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PHYSICAL PROPERTIES OF LI ION CONDUCTING POLYPHOSPHAZENE BASED POLYMER ELECTROLYTES

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ABSTRACT

We report a systematic study of the transport properties and the underlying physical chemistry of some polyphosphazene (PPhz)-based polymer electrolytes. We synthesized MEEP and variants which employed mixed combinations of different length oxyethylene side-chains. We compare the conductivity and ion-ion interactions in polymer electrolytes obtained with lithium triflate and lithium bis(trifluoromethanesulfonyl)imide (TFSI) salts added to the polymer.

The combination of the lithium imide salt and MEEP yields a maximum conductivity of $8 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$ at room temperature at a salt loading of 8 monomers per lithium. In one of the mixed side-chain variations, a maximum conductivity of $2 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ was measured at the same molar ratio. Raman spectral analysis shows some ion aggregation and some polymer - ion interactions in the PPhz-LiTFSI case but much less than observed with $\text{Li CF}_3\text{SO}_3$. A sharp increase in the T_g as salt is added corresponds to concentrations above which the conductivity significantly decreases and ion associations appear.

INTRODUCTION

Solid polymer electrolytes (SPE) have been of interest for use in lithium secondary batteries. However, most SPE's have relatively low ionic conductivities. The highest ionic conductivities reported for non-plasticized polymer electrolytes have been in the $10^{-4} \Omega^{-1}\text{cm}^{-1}$ range. These are an order of magnitude or more lower than the typical conductivity of gelled electrolytes and liquid electrolytes.

Shriver, Allcock and coworkers have reported the use of electrolytes, such as poly bis 2(2methoxyethoxy ethoxy)phosphazene (MEEP), which are built on poly(phosphazene) (PPhz) backbones. The resulting polymer electrolytes exhibit good conductivity but poor mechanical properties. The PPhz is a highly flexible, low T_g polymer which allows significant synthetic versatility--variants of MEEP are relatively easily synthesized. We are exploiting that versatility to probe the effects of various side-chain structures on transport properties of the polymer electrolytes.

In oxyethylene-based SPEs, lithium interacts to a certain extent with oxygens in the oxyethylene segment. In the conduction process, the lithium ion moves from one

oxygen coordination site to another assisted by polymer motions. For lithium to move, a fluctuation of the polymer leading to a configuration which allows lithium to slip from one O site to another must be achieved. Thus, the lithium lifetime near any given site is determined by the strength of its interactions in that site, which is controlled by the O-Li interaction and the polymer dynamics. This picture amounts to a dynamic complexation of the lithium.

We have synthesized several different PPhz-based polymers, including poly bis- 2(2methoxyethoxy ethoxy)phosphazene (MEEP) and two variants of MEEP in which the etheric side chain lengths are mixed and varied. The first variation (Mixed MEEP A) has methoxy end-capped ethoxy chains of lengths 2,3, and 7 in 1/6, 1/6, 1/6 ratios, respectively, with the remaining 1/2 of the side chains methoxy and ethoxy moieties. The second variation (Mixed MEEP B) has methoxy end-capped ethoxy chains of length 2,3, and 7 in 1/3, 1/3,1/3 ratios, respectively.

The PPhz-based polymer used are comb-type, with lithium ions interacting with oxygen sites in the between the teeth of the comb. The mixed side-chains are employed in the hope of achieving structures with poorer side-chain packing, allowing lithium ions to more easily slip along the polymer because of constraints on the formation of the dynamic complex as well as because of more facile passing along of the lithium.

Two different salts were used in this work: lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium trifluoromethane sulfonate (triflate or LiTf). The TFSI anion is quite bulky with a delocalized electron density, promoting a high degree of dissociation, and plasticizes the polymer.

