building blocks that facilitate cell ingrowth and reduce inflammation. Although bulk gelatin methacryloyl (GelMA) hydrogel scaffolds have been extensively used for wound healing, the potential of GelMA GHS for this purpose remains unexplored. In this study, we fabricated GelMA HMP to form GHS and performed mechanical characterization on GHS with two different HMP sizes. The median pore equivalent diameter and compression modulus of GHS were analyzed to optimize scaffold porosity for cellular infiltration and proliferation. The effect of porosity on macrophage behavior was compared with bulk GelMA, which represents nanoporous scaffolds. The effect of porosity on wound healing was assessed in vivo in a murine model of full-thickness skin injury. Although the rate of wound closure was not affected by porosity, hematoxylin and eosin (H&E) staining and immunofluorescence staining 11 days post-implantation showed a thicker granulation tissue, which attested to an improved wound healing quality for GelMA GHS compared with the bulk scaffold. In vitro and in vivo results consistently show that GelMA GHS supports tissue regeneration. This study lays the foundation for engineering regenerative GelMA GHS.</p>

17	Engineering the Porosity of Photocrosslinkable Protein-Based Granular Hydrogel Scaffolds	Arian	Jaberi	<p>Over the past few years, granular hydrogel scaffolds (GHS) have been used for various biomedical applications. GHS are fabricated by placing hydrogel microparticles (HMP) in close contact, followed by physical and/or chemical interparticle bond formation. Various techniques have been used for confining the HMP in close-packed conditions, including centrifugation and compression. Studies have shown the effect of centrifugal speed on the porosity of GHS with different HMP sizes and/or stiffness. However, the effect of HMP deformation using external forces on the porosity of photocrosslinkable gelatin methacryloyl (GelMA) GHS is unexplored. GelMA, synthesized by methacrylate modification of gelatin, was used to fabricate uniformly sized HMP via a step-emulsification microfluidic device. To investigate the effect of packing on GelMA GHS porosity and mechanical properties, GelMA HMP were packed at different centrifugal forces and durations. Our results showed that increasing centrifugation time resulted in a higher degree of HMP packing, leading to a decrease in the void fraction and median pore diameter and an increase in compressive and storage moduli. In vivo subcutaneous implantation will be conducted on the two extreme conditions with the highest and lowest packing density to study the effect of packing on tissue integration. In conclusion, we engineered GelMA GHS porosity by applying centrifugal force to induce HMP deformation and showed how mechanical and biological responses are affected by the packing. This research is a step forward in engineering GelMA GHS via external stimuli for tissue engineering.</p>
18	A photoreactive biomaterial crosslinker with broadband fluorescence	Anthony	Berardi	<p>The modular synthesis and photophysical characterization of a photoreactive, intrinsically fluorescent, dithiomaleimide (DTM)-based biomaterial crosslinker platform is presented. DTMs with alkyl substituents are a novel class of highly emissive, photostable small molecules and have been shown to exhibit distinct fluorescence anisotropy decay signatures depending on their physical state - for example, as a free molecule in solution compared to covalently immobilized in a material. This crosslinker was employed to stabilize a variety of synthetic polymers, proteins, and nanoparticles relevant in biomedical applications. Fluorescence anisotropy spectroscopy and fluorescence lifetime imaging were used to characterize the resulting spectroscopic properties of these materials. In summary, we've designed a single, versatile molecular platform that addresses the following criteria common to those engaged in biomaterial design: 1) scalable, facile synthesis, 2) rapid and efficient material crosslinking, 3) intrinsic fluorescent emission, and 4) self-reporting of material state.</p>

