

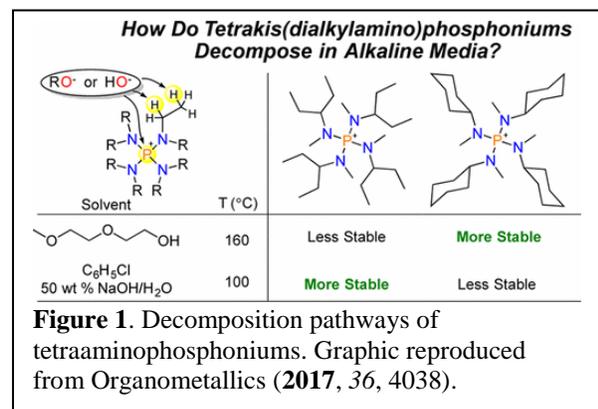
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Title: Controlled Polymerization Approaches to Polyelectrolytes with Resonance-Stabilized Phosphorus Cations
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The incorporation of ionic groups into polymeric materials has been of significant interest to both academia and industry. Electrostatic interactions of ions along a polymer chain alter the chemical and physical properties of a material relative to its neutral derivative. Polyelectrolyte properties are also dependent on the ion tethered to the polymer, as well as its counterion. While most stable cationic polymers are based on quaternized nitrogens, there is also significant interest in exploring 4-coordinate phosphonium-based materials since the larger atomic size and lower electronegativity alters the charge distribution and subsequent properties of the material.

The tetraaminophosphoniums ($[P(NR_2)_4]^+$) are derived from a class of organic superbases known as phosphazenes. These resonance-stabilized cations exhibit excellent chemical stability to caustic anions such as hydroxide they have been employed in phase-transfer catalysis, as well as delivery of reactive anions in organic transformations. In this proposal, we outlined our plans to incorporate tetraaminophosphonium cations into well-defined polymers to afford stable membranes for delivery and transport of reactive anions. Our goal was to use the tools of organic and main group synthesis to build cationic monomers and then employ specific polymerization strategies (controlled radical polymerization) to optimize ion-conduction in these phosphonium-based materials. We anticipated that block copolymers would enable good control over the nanoscale morphology of the final materials and these architectures were the second major objective of this work.

Accomplishments

In the first twelve months, we added an aim to the project since we wanted to obtain a better understanding of how the chemically resistant tetraaminophosphoniums degrade under alkaline conditions. We felt this was critical



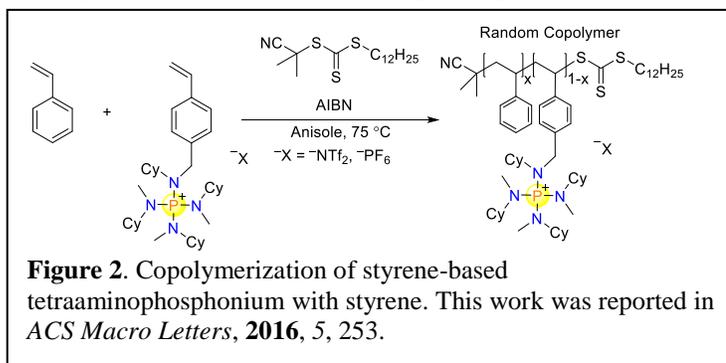
for appropriate cation selection prior to monomer and polymer synthesis. We synthesized a family of eight different cations and explored degradation in alcoholic solvents and under phase transfer conditions. We discovered that in alcoholic solvents, β -elimination seems to be the most prevalent decomposition pathway while in two-phase systems (chlorobenzene and 50% NaOH/H₂O), direct attack at phosphorus was most common. Harsh conditions were employed to bring about degradation (Figure 1), which speaks to the impressive alkaline resistance of these cationic species. The goal of this study was to elucidate how these molecules break down to enable future design improvements and it illustrated how steric constraints around the framework could be used to

improve stability. This paper was published as an article in *Organometallics* last year (2017, 36, 4038).