EXPERIMENTAL

Materials

MEEP and the mixed length etheric side chain polyphosphazenes were synthesized by first using sodium salts of the appropriate etheric alcohol to replace the chlorines on the cyclic dichlorophosphazene trimer. To ensure that all the chlorine had been replaced, an excess amount of the sodium etheric alcohol was added. For the mixed side chain lengths, three sodium etheric alcohols were introduced in a non-sequential substitution. Each was stoichiometrically 1/6 for mix A and 1/3 for mix B of the total solution used in the substitution. For mixed MEEP A the remainder of the substitution was with sodium methoxide and sodium ethoxymethoxide. After the substitution, the trimer underwent a ring opening polymerization. The polymers were extensively purified and then dried under vacuum.

$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ was obtained from 3M and used as received. $\text{Li CF}_3\text{SO}_3$ (Aldrich) was dried under vacuum for 48 hrs. at 60°C. THF (Aldrich) 99.9% was used as received.

Sample Preparations and Testing

All sample preparations were done in an Argon filled Vacuum Atmosphere Company glove box, using standard air and moisture sensitive techniques. The polyphosphazenes were dissolved in THF. The polymer, in solution, was mixed with appropriate amounts of salt to give the desired monomer: mole ratios. The polymer:salt solutions were mixed and let stand for 24 hr.

Conductivity/AC Impedance. Polymer:salt complexes in THF were solution cast onto stainless steel discs. The samples were dried using an absorption pump and heat (60 °C), for 12 hr. Once the sample was dry, a second stainless steel disc was placed on top of the polymer. The sandwiched sample was placed in a conductivity cell designed and built in house. This cell keeps the sample at constant contact pressure, while allowing the thickness to be measured in situ. Temperature was controlled using a stainless steel casing enshrouded in heating tape. Samples were allowed to equilibrate for 30 min. before a measurement was taken. AC impedance measurements were taken using a Solatron 2000 impedance analyzer from 1 MHz to 1 Hz. The Nyquist plot gives a linear relation. The resistance was taken as the intercept of the real axis.

Differential Scanning Calorimetry. Polymer: salt complexes were cast into pre-weighed aluminum pans and allowed to dry. The pans were then hermetically sealed and weighed. The measurements were made on a Perkin Elmer DSC7 fitted with a cryogenic head and nitrogen atmosphere. Scans were taken from -100 °C to 0 °C at a rate of 10 °C/min.

Raman Spectroscopy. Raman samples were prepared using low grade Kontes NMR tubes (5 mm). Solutions of the polymer:salt complexes were poured into the tubes and the excess solvent taken off by an absorption pump and heating (60 °C). This process was repeated until the amount of sample needed was obtained. Spectra were measured using a Nicolet from 3500 cm^{-1} to 100 cm^{-1} .

RESULTS

Conductivity

Conductivities were determined by AC impedance analysis. We varied the composition from 2:1 to 16:1 (Monomer: LiX) for each polymer and each salt. The temperature was modulated from room temperature (23 °C) to 80 °C. Figure 1 shows how composition changes influence the conductivity. In each system, we observe a maximum in conductivity at approximately 8:1 (Monomer : LiX). These measurements were taken at room temperature (23 °C). The MEEP : $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ maximum value is 8.0×10^{-5} S/cm. The mixed side chain length systems give values of 1.0×10^{-4} s/cm for A and 2.1×10^{-4} S/cm for B. These are some of the highest reported room-temperature conductivities for non-plasticized solid polymer electrolytes. Figure 2 shows the temperature dependence of several concentrations of lithium imide in mixed MEEP B. These curves follow an Arrhenius function. Note that at 60 °C, the

conductivity is in the 10^{-3} S/cm range for majority of the concentrations studied. Curves for MEEP and mixed MEEP A are similar.

Differential Scanning Calorimetry

Differential scanning Calorimetry was used to determine the glass transition temperatures of the polymer : salt complexes. Figure 3 shows the T_g as a function of concentration for regular MEEP and Mixed MEEP A with lithium imide. The T_g of the Mixed MEEP is higher than that of the regular MEEP due to the lengthy side chains. Note the sharp increase in T_g of each polymer type with increasing salt loading above roughly 8:1 monomer : salt ratios. This corresponds to the ratios at which conductivity starts to decrease. This suggests that the salt is hindering polymer motions and in effect decreasing the conductivity.