19 Patient-derived Ovarian Cancer Tumoroids for Studying the Tumor Microenvironment Kathleen Burkhard

The deadliest cancer of the female reproductive system is ovarian cancer. New targeted treatments have been developed; however the overall survival rate remains unchanged. There is a critical need for more physiologically relevant patient-derived models in order to improve preclinical testing success. To meet this goal, we created a patient-derived 3D tumoroid model to evaluate the impact of non-tumor cell types from the tumor microenvironment on tumor cells and uncover the molecular pathways involved. Tumoroids were generated in hanging drop arrays by incorporating controlled ratios of mesenchymal stem cells, endothelial cells, and immune cells with patient-derived tumor cells into self-assembled tumoroid microtissues. Single cell RNA sequencing and quantitative polymerase chain reaction was used to evaluate gene expression in spheroids and tumoroids. Tumorigenic potential was assessed by subcutaneous injections of patient-derived tumoroids and spheroids into NSG mice. All animal work was conducted at the University of Michigan under an IACUC approved protocol and adhered to the guidelines established by the National Academy of Sciences. Additionally, in vitro response of patient-derived tumoroids and spheroids to chemotherapeutics and novel biologics was quantified using MTS assays. We demonstrated that the patient-derived tumoroids have increased tumorigenic potential in mice, forming more tumors and reaching the tumor burden threshold more quickly. Additionally, tumoroids displayed increased resistance to chemotherapies and biologics. The single cell RNA sequencing revealed epithelial to mesenchymal transition (EMT) and increased matrix expression in tumoroids compared to spheroids or 2D cells. In conclusion, this work shows that the non-cancer cells in the tumor microenvironment are linked to clinical outcomes through their role promoting tumorigenesis, chemoresistance, EMT, and extracellular matrix remodeling. Our patient-derived 3D tumoroid model incorporates the complex cell-cell interactions of the tumor microenvironment while maintaining control over experimental variables, which is lacking in patient-derived organoids and xenografts.

20	Design and Electrochemical Study of Multidimensional Polymeric Architectures for Electrocatalytic CO ₂ Reduction	Jukai	Zhou	<p>Electrochemical CO₂ reduction reaction (CO₂RR) is a promising strategy for the conversion of waste CO₂ into value added products. A terthiophene modified cobalt pyridylidimine complex (CoTTPDI) has been prepared and shows high catalytic activity for electrochemical CO₂ reduction in acetonitrile with proton source. Our current efforts are focused on extending this CoTTPDI complex into one or two dimensional (1D/2D) polymeric architectures, with a desire to integrate the advantages of both homogeneous and heterogeneous catalysts. 1D polymeric architecture (1D-polyCoTTPDI) has been prepared by electro-polymerization of CoTTPDI on glassy carbon electrode. The 1D-polyCoTTPDI shows greater catalytic activity for CO₂RR than its precursor CoTTPDI. This improvement is endowed by the high coverage density of CoTTPDI on the electrode surface and the good conductivity of polyterthiophene. The catalytic activity can be further enhanced by adding water as a cheap proton source into the catalysis system. In addition, 2D polymeric architecture (2D-polyCoTTPDI) is prepared by electro-copolymerization of CoTTPDI with several crosslinkers. The porous structure of 2D-polyCoTTPDI can provide more active catalytic sites exposed to substrates, contributing to increased catalytic activity. As numerous metal complexes are known for a broad scope of electrocatalytic transformations, these extended polymeric architectures are anticipated to serve as a platform for future studies.</p>
21	A FACILE WATERBORNE STRATEGY FOR INCREASING OIL FOULING RESISTANCE OF POLY(VINYLDENE FLUORIDE) MICROFILTRATION MEMBRANES	Moustafa	Zagho	<p>Membrane technology is widely utilized for producing an industrial-grade water for numerous applications. Poly(vinylidene fluoride) (PVDF) is one of the most commonly used polymers in various separation membranes due to its low cost, high mechanical strength, superior thermal stability, and excellent chemical resistance properties. However, PVDF membranes mainly suffer from oil fouling due to their hydrophobic nature. Herein, an oil fouling-resistant coating based on biodegradable polydopamine (PDA) was designed by co-deposition on the surface of PVDF microfiltration membranes. The PDA layer was used as a template to introduce other hydrophilic materials to further improve the hydrophilicity of the membranes. Second generation hyperbranched BoltornTM polyol (H₂O) and MXene were incorporated in combination with PDA to compare their effect on enhancing the oil separation performance of PVDF membranes. Compared to MXene, the incorporation of H₂O demonstrated a remarkable boost in the separation of oil from water in tight emulsions while displaying surprisingly high resistance to fouling over five runs.</p>

