Macromolecules **1996,** *29,* 3499−3506

Effect of Plasticizers on Ionic Association and Conductivity in the $(PEO)_9LiCF_3SO_3$ System

Sangamithra Chintapalli and Roger Frech*

Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, Oklahoma 73019

Received October 23, 1995; Revised Manuscript Received February 5, 1996⊗

ABSTRACT: Infrared spectroscopic studies of the effect of the plasticizers ethylene carbonate, tetraethylene glycol, and tetraethylene glycol dimethyl ether on the $(PEO)_xLiCF_3SO_3$ system are reported. These data are augmented by measurements of the ionic conductivity. Relative concentrations of the various ionic species present have been determined as a function of plasticizer content. The plasticizers appear to preferentially interact with the crystalline PEO phase in the $(PEO)_xLiCF_3SO_3$ complexes, although the relative amount of the compound $(PEO)_3LiCF_3SO_3$ decreases with addition of plasticizer. The net effect of the addition of plasticizer is to create ionically-conducting pathways of amorphous PEO containing dissolved ionic species.

1. Introduction

The ion transport properties of lithium ion polymer electrolytes have led to their use in high-energy density batteries and other solid state electrochemical devices.[1−3] However, Li^+-based polymer electrolytes exhibit disadvantages which affect the commercialization of such cells.[4,5] One such drawback is the low ionic conductivity of the electrolyte at ambient temperature. In particular, poly(ethylene oxide)−lithium salt-based electrolytes have been the focus of a wide variety of fundamental and application-oriented studies.[6−11]

Although PEO is a good solvent for alkali metal salts owing to its excellent solvating properties, its crystallinity is a drawback for electrochemical applications because ion conduction appears to occur in the amorphous domains.[12] Structural and phase diagram studies indicate that at least three phases can be present in the PEO−$LiCF_3SO_3$ system: (a) crystalline PEO below the melting point at 60 °C, (b) the crystalline compound $(PEO)_3LiCF_3SO_3$, and (c) amorphous PEO with dissolved salt. It is this latter phase that is believed to be responsible for the ionic conduction.[12−14]

Electrolytes with higher ionic conductivities can be made by introduction of plasticizers, which are often low molecular weight aprotic organic solvents such as propylene carbonate (PC), ethylene carbonate (EC), or oligomeric poly(ethylene glycols) and their derivatives.[2,4] Plasticizing additives increase the free volume of the polymer and hence lower the glass transition temperature of the polymers.[15] DSC studies by Wang et al.[16] revealed that additives reduce the content of the PEO crystalline phase in polymer electrolytes at room temperature. It was also shown in their work that the endothermic peak corresponding to the $(PEO)_3LiCF_3SO_3$ crystalline compound did not change with the addition of plasticizers. However, the glass transition temperature was lowered to a great extent.

There have been several reports describing the effect of plasticizers in polymer−salt complexes using conductivity, EXAFS, DSC, and X-ray diffraction techniques.[15,17−22] Several characterization methods such as vibrational spectroscopy, NMR, conductivity, and viscosity have been utilized to study mixed solvent systems with dissolved lithium salts.[23−26] There are a few reports[16,18,22] of studies involving DSC, conductivity, and electrochemical applications of plasticized PEO−$LiCF_3SO_3$ electrolytes. The conductivity studies show that the ionic conductivity is enhanced by orders of magnitude with the addition of plasticizer.

In this paper a vibrational spectroscopic study of the role of plasticizers in the PEO−$LiCF_3SO_3$ system is reported. The results of conductivity measurements are also utilized. The plasticizers used in this study are ethylene carbonate (EC), tetraethylene glycol (TEG), and tetraethylene glycol dimethyl ether (TEGDME). The 9:1 PEO:$LiCF_3SO_3$ composition was chosen for this study, although the effect of EC in the PEO:$LiCF_3SO_3$ system was also studied as a function of O:M ratio.