The glass transition temperatures are well below room temperature (-80 °C for MEEP, -70 °C for mixed MEEP A). Thus, our polymers are amorphous and flow under slight pressure at room temperature. Mechanically these polymers are unfavorable for batteries. However, this can be helped somewhat by cross linking and other measures. Our main objective in this work is to understand the relationship between structures we build in the polymer and the conductivity or underlying properties.

Raman Spectroscopy

Raman spectroscopy was used to study the effects of ion associations and ion polymer interactions. There are three regions of interest in the spectra; the SO_3 symmetric stretching mode in the lithium triflate, the CF_3 bending modes in both the lithium imide and the lithium triflate, and the Li - O stretching mode of the polymer with both salts. Both the SO_3 symmetric stretching modes and the CF_3 bending modes and their sensitivity to ion - ion interactions have been discussed previously by Schantz and Torell (1-3), and Frech (5 & 6), respectively. These bands were analyzed by modeling and group theory. These previous analysis have mainly focused on the Li Triflate salt. Very little work has been done previously on Li TFSI. The Li - O stretching mode was assigned by Shriver (7). The SO_3 and CF_3 regions give information on ion associations such as ion pairing and ion aggregation. The Li - O region gives information on the ion - polymer interactions. Figure 4 shows the spectra of the salt free polymer and the two salts studied, with the areas of interest marked.

Figure 5 shows the symmetric stretching mode of SO_3 from the lithium triflate. At low salt loadings (16:1) the spectra shows about 50% free ions (1030 cm^{-1}) and 50% ion pairs (1040 cm^{-1}). As the salt concentration is increased the amount of free ions decrease and ion aggregates start to appear at 1055 cm^{-1} . This is consistent with previous work of Schantz, Torell, Jacobsson, and Frech (1-6). The same general trend is seen in the CF_3 bending region (5 & 6) (figure 6), although much less ion association are seen with the lithium imide. In fact only a small portion is seen to form

ion pairs and there is no evidence of ion aggregates. The same region with lithium triflate (figure 7) shows much more significant ion pairing. Notice that the ion pairing and ion aggregates become significant at ratios of about 8:1 monomer : salt. This corresponds to the decrease in conductivity. In figure 8 we see the effects the salt has on the polymer. The Li - O stretching becomes more pronounced above a salt concentration of 8:1 monomer : salt, indicating that the lithium ion is more strongly interacting with the polymer. The ratio where this becomes apparent correlates with the increase in Tg and the decrease in conductivity.

CONCLUSIONS

In all of the polymer : salt systems we have studied, we see a maximum in conductivity around 8:1 monomer to salt ratios. At higher concentrations of salt, the conductivity decreases significantly. Concentrations higher than 8:1 also exhibit ion pairing, ion aggregation and strong ion - polymer interactions. At these concentrations the polymer is rapidly increasing in structure as seen by the glass transition temperatures. The ion associations with other ions and with the polymer, as well as the polymers mobility have a significant impact on the conductivity.

In varying the etheric side chain lengths we have improved the conductivity by a factor of about 3. The mixed MEEP B, which had all long chains, showed the best conductivity of the three polymers studied. Mixed MEEP A, which contained half long chains and half really short side chains, showed slightly lower conductivities and the conductivity decreased faster than the other polymers. MEEP, with all side chains of the same length, exhibited the lowest conductivity of them all. Since signs of ion associations appear at the same concentrations and are about the same intensity for each of the polymers, the trend suggests that the different side chain lengths are assisting in Li⁺ motions. The short chains in mixed MEEP A may be trapping some of the ions thus decreasing the conductivity. There may also be a deficiency of oxygens to coordinate the lithium ions thus causing the rapid decrease in conductivity at high concentrations.