- 22** In situ observation of solvent exchange kinetics in a coordination polymer Hochul Woo
- The solvent exchange of porous coordination polymers, known as metal-organic frameworks (MOFs), is critical to achieve an optimal surface area by facilitating solvent evacuation. In the case of MOFs with coordinatively unsaturated sites (CUS), strongly bound solvent molecules can be particularly difficult to remove. HKUST-1, which is an iconic MOF system with Cu-paddlewheels, was explored in this experiment. Previously, N,N-dimethylformaldehyde (DMF) retained by HKUST-1 was reported to be mostly replaced with ethanol (EtOH) or dichloromethane (DCM). In order to compare these solvent exchange systems, deuterated solvent was used to provide a unique spectroscopic signature from the C–D stretch. It is demonstrated that DMF concentration reached equilibrium faster when it exchanged with DCM, yet more DMF remains during DCM replacement compared to EtOH exchange. Moreover, Cu–Cu stretch change revealed that CUS-bound solvents were only replaced during EtOH exchange. This research indicates that CUS-bound solvent exchange takes more time than pore-filled solvent exchange, and will only occur when a solvent with sufficient affinity for CUS is introduced.
- 23** Biomass-Derived Polymer Precursors as Lithium-ion Solid Electrolytes Mengjie Yu
- The urgent quest for new energy sources to alleviate environmental concerns couples strongly with sustainability in the search for new energy storage methods. Given the significant greenhouse gas emissions that occur coincident with current battery production and operation processes, the introduction of renewable biowaste rice hull ash (RHA) as a source for battery components could allow true realization of green and sustainable energy storage. We have learned to catalytically dissolve SiO₂ in RHA with hexylene glycol, forming spiroxiloxane [(C₆H₁₄O₂)₂Si] that can be distilled directly at 200 °C. The spiroxiloxane can be lithiated using controlled amounts of LiNH₂ to produce Li_xSiON, which is a series of Li⁺ conducting oligomer/polymer precursors. Li₆SiON polymer impregnated in a Celgard separator offers high conductivities up to 6.5 × 10⁻⁶ S/cm linked to higher Li⁺ concentrations. The Li⁺ transfer numbers (t_{Li}) of >0.73 indicates electrostatic interactions between Li⁺ and SiON afford high Li⁺ mobility. Traditional liquid electrolytes often exhibit t_{Li} <0.5 due to electro-polarization from anion buildup decreasing electrochemical performance due to high internal resistance, voltage losses, and dendritic growth. Li_xSiON solid electrolytes appear to overcome issues faced with liquid electrolytes. Most important, Li₆SiON forms with polyethylene oxide (PEO) solid solution electrolytes in membrane formats with 2 order magnitude conductivity improvements. A number of aspects of these efforts will be presented.

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| 24 | Hybrid Nanostructures with liquid metal core and functional polymer shell for flexible energy storage and electronics | Jinyu | Bu | Gallium based alloy, namely eutectic gallium indium, has seen a vase application to energy storage devices. Its fluidic nature enables simple fabrication method and easy integration into matrix material and with other functional fillers. However, its intrinsic oxide formation on the surface, and its poor stability hinders its mass application as an efficient candidate for energy storage devices. Here, a core-shell structured EGaIn liquid metal (LM) nanoparticles (NPs) are introduced. The core-shell LM NPs were fabricated using Layer-by-Layer (LbL) method to deposit polysaccharide pair using electrostatic interactions between chitosan and dextran. The as fabricated core-shell LM NPs are exposed with several post treatment techniques including hydrothermal carbonization and high temperature calcination to convert the polysaccharide layer to amorphous and graphitic carbon respectively. Electron microscopy and Raman spectroscopy confirmed the successful formation of the core-shell structure and the conversion from polymer to amorphous and graphitic carbon. As a proof of concept, we further tested the electrochemical performance of such core-shell particles using three-electrode method. The graphitic carbon-coated LM NPs showed one-fold increase in the capacitance compared with the pristine LM NPs. Such particles are believed to be a promising candidate as the active material for the micro-supercapacitors. |
| 25 | Metal-Organic Framework-Based Mixed Matrix Membranes for Nonaqueous Redox-Flow Batteries | Cassidy | Carey | Nonaqueous redox flow batteries (NARFBs) show great promise in energy storage applications due to their wide range of operating temperatures, high cell voltages, and high energy density. While interest in developing NARFBs has increased in recent years, the lack of an efficient membrane that allows fast conduction of supporting electrolyte ions while simultaneously blocking crossover of redox active species prevents their broader implementation. Existing commercial membranes for NARFBs permit fast conduction of supporting electrolyte ions, but lack the microporosity required to reject redox active species. Metal-organic frameworks (MOFs) are porous coordination polymers formed from metal-cluster nodes linked by multifunctional organic linkers. Their chemical versatility and well-defined pore sizes make them viable candidates for size selective applications. Recently, MOFs have been implemented into mixed-matrix membranes (MMMs) for NARFBs, but the effects of MOF linker functionality on MMM performance are not well-understood. In this work, we developed a series of MOF-based mixed matrix membranes by blending functionalized MOFs with chemically stable polymers. The MMMs demonstrated size-selective blocking of redox active oligomers in diffusion studies, and we found that MOF linker functionality can influence membrane ionic conductivity. This work provides a platform on the design of efficient MMMs with both ion exchange and ion-sieving functionality for NARFBs. |

26 Biowaste Modified Philyong Kim
Sulfurized Polyacrylonitrile
Cathodes Toward Stable
Lithium-Sulfur Batteries

The lithium-sulfur (Li-S) couple offers a high theoretical specific capacity (1675 mAh/g-1) and energy density (2600 Wh/kg-1) based on readily available low-cost materials and significant promise for next-generation systems for Li-ion batteries (LIBs). The motivation comes from the fact that current LIBs are reaching a limit of ~600 Wh/kg-1 deemed insufficient for newer electric vehicles and energy storage systems.