2. Experimental Section

PEO (MW 4×10^6, Aldrich), TEG (194, Aldrich), TEGDME (222, Aldrich), and EC (Aldrich) were used as received. Lithium triflate (Aldrich) was dried at 100 °C in vacuum. A solution of the desired amounts of PEO, plasticizer, and lithium triflate dissolved in a sufficient amount of acetonitrile was stirred overnight at room temperature. After continuous stirring, the solution was allowed to stand at room temperature for 24 h to facilitate degassing. To obtain thin films, the gelatinous polymer solution was cast on a Teflon support. Solvent evaporation led to pinhole-free films of uniform thickness (on the order of 10−20 μm). The films were then dried in a vacuum oven at ∼100 °C for ∼20 h.

For infrared studies, thin films were made on CsI windows of dimensions 38 mm × 19 mm × 4 mm and dried at ∼80 °C under vacuum for 30 min. However, samples involving EC were blow-dried at room temperature to avoid loss of EC. The IR studies were carried out with a Digilab FTS-40 Bio-Rad infrared spectrometer in the absorbance mode in the region 4000−400 cm^{-1} and at a resolution of 2 cm^{-1}. Conductivity measurements were made using a Hewlett-Packard 4192A LF impedance analyzer in the temperature range 25−100 °C controlled to an accuracy of ±1 °C with a Cole-Parmer Digi Sense temperature controller. The frequency range used for this study was 5 Hz−13 MHz. The thin films prepared as described above were used for these measurements. Alternately, films were directly cast in the sample holder.

In the EC samples, the PEO:Li ratio is maintained at 9:1. An amount of EC has been added which is expressed as a weight percent of the PEO present:

$$y\,\% = Wt_{EC}/Wt_{PEO} \times 100$$

The composition is represented as $(PEO)_9LiCF_3SO_3 + y\,\%$ EC. In the TEG and TEGDME samples, the overall ether oxygen:

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

S0024-9297(95)01564-6 CCC: $12.00

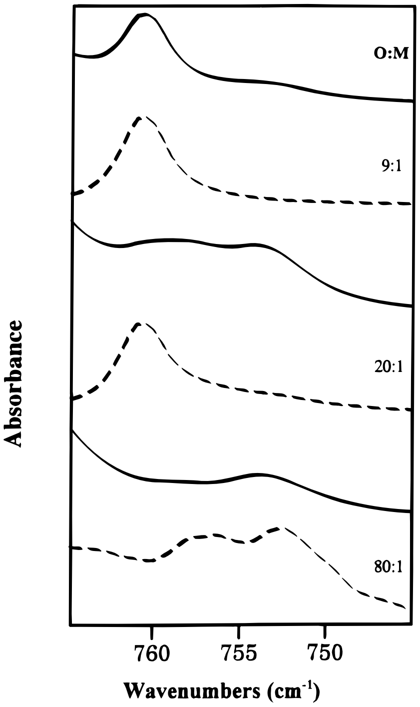

Figure 1. Comparison of IR spectra of $(PEO)_xLiCF_3SO_3 + 50$ wt % EC (solid lines) and $(PEO)_xLiCF_3SO_3$ (dashed lines) at different O:M ratios in the $\delta_s(CF_3)$ spectral region.

Li ratio is maintained at 9:1. However, a portion of the ether oxygens are supplied by the host PEO and a portion by the plasticizer P. The ratios of the PEO to P ether oxygens used in this study are 3:1, 1:1, and 1:3. The compositions are represented as $(PEO+P)_9LiCF_3SO_3$, where P = TEG or TEGDME. TEG and TEGDME were used as substituents while EC was used as an additive.