The two salts used behaved as expected. The Li TFSI, with its bulky anion, gave at least an order of magnitude higher conductivities than the lithium triflate. Ion pairing and ion aggregates were significantly more abundant with the lithium triflate, while very little was seen with the Li TFSI. The Arrhenius behavior of the polymer: salt complexes suggest that the lithium is not going far between the side chains but is staying at the outer edges. This implies that the use of an even larger anion may increase the conductivity even more. This is clearly an area which need to be studied further.

We have seen that by varying the length of the etheric side chains on polyphosphazene backbones and by using salts with bulky anions that dissociate well, we can improve the conductivity by about a factor of 3. Further work is needed to determine the optimum side chain lengths and ratios of lengths, determine the effects of larger anions, and improve on the mechanical properties of the polymers and the effects the improvements have on the transport processes.

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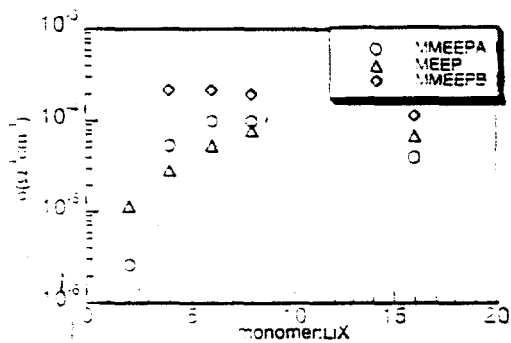


Figure 1. Concentration dependence for conductivity of polyphosphazenes with Li TFSI.

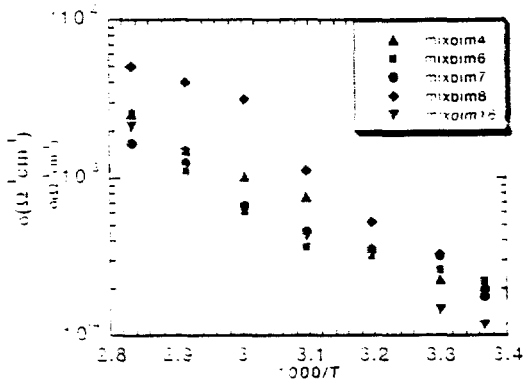


Figure 2. Temperature dependence of Mixed MEEP B with Li TFSI at different concentrations.

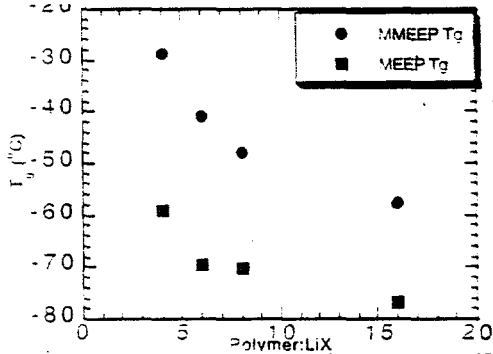


Figure 3. Glass transition temperatures as a function of concentration of Li TFSI.

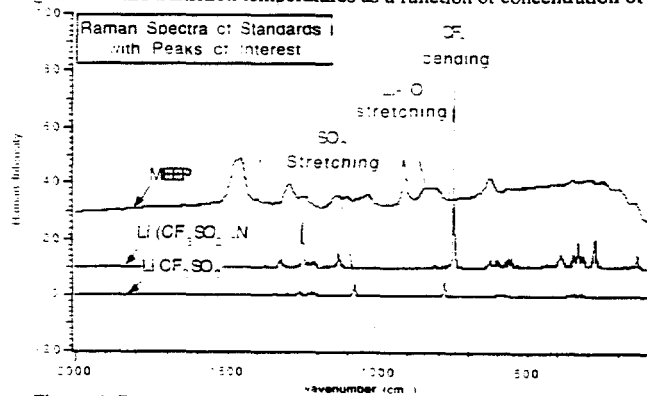


Figure 4. Raman spectra of polymer and salt backgrounds.