Broadly, two different types of S composites have been explored in the development of Li-S batteries. One type uses elemental S8-impregnated carbon composites. The second can be described as sulfurized polyacrylonitrile (SPAN) composites in which small S_x chains (1 ≤ x ≤ 4) are linked covalently to cyclized PAN. However, two major obstacles to the realization of commercial Li-S batteries arise from lithium polysulfide (LiPS) shuttling and volume expansions of up to 80% during battery cycling. In part, the former is alleviated by SPAN because the solubility of short LiPSs (LiS₂₋₄) is poor in typical carbonate electrolytes. However, Li-SPAN batteries experience the volume issue based on density differences between S and Li₂S (2.07 and 1.66 g/cm³ respectively) during cycling. Thus, pristine SPAN still suffers from capacity fading in carbonate electrolytes.

In this work, we show the introduction of biowaste and very cost-effective silica-depleted rice hull ash (SDRHA) which is a porous material with ~460 m²/g-1 of surface area. SDRHA can disperse SPAN and introduce a high specific surface area carbon-silica nanocomposite that appears to buffer the volume change during cycling.

The SPAN with SDRHA (SPAN/SDRHA) electrode can deliver a ~1200 mAh/g-1 of discharge capacity, compared to ~780 mAh/g-1 for SPAN-only electrode, demonstrating improved electrochemical performance by 50% when they were tested at 1C for 300 cycles. In addition, when the SPAN/SDRHA pairs with a polyacrylic acid binder, the cathode can deliver a ~800 mAh g-1 of discharge capacity at 2C for 300 cycles.

27

Crosslinked-Monovalent
Selective Ion Exchange
Membranes

Lisby

Santiago-Pagán

Ion exchange membranes (IEMs) have gained increasing attention over the past years due to their applications in a variety of water treatment and energy storage/production technologies. Their usefulness arises from having acidic or basic functional groups covalently bound to a hydrophobic polymer backbone. The functional groups ionize in the presence of water, which allows for the transport of counter-ions, and rejection of co-ions. Although IEMs provide good selectivity for counter-ions over co-ions, they cannot efficiently separate similarly charged counter-ions having different valences. Recent attempts have been made to achieve selectivity for monovalent ions over divalent ions in IEMs, but the performance of these membranes is limited by a tradeoff between achieving high selectivity and maintaining good ionic conductivity, as well as inadequate long-term stability. Further, the scarce fundamental and systematic studies on these types of systems make it challenging to modify them for higher selectivity demands. The present work introduces a novel synthetic approach for achieving monovalent-ion selectivity through the photochemical polymerization of a thin oppositely charged layer on top of a base IEM. Both layers were synthesized via free radical photopolymerization of commercial charged monomers 3-sulfopropyl methacrylate (SPM) and 2- (methacryloyloxy) ethyl trimethylammonium (MOETMA) with cross-linker glycerol dimethacrylate (GDMA). Individual IEM layers were synthesized with precise control of charge density, over a wide range of water volume fractions (0.2-0.5). Having a systematic control of these two structural properties, which largely dictate ion transport and selectivity in the membrane, enabled us to establish an understanding of how the membrane structure impacts its performance. The design of these novel membranes and the understanding of their structure-property relationships will give us the tools to advance this material space and enhance the efficiency of current and future separation technologies.