3. Results and Discussion

3.1. Ethylene Carbonate as a Plasticizer. 3.1.1. Effect of EC on Ionic Association. In Figure 1, the infrared spectra (solid line) of $(PEO)_xLiCF_3SO_3 + 50$ wt % EC with different O:M ratios (or x values) in the region 775−745 cm^{-1} are shown. In addition, the infrared spectra of the analogous complexes without EC are given for comparison (dashed lines). In these latter spectra it is seen that more highly associated ionic species are formed with increasing $LiCF_3SO_3$ concentration, as has been previously observed.[27,28] The bands at 753, 757, and 760 cm^{-1} correspond to the symmetric bending mode of CF_3 [denoted as $\delta_s(CF_3)$] of the “free” triflate ion, ion pair, and the compound, $(PEO)_3LiCF_3SO_3$, respectively. These assignments are consistent with an ab initio calculation[29] and a normal coordinate analysis.[30] Here, “free” triflate ion refers to the triflate species with no degree of ionic association but which may exhibit weak interactions with the polymer host. In the 9:1 sample, the band at 760 cm^{-1} due to the 3:1 compound is present even after the addition of the EC; however, there is a slight increase in the intensity of the “free” ion band at 753 cm^{-1}. The addition of EC to the 20:1 complex is more dramatic. The 760 cm^{-1} band decreases remarkedly in intensity, with a pronounced increase in the “free” ion band at 753 cm^{-1} and a broad feature at roughly 757 cm^{-1}. There is no trace of the 3:1 compound in the 80:1 complex. Instead, the ion pair band at 757 cm^{-1} and the “free” ion band are the prominent features. With the addition of EC, the intensity of the “free” ion band increases at the expense of the ion pair band.

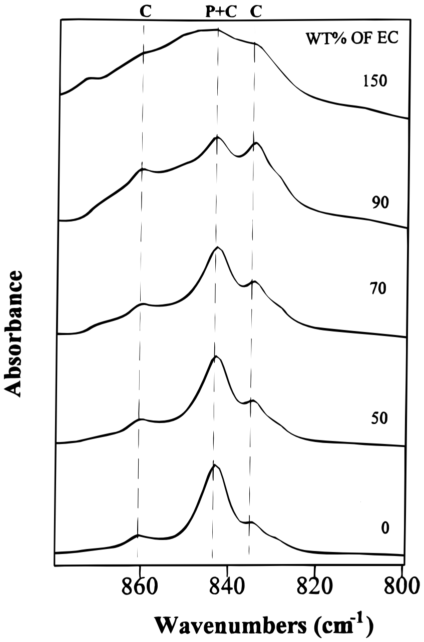

Figure 2. IR spectra in the spectral region 880−800 cm^{-1} as a function of EC wt % for the system $(PEO)_9LiCF_3SO_3 + y$ % EC. C = crystalline compound; P = crystalline PEO.

3.1.2. Effect of EC on Local PEO Conformation. Vibrational bands in the region 1000−800 cm^{-1} (Figure 2) are associated with vibrational modes due to CH_2 rocking coupled with C−O stretching vibrations of the PEO molecule.[31] The band at 844 cm^{-1} is ascribed primarily to the rocking motion of CH_2 units [symbolized as $r(CH_2)_a$]. This band is sensitive to the interaction of the cation with the polymer backbone[31] and hence is ideal for monitoring the changes in the conformation of PEO with the addition of EC. Temperature-dependent infrared spectroscopic studies of $(PEO)_9LiCF_3SO_3$ suggest that the 844 cm^{-1} band contains contributions from both the 3:1 compound and the pure PEO phase.[32] There are, in addition, two very weak bands present at 857 and 828 cm^{-1} which are due to pure PEO and can be seen only in an expanded scale. Upon complexation with lithium triflate, two peaks become visible at 833 and 860 cm^{-1} which are due to the compound $(PEO)_3LiCF_3SO_3$ and result from the coordination of the Li^+ ion by the PEO chain. These assignments are consistent with the composition-dependent spectroscopic studies in the $PEO-LiCF_3SO_3$ system.[32,33] Figure 2 shows that there is no significant change in the bands at 833, 844, and 860 cm^{-1} up to 50 wt % EC. Beyond this limit, the band at 844 cm^{-1} begins to decrease in intensity. The absence of any change up to 50 wt % suggests that the Li^+ ion continues to interact with the PEO rather than the EC up to this composition.

