Developing Rigid Polymer Electrolytes

by James F. Snyder

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ABSTRACT

This report is a reprint of a paper published in Polymer Preprints, Vol. 45, No. 2, by the American Chemical Society in Fall 2004. The focus of this research is the synthesis and characterization of highly conductive rigid polymer electrolytes. Traditional solvent-free polymer electrolytes allow for long-range ion diffusion by means of ion-polymer coupling in the amorphous phase of the polymer host. Coupled systems typically require low glass transition temperatures for fast ion diffusion, resulting in poor mechanical properties when fillers are not added. The effort described here explores polymer electrolytes in which ion diffusion is decoupled from polymer motion. These materials allow for the development of polymers with desirable structure and fast ion transport at low temperatures. This is accomplished through the design of high dielectric polymer hosts with large internal free volume. The recently reported step polymerization using vinylene carbonate and oxalic acid derivatives was modified to eliminate the formation of a dominant byproduct, and extended to include more robust but less reactive monomers, including derivatives of 3-sulfolene, maleimide, and maleic acid.

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DEVELOPING RIGID POLYMER ELECTROLYTES

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Introduction

Polymer systems have undergone development in recent years for use as electrolytes in modern power source applications such as fuel cells and secondary batteries. Polymer electrolytes have many physical advantages over other types of electrolytes, including the ability to be modified to exhibit a broad range of mechanical properties and the ability to be cast into thin films for use in portable or flexible applications. Significant focus in the literature has been to improve electrochemical performance while maintaining reasonable mechanical properties. Less attention has been given to providing enhanced structural properties to the membrane. One reason for this concerns the mechanisms for ion diffusion in polymer systems. Ion diffusion in solvent-free polymer electrolytes has been shown to occur by means of short-range polaron hopping, long-range ion hopping, and long-range conduction dependent on segmental motion of the polymer host. An increase in polymer segmental mobility, reflected in depression of the polymer glass transition temperature, generally leads to an increase in ion conductivity and a decrease in polymer structure. An apparent interaction exists between rigid structure and ion diffusion for solvent-free polymer electrolytes.

A common solution to providing enhanced electrochemical properties has been to add plasticizers to thin film membranes. The addition of liquid plasticizers to polymer scaffolds such as PVDF results in gels with high ion conductivities. However, gels have added complications with solvent flammability and solvent management. The addition of small particle inorganic plasticizing fillers to solvent-free polymers typically results in more robust membranes, but conductivities are lower than those observed in gels. Another method for developing structural electrolytes involves the synthesis of high dielectric polymers with rigid architecture that have a large internal volume and ion diffusion decoupled from polymer motion. Although a solvent-free and particle-free highly conductive rigid polymer electrolyte is still unreported, several advances have been made in designing these systems. Examples include glassy electrolytes, polymer-in-salt systems, and polymers based on common solvents such as poly(vinyl alcohol) and poly(vinyl carbonate). The project presented here is based upon the latter technology.

Experimental

Materials. All of the reagents used in this study were purchased from Alpha Aesar and used without further purification, except where noted.

Methods. Step polymerization of cyclic monomer vinylene carbonate or 3-sulfone with oxalic acid or malonic acid was attempted by chemical reaction according to method described in the literature, with variations as described below. The anticipated polymers are shown in Figure 1. Cyclic monomers, including vinylene carbonate and 3-sulfone, were quantitatively brominated on a 10 g scale using 1.2 molar equivalent of liquid bromine in 50 mL of carbon tetrachloride (vinylene carbonate) or 50 mL of 40% chloroform in carbon tetrachloride (3-sulfone). The variation in reagent polarity accounts for the different choice of solvent. Dibromo-vinylene carbonate (1) was purified by distillation under vacuum. Dibromo-sulfone (2) was purified by recrystallization from methanol. Silver salts of the diacid monomers were accomplished by addition of silver nitrate and oxalic acid to form PSOX (PVICOX, including DSC of the pure polymer and impedance measurements of the polymer mixed with lithium triflate. However, repeating the reaction with substitution of vinylene carbonate by 3-sulfone to form PSOX also resulted in generation of the same product. In some cases, small amounts of minor product was collected that may correspond to the expected polymers. Apparent byproduct of the cyclic reagent was also recovered. Analysis of the major product was undertaken to evaluate the side reaction that occurred and correct for it.

Results and Discussion

The literature reaction to form the AB polymer of vinylene carbonate and oxalic acid, referred to as PVICOX and shown in Figure 1a, was explored in depth and extended to less reactive monomers to form compounds such as that in Figure 1b, referred to as PSOX. Reaction between a brominated cyclic alkene and the silver salt of a diacid is not evident elsewhere in the literature and is of interest for development of similar materials.

The reaction under the reported conditions was found to apparently proceed to a nonpolymer byproduct exhibiting properties similar to those expected of PVICOX. Characterization is similar to that reported of PVICOX, including DSC of the pure polymer and impedance measurements of the polymer mixed with lithium triflate. However, repeating the reaction with substituted vinylene carbonate by 3-sulfone to form PSOX also resulted in generation of the same product. In some cases, small amounts of minor product was collected that may correspond to the expected polymers. Apparent byproduct of the cyclic reagent was also recovered. Analysis of the major product was undertaken to evaluate the side reaction that occurred and correct for it.