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|----|---|----------|----------|---|
| 28 | Highly Charged Ion-Exchange Membranes for Treatment of Highly Impaired Waters via Electrodialysis | Carolina | Espinoza | <p>A better understanding of the interconnection between membrane structure and transport properties is required to better guide future IEM development. Technologies, such as electrodialysis, for brine disposal, require membranes that are highly permeable and highly selective. Typical membranes used for brine application have a lower degree of swelling. However, there is a poor understanding of ion transport in the region of low swelling, making it difficult to rationally design membranes with desired transport properties. In this work, we have successfully synthesized a series of highly charged cross-linked AEMs and CEMs with varying degrees of swelling and constant fixed charge concentration. The membrane ion transport properties were measured at salt concentrations indicative of highly impaired waters. The membrane selectivity (counter-ion over co-ion) was calculated using ion concentrations and diffusion coefficients in the membrane. Overall, there was little change in selectivity as membrane swelling increased, although counter-ion throughput increased about one order of magnitude. Membrane selectivity was greatly affected by the external salt concentration. We saw a decrease of approximately one order of magnitude in membrane selectivity increasing the external salt concentration from 1 to 5 molal NaCl. The overall membrane selectivity was decoupled into ion sorption and diffusion coefficient selectivity. For all membrane swellings and salt solution concentrations, the ion sorption selectivity had a greater contribution to the overall membrane selectivity. This project aims to address knowledge gaps in the fundamental understanding of transport phenomena in charged polymer membranes with varying degrees of swelling.</p> |
| 29 | Open-cell PDMS polyHIPEs using PMVS to | Anthony | Smith | <p>Polymerized high internal phase emulsions (PolyHIPEs) are porous polymers made from emulsion templates. PolyHIPEs prepared using polydimethylsiloxane (PDMS) are typically</p> |

30 Streptococcus mutans Jeongmi Moon
Aggregation in Biofilm
Model System Driven by
Depletion and Bridging.

S. mutans is a cariogenic bacterium prevalent in oral cavity. In order to investigate and understand bacterial aggregation and their behavior in biofilm, *S. mutans* was used. EPS, which takes approximately 80-90% of biofilm, consists of glucan, eDNA etc. *S. mutans* have glucan binding protein on its cell wall, so *S. mutans* binding with glucan in EPS and the stickiness glucan provides have been the dominant theory explaining bacterial aggregation in the biofilm. However, how they reproduce while living in sticky environment of the biofilm is not much studied.

Here, we adopt depletion force driven aggregation in colloidal science to understand better about bacterial aggregation. Dextran, PEG(Poly ethylene glycol), PSS(Poly styrene sulfonate), PEI(Poly ethylene imine) were used to cause the aggregation. Dextran was used as a replicate glucan in EPS, and PSS was used as eDNA. After grown for 24 hours, *S. mutans* was washed 3 times with sterile PBS. After washing, *S. mutans* was mixed with each different polymers and incubated for 6 hours in room temperature.

Upon observation, all different polymers caused bacterial aggregation but microscopic view of *S. mutans* showed interesting results. In the presence of dextran, as the concentration of dextran got higher, the space between *S. mutans* chains got bigger. In the presence of PSS, the more PSS there is, the more the bacterial chains were packed. It is our understanding that as dextran and PSS acts similar as glucan and eDNA in EPS, through this experiment and observation we understand better how *S. mutans* enable room for new cells in biofilm.

31 Thermally, UV, and
Moisture Curable Novel
Family of Versatile
Oligomers

Neda

Hayeri

Binders are the essential ingredients in every coating formulation and primarily define the properties, applications, and curing technologies of the coating system. The most popular and commonly used binders in conventional coatings are usually designed to be cured by one specific curing mechanism, such as thermal curing, radiation curing, or ambient temperature curing. Some inherent limitations are brought to the system with binders that can be cured only with one curing mechanism, such as balancing hardness and flexibility, substrate characteristics, leveling and wettability, complete surface, and through curing with no apparent defect, and poor adhesion to substrates in some cases, which limit the coating application spaces.

We have developed a family of new-generation oligomers that are not dependent on a single-cure mechanism but are capable of curing independently by multiple cure mechanisms. A broad range of alkoxy-silane functional oligomers/polymers has been meticulously designed and synthesized with varying backbone structures and functional group contents. Oligomers containing bio-based resources have also been synthesized to reduce their environmental impact. By using a variety of catalysts and unique cure-chemistries we have successfully demonstrated coatings cured by thermal-curing, UV-curing, as well as ambient-temperature curing. Furthermore, these cure processes can also be combined to afford dual-cure capabilities, which overcome many issues such as oxygen inhibition, uncured shadow areas, depth-of-cure, volume shrinkage, and chemical adhesion on various surfaces.

The cured coatings are characterized by the extent of the cure and the mechanical and thermal properties of the cured films. Comparison of results for coatings cured with different curing techniques provides an insight into the curing mechanism and its effect on film properties.

