

Synthesis of PEGylated Poly(lactic acid) for Controlled Drug Delivery

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Poly(lactic acid) (PLA) has great potential for use in controlled drug delivery.¹ This is because of its biodegradability and bioresorbability,² which enables drug delivery systems to release drugs upon reaching their destination. Moreover, PLA is synthesized from lactic acid, which comes from renewable sources (e.g. corn).³ When PLA is copolymerized with 2-bromo-3 hydroxypropionic acid, it creates functional sites along the PLA backbone. These sites can be used to covalently attach drugs, small molecules or other polymers. Using poly(ethylene glycol) (PEG) helps to increase the time the drugs spend in the bloodstream before they're broken down. In this project, halogenated PLA was synthesized. PEGylated 2,2,6,6-tetramethyl-1-oxyl (TEMPO-PEG) was grafted onto the halogenated PLA to create micelles for drug delivery purposes.

[1] Spenlehauer, G.; Vert, M.; Benoit, J.R.; Chabot, F.; Veillard, M. *J. Cont. Rel.* **1988**, *7*, 217-229.

[2] Rasal, R.; Janorkar, A.; Hirt, D. *Prog. in Polym. Sci.*, **2010**, *35*, 338-356.

[3] Darensbourg, D.J. *J. Am. Chem. Soc.*, **2011**, *133*, 7237-7237

Synthesis of Poly(urea-amidoamine) (PURAM) Dendrimers using Convergent and Divergent Methods

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Dendritic polymers, or dendrimers, have become major macromolecules of interest due to very precise control of their construction and ligand functionality, a feature that is leading to applications in drug delivery, metallocyclic architectures, and the production of synthetic blood. [1] Named after their unique branching structures, reminiscent of a tree, dendrimers exhibit repeating branching motifs with monomeric units known as dendrons comprising the structure. [2] While many previous dendrimers have exhibited a 1→2 branching motif, poly(urea-amidoamine), or PURAM, exhibits both a 1→3 branching pattern and amino terminated end groups, providing significant functionality compared to its dendrimer predecessors due to an increased amount of surface endgroups. Multiple nitrogen atoms also allow for the coordination of metal atoms, adding to the functionality of the PURAM dendrimers. By employing convergent and divergent methods of synthesis, a new molecular species will be created.

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[2] Perera, S.; Moorefield, C., Newkome, G.; *Dendrimer Chemistry: Supramolecular Perspectives and Applications. Dendrimer Based Drug Delivery Systems: From Theory to Practice*. Wiley and Sons, 2012.

High Surface Area, Flexible Mesoporous Films on Polymer Substrates for Energy Storage

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Mesoporous (MP) materials are of interest for many applications. The focus of this research is on utilizing a high surface area film that can be more easily utilized for energy storage in the form of a supercapacitor. Similar MP carbon films are typically cast onto a rigid substrate in a bulky apparatus. By dip coating onto a thin plastic roll (Kapton - polyimide), a final electrode was produced that could be flexed to moderate angles. TEM and N₂ sorption testing show an ordered nanostructure and reasonable surface area respectively. By adding multiple layers of film the thickness of the active layer was increased. Initial testing shows a slight increase in capacitance. To further increase capacitance Cobalt was added to the films with 10wt% solids being the Co salt. Identical coating methods were used. Surface area of the Co/C nanocomposites dropped slightly. Likely due to graphitization caused by the Co atoms. Capacitance was increased by a factor of ~5. Further work is being done to determine the impact of the cobalt precursor.

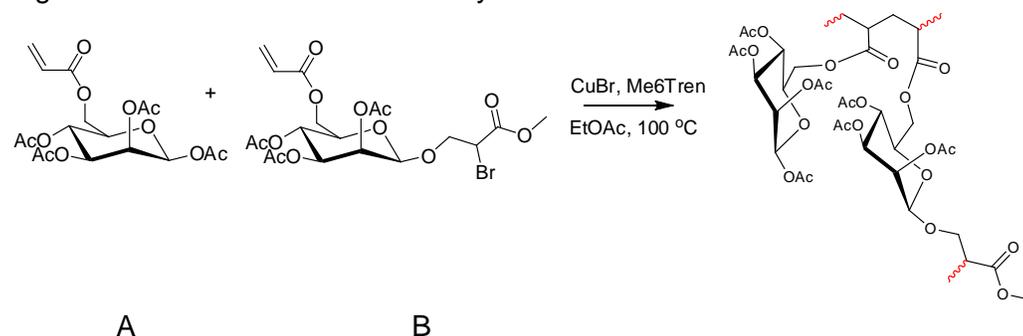
Mass Spectrometry of Glycopolymers

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Glycopolymers synthesized by atom-transfer radical polymerizations of acetyl protected β -D-mannopyranosides were studied using mass spectrometry. Electrospray ionization and matrix-assisted laser desorption/ionization were implemented into the analysis of the synthesized structures. The MALDI MS/MS fragmentations of the molecules composed of A₁B₁, A₂B₁, and A₂B₂ were examined to deduce their structures.

