Synthesis and Characterization of Poly(arylene amine sulfone) Copolymers for Proton Exchange Membrane Fuel Cells (93)

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Proton exchange membrane fuel cells (PEMFCs) have been the focus of much scientific research because of their ability to produce renewable energy by the conversion of chemical energy to electrical energy. An integral component of PEMFC is the polymer exchange membrane which facilitates ion transportation from the anode to the cathode. Successful synthesis of membranes that can sustain mechanical strength for long periods of time has been a limiting factor in the advancement of fuel cell technology. The purpose of this research project is to synthesize poly(arylene amine sulfone) (PAAS) copolymers and physical blends with enhanced proton conductivity and mechanical strength to be used as membranes for fuel cells. Unsulfonated and disulfonated PAAS homopolymers and copolymers were prepared by reacting ammeline, dichlorodiphenyl sulfone (DCDPS) and sulfonated dichlorodiphenyl sulfone (SDCDPS) in the presence of either 18-Crown-6 (18-C-6) or tetraethylammonium chloride (TEAC). The introduction of catalysts to nucleophilic aromatic substitution reaction mixture will allow for high molecular weight PAAS polymers with improved mechanical strength to be obtained at shorter reaction times as demonstrated in literature. Future analysis to confirm PAAS structure and the retention of hydroxyl groups for post-modification from ammeline using NMR will be investigated. Studies to understand the effect of catalysts and concentration of sulfonated dichlorodiphenyl sulfone (SDCDPS) on the molecular weight, structure-property relationships, proton conductivity, and fuel cell properties of PAAS copolymers will also be carried out.

Key Words: PEMFC, fuel cells, membrane, ammeline, DCDPS
Synthesis and Characterization of Sulfonated Poly (arylene ether sulfone 2-chloro-4, 6-diamino-1,3,5-triazine) Hybrid Copolymers. (98)

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Poly (arylene ether sulfones) (PAESs) derived from 4,4’-dichlorodiphenyl sulfone (DCDPS) are engineering thermoplastic widely used in industries due to its high glass transition temperature, high thermal stability, good mechanical properties and excellent resistance to hydrolysis and oxidation. In fuel cell, sulfonation of PAES using disulfonated DCDPS (SDCDPS) give membranes with good proton conductivity and mechanical stability at sulfonation levels <50%. Higher degree of sulfonations, disulfonated PAES become mechanically unstable and lose membrane integrity. The goal of this research is to prepare sulfonated poly(arylene ether sulfone 2-chloro-4, 6-diamino-1,3,5-triazine) (PAES-CDT) hybrid copolymers membranes for proton exchange membrane fuel cells. The driving force behind the proposed research is to enhance the fuel cell properties of PAES membranes using a pendant sulfonic acid group. The synthesis of sulfonated PAES-CDT copolymers will be accomplished by adhering either aniline-2-sulfonic acid or 3-aminobenzenesulfonic acid pendant sulfonic acid groups to PAES-CDT backbone to promote proton conductivity. PAES-CDT homopolymers were synthesized via nucleophilic aromatic substitution reaction conditions in the presence of phase transfer catalysts, tetraethylammonium chloride (TEAC) catalyzed or 18-Crown-6 ether (18-C-6). The confirmation of PAES-CDT chemical structure was verified by ATR-FTIR analysis by the appearance of a peak around 2,200-2,250 cm⁻¹ in signaling the formation of the N-C between CDT to DCDPS monomers. Additionally, the retention of the C-Cl bond on the CDT was also demonstrated by the presence of a peak at less than 600 cm⁻¹. Further analysis to confirm the effect of catalyst and pendant groups on the molecular weight and other structure-property relationships will also be investigated.

Key Words: Poly (arylene ether sulfone) (PAES), Triazine, Polymer electrolyte fuel cell (PEMFC), Polymer chemistry, Sulfonated poly (arylene ether sulfone) (SPAES) synthesis

Synthesis of poly(xylitol sebacate) to generate nanoparticles with improved mechanical properties for targeted drug delivery (100)