Further evidence for the preferential interaction of the EC with the crystalline PEO phase rather than the 3:1 compound can be seen in Figures 3 and 4, which show infrared spectra in the CH_2 wagging region. The bottom curve of Figure 3 is the spectrum of pure crystalline PEO, while the bottom curve of Figure 4 shows the 9:1 complex without any EC present. A comparison of these two spectra establishes that the bands at 1360 and 1343 cm^{-1} in the latter spectrum are due to the crystalline PEO phase, while the bands at 1353 and 1340 cm^{-1} originate in the 3:1 compound. Upon addition of EC to the 9:1 complex, the bands of the 3:1 compound persist to the addition of 150 wt % EC, while the bands due to crystalline PEO slightly

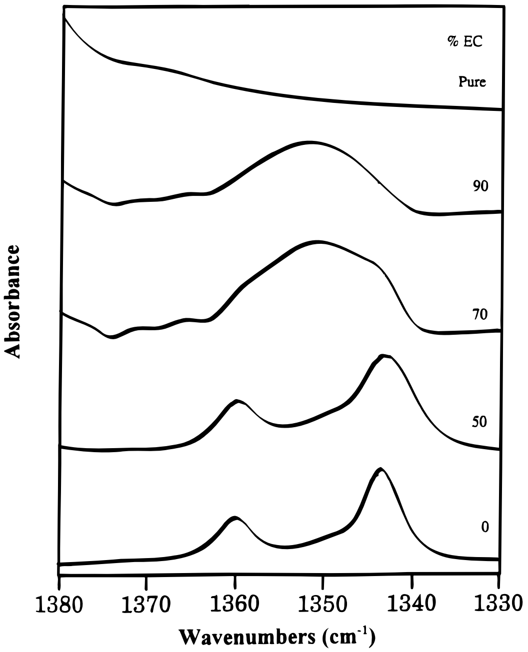

Figure 3. IR spectra of PEO with EC as a plasticizer in the 1380−1330 cm^{-1} spectral region. The wt % of EC is indicated for each curve.

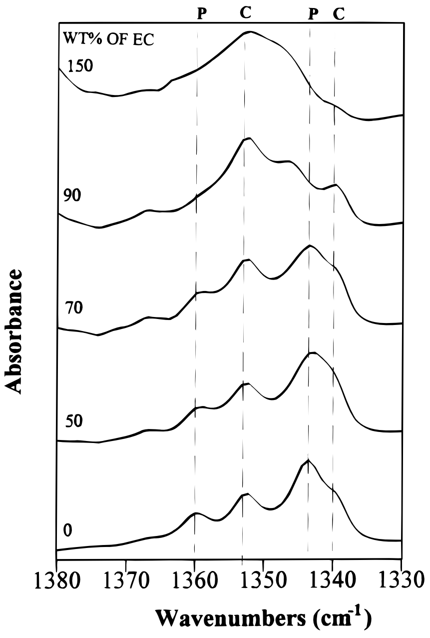

Figure 4. IR spectra of $(PEO)_9LiCF_3SO_3$ with EC as a plasticizer in the 1380−1330 cm^{-1} spectral region. The wt % of EC is indicated for each curve. C = crystalline compound; P = crystalline PEO.

decrease in intensity relative to the bands of the 3:1 compound up to 70 wt % and essentially disappear at 90 wt %, being replaced by a broad band roughly centered at 1350 cm^{-1}. A similar pattern with increasing amounts of EC is seen in the spectrum of pure PEO (Figure 3), where at 70 wt % EC the intensities of the crystalline PEO bands have decreased and a broad band at approximately 1350 cm^{-1} has grown in. At 90 wt % the new broad band dominates this spectral region.

3.1.3. Interaction between EC and Lithium Triflate. In order to understand the various interactions in the plasticized system, it is essential to understand the interaction between $LiCF_3SO_3$ and EC itself. An infrared study of the EC−$LiCF_3SO_3$ system shows that, with an increase in concentration of $LiCF_3SO_3$, the peaks corresponding to ion pairs and aggregates increase in intensity, while at very low concentrations free ions dominate (these spectra are not shown). This result demonstrates that triflate ions are increasingly coordinated with Li^+ ions at higher salt concentrations. Similar concentration-dependent behavior has also been observed in the PC-$LiCF_3SO_3$ system.[28]