Increases in temperatures appear to reduce the yield of all products by catalyzing the decomposition of silver oxalate. However, temperatures higher than 50°C were necessary to catalyze reactions involving the 3-sulfone derivative. GPC analyses of the major product were inconclusive, although no evidence was found for polymer above MW 1000. Extensive 1H NMR using a Bruker 600 MHz AVANCE system revealed only two peaks in the major product, δ161 (quaternary carbon) and δ45 (CH3). The quaternary peak corresponds to oxalate, but the absence of peaks corresponding to vinylene carbonate further suggest that the cyclic reagents are not included in the major product. The carbon peak at δ45 is unknown. 13C NMR revealed only one peak, δ25 (s), apparent through comparison of individual spectra generated using water and DMSO as solvents. Comparison was made to the theoretical spectra of a variety of oxalate and urea derivatives using ChemDraw’s NMR prediction capabilities. It was found that both the 1H and 13C NMR spectra exactly match the expected spectra for tetramethyloxamide, the dimer form of DMF.

Since the reagents may have reacted with the solvent, the solvent system was varied from the DMF/water solution. The only two systems found to appreciably sustain reactions were DMAC/water and DMSO/water. In both situations the unknown byproduct described above was not observed. The resulting products had NMR spectra similar, but not exactly corresponding, to those expected of the polymers.

Table 1 lists the results from elemental analysis. The data in Table 1 was generated using a Perkin Elmer Series II CHNS/O Analyzer, model 2400, in CHNS mode. Samples were dried under vacuum to constant mass prior to analysis. Each data point is an average over two samples. Deviation from the average is limited to ±0.5 wt% for each data point. The mass that is unaccounted for may be attributed primarily to oxygen. The sulfur content in samples 1-3 correspond to a very low number of sulfur atoms and may be attributed to artifacts or noise. This is particularly true for trial 1, in which no sulfur bearing compound was introduced into the reaction. Comparing sample data taken from the brominated sulfone reagent with the theoretical expectations confirms that the instrument is accurate at moderate sulfur content.

The results in Table 1 support the hypothesis that silver oxalate reacts with DMF to form a byproduct. The data in trials 1 and 2 are within experimental error of each other, and the hydrogen and nitrogen contents are very different from those expected of PVICOX or PSOX. Residual DMF or water cannot account for the discrepancy, and the samples were prepared in such a way that there is little residual solvent expected. The data does not correlate exactly to that expected of tetramethyloxamide either, but it is a much better fit. The product is still considered to be unknown at this time and further tests are underway.

Switching the solvent appears to eliminate formation of the unknown product. Trials 3 and 4 show a much different elemental ratio than trials 1 and 2, and they are also different from each other. Although they do not correspond exactly to the expected spectra for PVICOX or PSOX, they are a better fit. These products are also considered to be unknown at this time and further tests are underway.
Table 1. Sample Properties by Elemental Analysis

<table>
<thead>
<tr>
<th>Trial</th>
<th>Cyclic Monomer</th>
<th>Solvent</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Vinylene carbonate</td>
<td>DME/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>34.7</td>
<td>6.1</td>
<td>9.1</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>Sulfolene</td>
<td>DME/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>32.6</td>
<td>6.1</td>
<td>9.4</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Vinylene Carbonate</td>
<td>DMSO/H&lt;sub&gt;2&lt;/sub&gt;O or DMAC/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>35.7</td>
<td>5.0</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>Sulfolene</td>
<td>DMAC/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>50.3</td>
<td>4.2</td>
<td>3.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Sample: 3-sulfolene, brominated (Theoretical)</td>
<td></td>
<td></td>
<td>17.3 (17.3)</td>
<td>2.0 (2.2)</td>
<td>0 (0)</td>
<td>11.3 (11.5)</td>
</tr>
<tr>
<td>Theoretical: PVICOX (dihydrate)</td>
<td></td>
<td></td>
<td>34.5 (28.6)</td>
<td>1.2 (2.9)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Theoretical: PSOX (dihydrate)</td>
<td></td>
<td></td>
<td>34.6 (29.8)</td>
<td>2.9 (4.2)</td>
<td>0 (0)</td>
<td>15.6 (13.3)</td>
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<tr>
<td>Theoretical: Tetramethyloxamide (dihydrate) (tetrahydrate)</td>
<td></td>
<td></td>
<td>50.0 (40.0)</td>
<td>8.4 (9.0)</td>
<td>19.4 (15.6)</td>
<td>0 (0)</td>
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Conclusions
Reactions between dibromo-substituted cyclic alkenes and diacid silver salts were explored as possible means to step polymerization. Apparent problems with published reaction conditions were elucidated and possibly eliminated. Further characterization of the products is underway. Further variation of both reagents is also underway, with particular emphasis on replacement of oxalate with malonate. Due to less activation of the end groups, malonate is found to react less readily than oxalate and requires addition of nonprotic bases such as triethylamine or pyridine to advance the reaction at room temperature.

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