Abstract

We previously demonstrated that phenyl and vinylsilsesquioxanes, [PhSiO_{1.5}]_{8,10,12} and [vinylSiO_{1.5}]_{8,10,12} functionalized with three or more conjugated moieties show red-shifted emissions that offer 3-D conjugation via a cage centered LUMO. Extending this work to corner missing [PhSiO_{1.5}]₇(OSiMe₃)₃ and edge opened and endcapped [PhSiO_{1.5}]₈(OSiMe₂)₂ cages likewise generated compounds presenting red shifted emissions again indicating 3-D conjugation and a cage centered LUMO. Extending this work to functionalized, endcapped or double decker (DD) silsesquioxanes again led to macromolecules exhibiting red-shifted emissions if functionalized more than three times suggesting a cage centered LUMO.¹ Copolymerization of the DD [PhSiO_{1.5}]₈(OSiMevinyl)₂ with multiple dibromoaromatics again offers emission red-shifts suggesting through chain conjugation even with two (O-Si-O) end caps likely via a cage centered LUMO. To assess conjugation limits, the ladder silsesquioxane, (vinylMeSiO₂)[PhSiO_{1.5}]₄(O-SiMevinyl) was copolymerized using the same protocols expecting elimination of a cage format would eliminate red-shifted emissions and LUMO formation. Instead, red-shifts were even greater for identical copolymers requiring a different explanation for this type of conjugation.¹⁻³

Here we assess the photophysical behavior of copolymers of two more extreme forms: expanded cage [PhSiO_{1.5}]₈(OSiMevinyl)₄ "Vy4XDD" even having double end capping [OSiMevinyl-O-SiMevinyl] units and the half cage [PhSiO_{1.5}]₄(OSiMe₂vinyl)₄, Vy₄HC. In both systems, we again see upto ~ 60 nm red-shifted emissions compared to their tetra-conjugated moiety- functionalized model compounds. To further explore conjugation in these compounds, column chromatography was used to separate fractions of the XDD-coStilbene/HC-coStilbene oligomer mixture, as examples, to assess the effects of chain length on photophysical properties. The emission wavelengths change from purple to greenish blue proving that as chain length is extended the emission band gap gets smaller. These results further support the existence of conjugation via Si-O-Si bonds and contrary to most traditional views of Si-O linked polymers.

- 33** Facilities for Procedurally Evaluating the Snow Shedding Behavior of Polymeric Surfaces Matthew Wu
- The large-scale accumulation of snow and ice on surfaces produces loads that can put structures at risk and hinder the efficiency of solar panels. While lowering the adhesion strength of ice to surfaces using polymeric coatings is well studied, quantitative studies into snow shedding surfaces are relatively rare. One of the difficulties in evaluating the snow shedding ability of different surfaces outdoors during a snow event is that variations in temperature, humidity, and wind speed can alter the formation, deposition, compaction and shedding of snow. To get consistent and replicable results a standardized form of snow and consistent shedding conditions are required to facilitate comparison between surfaces. In this study, a nozzle-based snowmaking system was constructed inside a walk-in freezer. Using controlled air and water flows, snow with properties resembling that of natural dry snow (liquid water content < 5% and density = 0.11 g cm⁻³) can be reproducibly made in large quantities. Additionally, force gauges mounted onto motor assemblies were constructed to evaluate the forces required to detach snowpacks of controlled lengths with a controlled speed from surfaces at subzero ambient temperatures. Using these facilities, some key differences between snow shedding and ice shedding have been observed. The highly porous structure of a snowpack can undergo relatively rapid isothermal sintering, which causes the snowpack to rapidly increase in density after forming. By this same process, the ice particles that make up snow can form attachments to a surface and reattach after being detached. Preliminary tests have found reduced adhesion of snow to certain polymer coated surfaces compared to uncoated surfaces under the same conditions. Further study could reveal the properties responsible for reduced snow adhesion and lead to the development of surfaces able to passively shed snow in its many forms.
- 34** The Flow Properties of Snake Venom: How Venom Adapts to Fang Morphology Madison Forstner
- Snakes across different species have evolved fang morphologies to penetrate different tissues depending on their diet. Different fang morphologies also come with different mechanism of administering venom, for example: solid fang, where the venom pools out around and into a bite wound; grooved fang, where there is a groove on the outside of the fang for venom to flow down; or hollow fang, where the venom is injected directly through channels inside the fang. Although the structural and mechanical properties of different types of fangs is well studied, the fluidic properties of their respective venom is not well understood. In this project, we are studying the non-Newtonian shear-dependent flow properties of snake venom from 14 different species (with eight of them being from the family Viperidae and the other six being from the family Elapidae). Through rheological characterization, we can compare the shear flow properties across species and families to gain a greater understanding of the role evolution played in the flow properties of snake venom. Ultimately, we will use this data to recreate the flow properties of various snake venoms in a “synthetic” venom that lacks the toxin proteins found in natural venom to perform experimentation and validation in 3D-printed fang models.