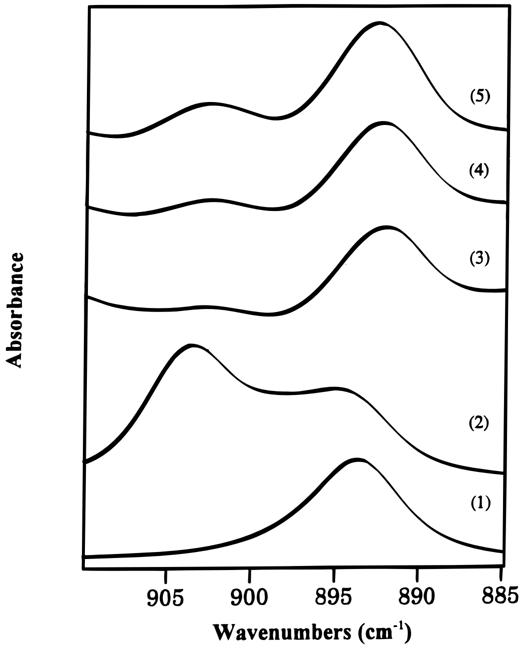

Figure 5. Comparison of the ring-breathing vibration region of EC in (1) pure EC; (2) EC−$LiCF_3SO_3$; and $(PEO)_9LiCF_3SO_3$ + *y* % EC with (3) $y = 50$; (4) $y = 70$; and (5) $y = 90$.

Useful observations can be made in the region characteristic of the EC ring breathing vibration mode (Figure 5) which occurs at 893 cm^{-1} in pure EC.[34,35] With an increase in $LiCF_3SO_3$ concentration, a band grows at 904 cm^{-1}, and the peak at 893 cm^{-1} also shifts to a higher frequency. The intensity of the peak at 904 cm^{-1} increases with increasing $LiCF_3SO_3$ concentration, demonstrating that it originates from the EC−Li^+ interaction. Additional support for this assignment comes from the results of Wawrzyniak et al.[36] who have reported that PC interacts with small cations but does not interact with anions and large cations such as tetrabutylammonium.

In Figure 5, a comparison of the spectrum of EC−$LiCF_3SO_3$ complex with that of the $(PEO)_9LiCF_3SO_3$ + 50 wt % EC complex suggests that the degree of interaction of EC with lithium triflate appears to be reduced in the presence of PEO. This is reflected in the weaker intensity of the band at 904 cm^{-1}. Also, the frequency shift of this peak is considerably reduced when compared with the EC−$LiCF_3SO_3$ complex. With increasing EC wt %, the peak shifts again toward higher frequency. Although the shift is small, it is an unmistakable trend. Similar behavior has been observed in the C=O bending mode of EC, which appears at 717 cm^{-1} in pure EC while an additional peak grows at 727 cm^{-1} with addition of $LiCF_3SO_3$. It may, therefore, be speculated that EC is not a good competitor against PEO in terms of Li^+ ion interaction.

Similar behavior has been observed in the studies of lithium perchlorate, $LiClO_4$, dissolved in EC[37] and PC.[38] In the study of EC−$LiClO_4$,[37] the peak at 907 cm^{-1} has been attributed to the EC molecules interacting with

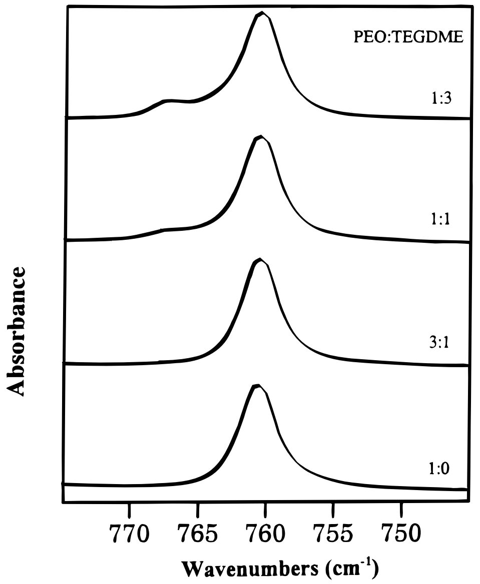

Figure 6. IR spectra of $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ in the $\delta_s(CF_3)$ spectral region. The PEO:TEGDME ratios of 1:0, 3:1, 1:1, and 1:3 correspond to x values of 0, 0.25, 0.50, and 0.75, respectively.