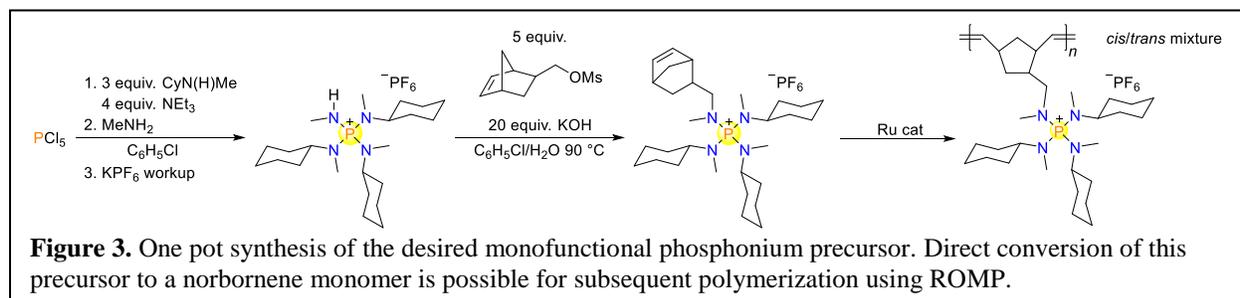
We have continued this stability investigation over the second twelve month reporting period. We have established a computational approach where we evaluate the reaction of hydroxide with phosphonium cations using DFT methods. This has provided additional evidence that attack at phosphorus is indeed the preferred pathway for decomposition, similar to our degradation studies under phase-transfer conditions, eventually leading to formation of the thermodynamically favored P=O bond (final product: $(NR_2)_3P=O$). The computational work has also revealed the stark contrast between alkyl and aminophosphoniums with respect to hydroxide attack. When decorated with dialkylamino substituents, a much higher activation barrier is observed for this direct attack pathway when compared to the simple alkyl substituents. This change in the energy of activation has been tentatively ascribed to the electronic donation (resonance stabilization) from nitrogen lone pairs to available orbitals on phosphorus, as well as the steric repulsion derived from these lone pairs repelling the anionic hydroxide. This work is nearly completed and a full write up as a manuscript is in progress. We are hoping for completion of this work within the next three months.

Our other accomplishments are directly related to incorporation of the phosphoniums into polymer materials. As shown in Figure 2, we discovered that styrene-based phosphonium systems could be employed as co-monomers with styrene in controlled radical polymerization using a typical trithiocarbonate chain-transfer agent (reversible-addition fragmentation chain-transfer polymerization or RAFT). We attempted some other strategies for polymerization of the styrenic phosphonium including atom-transfer radical polymerization and nitroxide-mediated polymerization, though these reactions did not afford the same degree of control as we observed when using RAFT.

As such, we used the RAFT strategy exclusively when trying to make different copolymers. We noted that random copolymers could be synthesized with styrene (as pictured) and with acrylates or methacrylates but concerns over the long-term stability of the acrylate functionality in the presence of reactive anions led us to focus on the styrenic copolymers. Unfortunately, the styrene membranes synthesized using this method were quite brittle and could not withstand mechanical stress. Efforts to make block copolymers of this structure with polyisoprene were envisioned and though the synthetic efforts were successful, the mechanical integrity and flexibility did not improve to the point where robust membrane materials were obtained. Additionally, while we could incorporate this unit into random copolymers with styrene, it was not possible to homopolymerize the phosphonium functionalized styrene monomer, which limited our ability to make tailored block copolymers. Furthermore, the synthesis of this monomer was four steps and required isolation of an air-sensitive intermediate.



To circumvent some of the issues, we developed a new phosphonium precursor synthesis (Figure 3). We can create a single reactive site on the phosphonium cation (N-H moiety) in a one-pot reaction that is amenable to further substitution by deprotonation and reaction with an appropriate electrophile. We have used this method to build styrene monomers for RAFT, but the issues mentioned above with membrane properties has led us to target other polymerizable monomers. We decided to explore norbornene since it is well known to undergo living ring-opening metathesis polymerization (ROMP) in the presence of ruthenium or tungsten/molybdenum initiators. The norbornene monomer can be synthesized according to the two-step sequence as shown in Figure 3, and polymerization of this molecule is facile using a variety of ruthenium-based initiators. Not only can the material be homopolymerized using this strategy, but random and block copolymers have also been synthesized successfully. Several different norbornene derivatives can be copolymerized with the phosphonium. The membrane properties of the hydrogenated copolymers are outstanding, particularly compared to the styrene materials described above. These materials are suitable for testing in fuel cell devices which is an ongoing collaboration with another research team at Carnegie Mellon (Shawn Litster, Mechanical Engineering). Moreover, our interest in the packing and organization of these copolymers has led to a collaboration with Tomasz Kowalewski's group in the Chemistry Department at Carnegie Mellon. We are intending to publish the new synthetic route to the monomer as well as the copolymer data within the next three months. All the synthetic work and characterization has been completed at this point.



Impact of the Research

The support from the ACS PRF has been instrumental in helping the PI establish a strong effort on polyelectrolyte materials and elevate our research profile in this area. The preparation of membrane materials has enabled us to establish new collaborations with research teams at Carnegie Mellon directly (Litster, Kowalewski), as well as collaborations with research groups at other institutions (Coates). Furthermore, this work also allowed us to successfully obtain funding for future support of membrane work in the group.

The student working on this project was able to focus nearly exclusively on research due to his reduced teaching obligations. This helped provide him with good training in synthetic polymer chemistry. Moreover, his efforts in this area helped him secure a postdoctoral position at NYU in macromolecular science. A second student has picked up this project and she was supported for her first summer as a graduate student and really enabled us to complete the block copolymer work.