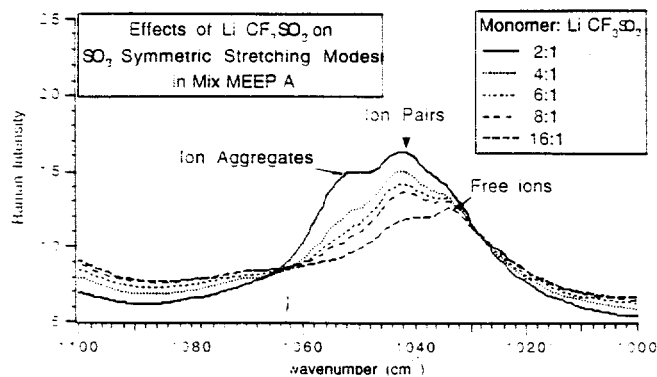


Figure 5. SO_3 symmetric stretching region of Mixed MEEP A with Li Triflate.

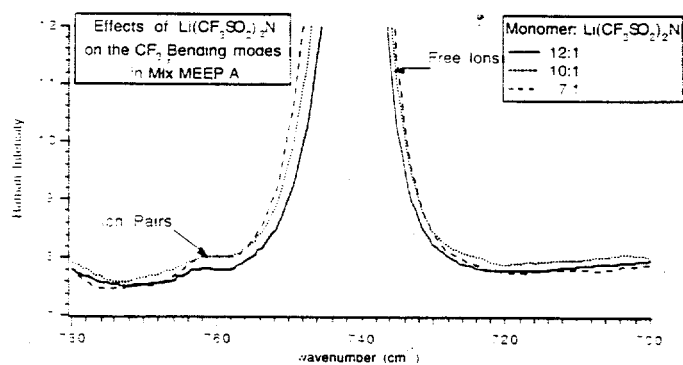


Figure 6. CF_3 bending region of Li TFSI in Mixed MEEP A.

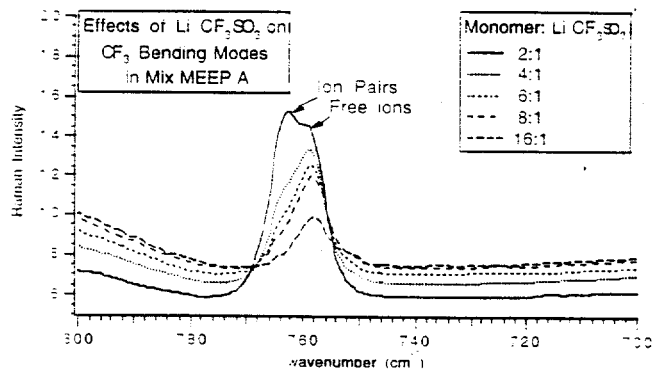


Figure 7. CF_3 bending region of Li Triflate in Mixed MEEP A.

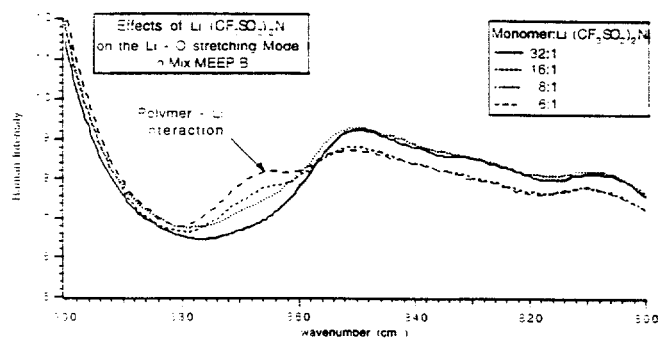


Figure 8. $\text{Li}-\text{O}$ stretching mode of LiTFSI in Mixed MEEP B.