- 35** Polymerized high internal phase emulsions to produce porous polymer beads with tunable mechanical properties Naomi Coutinho
- Porous polymer beads possessing tunable properties such as mechanical strength and morphology are needed for applications including tissue engineering, absorbents, and size exclusion chromatography. The polymerized high internal phase emulsions (polyHIPE) method has gained interest in producing porous materials with controlled morphology. However, polyHIPE beads are not well characterized by their mechanical strength. In this work, polydimethylsiloxane (PDMS)-based polyHIPE beads with controlled mechanical behaviors have been synthesized and compared to monoliths of the same formulation. The total porosities and mechanical strengths of the polyHIPEs are controlled by varying the volume of the aqueous dispersed phase in the emulsion. Analysis of SEM images and compression tests of polyHIPE beads proved the total porosity values and the storage moduli are tunable. This work provides a simple technique to prepare porous PDMS-based polyHIPE beads having a Young's Modulus of ~0.2 KPa which correlates to ~30 KPa of its respective monolith. The lower dispersed phase monolith could experience ~35% strain and the higher dispersed phase monolith could experience ~55% strain, whereas all the beads did not show breakage until almost 100% strain.
- 36** Porous polyurethane with monodisperse porosity and controllable mechanical properties using water-in-oil high internal phase emulsion templating Vindya Dikella
- Polyurethanes (PUs) are a versatile class of polymer with numerous applications including automobiles, aeronautic and biomedical field due their high mechanical strength, durability, flexibility, and biocompatibility. Porous PU foams have been receiving a great attention as a result of their low density light weight and high surface area. However, preparing PU foams with small, uniform, pore morphology is often difficult with commonly used methods like gas foaming, salt templating, and ice-templating. In this work, highly controllable porous PU with regular pore structures, and tunable material properties have been synthesized using emulsion templating polymerization known as polymerized high internal phase emulsions or polyHIPEs. Highly interconnected open cell pore morphology that originated only from emulsion templating are observed for PU polyHIPEs from analysis of SEM images. Mechanical properties of prepared PU-polyHIPEs are tailored by varying the type of diisocyanate, volume of aqueous dispersed phase in the emulsion, and thiol to ene ratio. This work presents unique and sustainable method to prepare PU-polyHIPEs with uniform porosity and tunable material properties.

37	Using Small-Angle Scattering and Rheology to Characterize Structure-Property Relation of Polymeric Latex Particles.	Kush	Patel	<p>Current formulations of many paints and coatings require high amounts of volatile organic compounds (VOCs) to achieve desired properties. Due to growing global concern over the negative environmental and health effects of VOCs, such as smog, cancer, and asthma, the EPA seeks to impose tighter restrictions on allowable levels of VOCs in such products. Our work is in collaboration with PPG Industries who, anticipating enhanced regulations of VOCs, aim to develop waterborne resins consisting of water-stable core-shell polymeric particles. The architecture of these engineered resins has been designed to respond to various stimuli - including salt concentration, pH, and solvent conditions - to achieve similar rheological properties as traditional solvent-borne resins which entail a low high-shear viscosity for ease of application and a high low-shear viscosity for quality appearance. While we can relatively easily predict the rheology of traditional solvent-borne resins by the molecular weight and total weight fraction of the polymer, several factors contribute to the rheology of these novel formulations. Our research therefore seeks to develop a framework for understanding the link between the rheology of these materials and their microstructure. I utilize small-angle scattering techniques at Argonne National Laboratory and Oak Ridge National Laboratory to probe microstructural responses to various stimuli. I determine that the shell component of the resin has a similar scattering contribution as a polyelectrolyte chain and confirm these results against rheology. The modification of pH or salt concentration influences the conformation of the polyelectrolyte shell component, whereas addition of inorganic solvents (such as 1-butanol) swells the polymeric core component. This work highlights the importance of scattering techniques in polymer research.</p>
38	Comparison of hydrophilic :	Mahek	Siwatch	<p>An emerging approach for low-pressure biological wastewater filtration is the self-forming dynamic membrane (SFDM) bioreactor, which accomplishes filtration via layers of microorganisms (i.e., biofilms) that form on a mesh support. This approach has garnered interest as a low-cost alternative to micro/ultrafiltration membranes. Materials such as polyvinylidene fluoride (PVDF) and polypropylene (PP) can be woven into a mesh with large pore sizes (e.g., 10-1000 μm) to support SFDM development. The critical challenge with the SFDM approach is fouling, which is indicated by an increase in filtration resistance and reduction in flux. Backwashing (i.e., flushing liquid back through a membrane) to physically dislodge foulants is a strategy to recover flux and reduce resistance. However, irreversible foulants that cannot be dislodged become a problem in long-term filtration. Previous studies have reported that hydrophilic micro/ultrafiltration membranes have less irreversible fouling because there is less hydrophobic interaction of foulants and membranes, and a less compact biofilm forms. Whether this phenomenon remains true for SFDM is currently unstudied. To elucidate the potential benefit of a hydrophilic polymer mesh to mitigate fouling in a SFDM, this study will filter municipal wastewater through hydrophobic PVDF and hydrophilic PP SFDM setups under the same operating conditions in short-term experiments conducted prior to this conference. For each mesh type, flux recovery after backwash will be monitored to determine irreversible fouling. Findings from this work will inform the relative fouling benefits of a more or less hydrophilic support material in SFDM wastewater filtration applications.</p>