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Breast cancer is the most common cause of cancer in women and the second leading cause of cancer deaths. HER-2 positive breast cancer is the most aggressive form of breast cancer. 1 in 5 breast cancers have an overexpression of HER-2. Current treatment of HER-2 positive breast cancer involves the use of chemotherapy, radiation, and surgery. The cytotoxicity of chemotherapy treatment creates a drive for the development of more target-specific drug delivery to allow for cancer cells only to be treated. The focus of this research is to improve the formation of biodegradable and biocompatible polymeric nanoparticles using a series of polyesters from various dicarboxylic acids with xylitol. Preliminary research shows that
stable nanoparticles can be synthesized from poly(xylitol sebacate) (PXS) and poly(xylitol suberate) (PXSsub), but not from poly(xylitol dodecanoate) (PXD). SEM imaging of PXS nanoparticles illustrated large nanoparticle formation (264nm) outside the desired nanoparticles size (100nm to 200nm) for chemotherapeutic. The inclusion of suberic acid resulted in smaller PXSub nanoparticles (147nm) were within the desired chemotherapeutic size range. The current research investigates the effect of branching and molar ratios of various diacids on nanoparticle formation, size and copolymer properties. Further studies on the use of protectant groups will also be studied.

**Key Words:** Targeted drug delivery, polymeric nanoparticles, poly(xylitol sebacate)

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**12:15 PM - 1:15 PM**

Investigating the network structure and transport properties of physically- crosslinked lignin-based composites (115)

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Lignin possesses several valuable characteristics, including biodegradability, antimicrobial properties, and chemical activity, that make it attractive for use in the fabrication of sustainable materials. However, the heterogenous nature of lignin has created a bottleneck in our understanding of how the introduction of lignin alters the network structure and ultimately the mechanical and transport properties of these soft composites. To address this issue, we have fabricated a series of lignin-poly(vinyl alcohol) (PVA) composite hydrogels using both crude bulk lignins (CBLs; raw lignin with high dispersity) and ultraclean lignins (UCLs; fractionated lignins with prescribed molecular weights and low dispersity). The soft composites were synthesized via the ‘Freeze-Thaw’ method, whereby physical crosslinks between PVA chains are created. Specifically, the lignin concentration and molecular weight were systematically varied, ranging in lignin concentrations of 20 wt% to 60 wt% and lignin molecular weights of approximately 1250 g/mol to approximately 4200 g/mol. To investigate the transport properties of these membranes, both the water uptake and permeabilities of model penetrants, such as methylene blue and bovine serum albumin were examined. Furthermore, to comprehensively probe the mechanical properties of the hydrogels, the Young’s modulus, shear modulus, as well as the loss and storage were characterized via mechanical indentation and dynamic mechanical analysis. Moreover, leaching of lignin from the lignin composite hydrogels were analyzed using UV-vis spectroscopy. Finally, the antimicrobial properties of the lignin-based soft composites were explored by culturing E.coli and Candida strains and counting the colonies of bacterial growth. Preliminary data indicates that the concentration, molecular weight, and dispersity of lignin modulates the degree of crosslinking, swelling, and mechanical properties of the soft composites.

**Key Words:** hydrogels, lignin, sustainable membranes, biopolymer
**Cyclic Olefin Copolymer Based Anion Exchange Membranes (126)**

*Mr. Jamie Gaitor, Graduate Research Assistant, Department of Chemistry, Carnegie Mellon University*

Ion-transport materials are essential components for a variety of applications including ion exchange membranes, fuel cells, and redox-flow batteries. Polymers bearing pendant ionic groups are viable options for these purposes because the polymer backbone provides mechanical integrity and the ionic groups provide paths for charge conduction. Both the backbone and ionic groups can be tuned toward optimized material properties, performance, and stability. These features have significantly impacted the development of alkaline anion exchanges membranes (AEMs). In alkaline fuel cells, AEMs serve as a solid cationic support for hydroxide transport from cathode to anode. Various polymer backbone and cation pairings have been investigated toward highly robust and conductive thin film membranes. Concerns to be addressed with these materials center around long-term mechanical integrity, alkaline stability, and hydroxide conductivity. Further understanding of how these aspects are influenced by backbone stiffness, cation identity, and polymer architecture would aid toward the fabrication of AEMs with improved mechanical and performance properties. We utilize ring opening metathesis polymerization (ROMP) to develop a series of AEMs derived from cyclic olefin copolymers (COCs). Rigid cyclic substituents are incorporated statistically along the polymer backbone, leading to high Tg (>100 °C) ROMP polymers with good mechanical and film forming properties. For the pendant ionic groups, we implement base stable tetra(dialkylamino)phosphonium cation derivatives as well as the ubiquitous trimethylammonium cation. Comparisons are made regarding the resulting polymer physical properties, ion transport capabilities, and alkaline stability.

**Key Words:** Polymers, Cation, Anion, Membrane, Conductivity