Figure 1. Atom-Transfer Radical Polymerization



The Effect of Fragility on Polymer Confinement

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It is known that confinement of a polymer alters the properties when compared to the bulk. What is not understood is what properties control the magnitude of these confinement effects. Reducing fragility, a measure of the temperature dependence of dynamics, has been shown to reduce the magnitude of these confinement effects in both simulations [1] and experiments [2] performed using additives. We employ molecular dynamics simulations to examine the effect of modifying fragility on confinement. We simulate freestanding polymer films using a coarse-grained bead-spring model and adjust the equilibrium bond length in order to selectively tune the fragility of the system. With reducing fragility we find increasing bulk like behavior near the free surface interface, suggesting a fragility dependence on confinement behavior.

[1] Riggleman, R. A., Yoshimoto, K., Douglas, J. F., and de Pablo, J. J.; *Physical Review Letters*, **2006**, 97, 0455021–0455024.

[2] Ellison, C. J., Ruskowski, R. L., Fredin, N. J., and Torkelson, J. M.; *Physical Review Letters*, **2004**, 92, 095702

AZOBENZENE MODIFIED LITHIUM-ION POLYMER ELECTROLYTE MEMBRANES: PHASE DIAGRAM AND IONIC CONDUCTIVITY

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Conventional liquid electrolyte for Lithium-ion batteries contains volatile solvent, which could bring severe safety problems. Compared with the liquid electrolyte, polymer electrolyte has excellent processability, flexibility and higher safety. They are potential replacement for their liquid counterparts. However, the crystalline nature of polymer been used (such as polyethylene oxide) has greatly limited the ion conductivity of the electrolyte. To overcome this difficulty, succinonitrile (SCN) plastic crystal has been heavily investigated. SCN can plasticize the polymer and ionize the lithium salt, which gives electrolyte a higher ion conductivity.

In this study, we mixed polyethylene glycol diacrylate (PEGDA), SCN, lithium bis(trifluoromethane)sulfonamide (LiTFSI), and azobenzene (AZO) and fabricated the solid state polymer electrolyte membrane (PEM) using photo polymerization. With the aid of ternary phase diagram, we are able to identify wide isotropic region that rendered the completely amorphous state. PEM with high ion conductivity was achieved upon photocuring.

Differential scanning calorimetry (DSC) was used for the construction of phase diagram. The establishment of the binary PEGDA/azobenzene and LiTFSI/azobenzene phase diagrams has been done. Subsequently, AC impedance measurement was performed to determine the ion conductivity of the PEM.

Studying the Adsorption of Polyelectrolyte on a Charged Surface in Aqueous Media

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Despite several bulk phase studies of polymer/surfactant complexes, fundamental understanding of adsorption of such complexes onto solid surfaces in aqueous media is not appreciable. Industries would benefit from a greater understanding by being able to optimize performance of polymer in their products[1]. The goal was to determine the interplay of polymer/surfactant complexes adsorption in aqueous environments on charged planar surfaces. Quartz crystal microbalance was used to determine the mass of polyquaternium-10, PQ-10, adsorbed to an Al_2O_3 surface. It was discovered that concentration of PQ-10 in solution does not affect adsorption. pH 8.5, where the Al_2O_3 surface is negatively charged, better facilitated adsorption than pH 4.5, where Al_2O_3 is positive. The strong coulombic attraction at pH 8.5 and repulsion at pH 4.5 between the surface and the cationic polymer were likely the cause of the results observed. Addition of 0.4 mM SDS increased adsorption at pH 4.5 and slightly decreased it at pH 8.5. This increase at pH 4.5 was likely caused by the SDS partially neutralizing the charge on PQ-10, making the repulsion force weaker and allowing adsorption. Changing the SDS concentration to 6 mM prevented adsorption at pH 8.5, probably because the excessive SDS presence caused PQ-10 to become negative and repelled from the surface. Future work in this area would include analyzing adsorption of the complex at various SDS concentrations.

[1] Ramon, Pamies, et. al. *Langmuir* 2010, 26(20), 15925-15932.