39	Investigating anti-bacterial and anti-COVID-19 virus properties and mode of action of Mg(OH) ₂ and copper-Infused Mg(OH) ₂ nanoparticles on coated polypropylene surfaces	Saleh	Alkarri	opulations in 24 h, while for thermally embossed NPs an 8 log reduction of E. coli populations was observed. In addition, the NPs exhibit anti-viral activity against SARS-CoV-2. Fluorescence microscopy revealed that reactive oxygen species (ROS) is the main mode of action through which Mg(OH) ₂ and Cu-Infused Mg(OH) ₂ act against microbes. Plastics with anti-microbial surfaces from where biocides are non-leachable are highly desirable. This work provides a general fabrication strategy for developing anti-microbial plastic surfaces.
40	Sustainable Packaging with Waterborne Soybean Oil	Vikash	Kumar	Packaging is responsible for 46% of total plastic waste, and thus sustainable packaging alternatives are urgently required. Reported herein is coated paper as a sustainable packaging material by using waterborne acrylated epoxidized soybean oil (AESO) to coat Kraft paper. The waterborne AESO was cast onto kraft paper and was then photo cured. Upon curing, the coated paper was tested for its oil and water repellency as well as its mechanical properties. Biodegradability studies were also conducted for the AESO-coated paper, and our findings suggest that its biodegradability reaches >90% within 90 days. The coating process was also evaluated for its compatibility with paper printing processes and its resistance to hot oil. Overall, the AESO-latex coated paper offers excellent water and oil-resistance, has the desired mechanical properties, biodegradability, and cost-effectiveness, and thus is a sustainable alternative to the current wasteful packaging made from plastic- or plastic-coated paper.
41	High-Density Polyethylene (HDPE)-	Ash	Subhaprad	High-Density Polyethylene (HDPE) is presently the most-used commodity plastic by volume, and it is frequently used in consumer goods, construction, and electrical industry. In this poster, I will present HDPE based vitrimers and the impact of grafting agents on the performance of these vitrimers. Interestingly, the crystallinity of the polymers decreased which might find a great application in 3D printing owing to warping issues with conventional HDPE.

Lipid nanoparticle (LNP) based vaccines and liver-trophic gene therapies are the first iteration of a new generation of biotechnology. Despite their many advantages, LNP vaccine platforms are limited by poor endosomal escape, liver tropism, and instability. Developing new, nonviral gene therapy platforms is critical to targeting cells outside the liver and expanding the possible cargos beyond mRNA. Polymeric systems offer such an alternative. Poly(β - amino ester) (PBAE) nanoparticles are a biodegradable, multifunctional platform which can deliver drugs and genes (DNA, RNA, or siRNA-based). However, the PBAE platform has been limited due to variability in polymer size and reproducibility. This variability is intrinsic to its' synthetic scheme: uncontrolled step -growth polymerization via Aza- Michael addition. To better understand the effects of formulation on nucleic acid payload encapsulation, cell uptake, and gene delivery variability in synthesis must be improved. To improve the reproducibility of PBAE synthesis, we are studying the effect of reaction parameters, such as temperature, concentration, and duration on polymer size and efficacy. We report detailed 1D and 2D $^1\text{H-NMR}$ analysis of neat and solvated reaction systems to establish structure, kinetic profile, and M_n parameter. NMR was validated with MALDI-TOF. Previously published GPC methods for analyzing dispersity in polymer size were found to be highly influenced by polymer/column interactions and an alternative method was developed. This data together informs a highly reproducible synthetic scheme. These highly reproducible polymers will be for library development of PBAEs to be tested in vitro. This system is amenable to incorporation of controlled RAFT chemistries paired with the current Aza - Michael addition to obtain micellar co-block polymers, which would provide a next-generation delivery vehicle for drugs and nucleic acids that improves upon existing LNP or PBAE formulations.

PBAE (poly(β -amino ester)) as