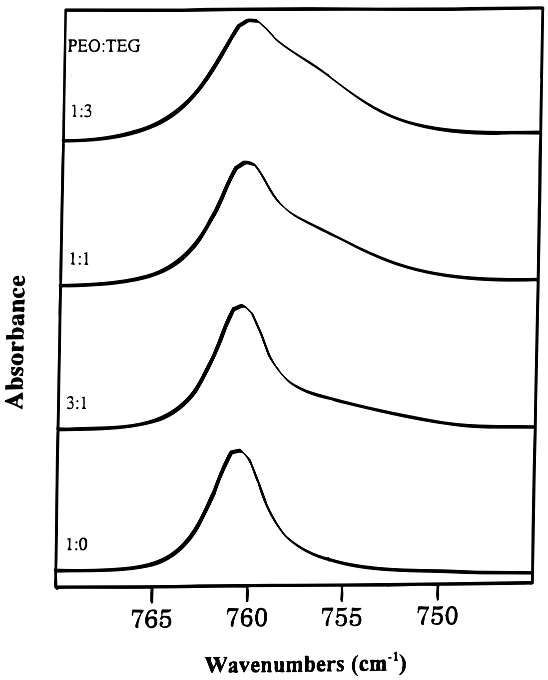

Figure 7. IR spectra of $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$ in the δ_s-(CF_3) spectral region. The PEO:TEG ratios of 1:0, 3:1, 1:1, and 1:3 correspond to x values of 0, 0.25, 0.50, and 0.75, respectively.

Table 1. Results of Curve-Fitting in the $\delta_s(CF_3)$ Region for the $(PEO+P)_9LiCF_3SO_3$ Complexes

composition	767 cm^{-1}	763 cm^{-1}	760 cm^{-1}	757 cm^{-1}	753 cm^{-1}
$(PEO)_9LiCF_3SO_3$			94.9	5.1	
$(3PEO+TEGDME)_9LiCF_3SO_3$			92.7	7.3	
$(PEO+TEGDME)_9LiCF_3SO_3$	8.3	1.7	90.0		
$(PEO+3TEGDME)_9LiCF_3SO_3$	11.0	7.2	81.8		
$(3PEO+TEG)_9LiCF_3SO_3$			76.1	8.4	15.5
$(PEO+TEG)_9LiCF_3SO_3$			68.7	19.8	11.5
$(PEO+3TEG)_9LiCF_3SO_3$			61.0	36.0	3.0

Li^+, while that at 898 cm^{-1} is due to EC molecules which do not interact with Li^+ ion. Hyodo and Okabayashi reported that the intensities of the bands at 898 and 907 cm^{-1} decrease and increase, respectively, with increasing electrolyte concentration (0.1−0.5 M).[37] The change in the relative intensities of the bands at 898 and 907 cm^{-1} has been ascribed to the existence of contact ion pairing.

When there is no compound formation, addition of even small amounts of a high dielectric solvent such as EC increases the average dielectric constant of the PEO matrix, with a corresponding decrease in the degree of ionic association. As a result, the intensity of the bands characteristic of “free” ions increases and the intensity of bands due to pair or triple ions decreases with increase in EC wt %.

3.2. Tetraethylene Glycol and Tetraglyme as Plasticizers. 3.2.1. Effect on Ionic Association. Complexes with an overall 9:1 ether oxygen:lithium ratio were studied with PEO:TEG (or TEGDME) ratios of 3:1, 1:1, and 1:3. Figure 6 shows spectra for the system $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ in the region 775−745 cm^{-1} where the $\delta_s(CF_3)$ mode is observed. The peak at 760 cm^{-1}, as mentioned before, is assigned to the $\delta_s(CF_3)$ mode of the compound $(PEO)_3LiCF_3SO_3$.[39] It may be noted that a peak starts growing at 767 cm^{-1} with increasing TEGDME concentration. This band has been previously assigned to a highly associated lithium triflate species, $[Li_3CF_3SO_3]^{2+}$.[29] To place these observations on a more quantitative footing, the spectral data in Figure 6 have been curve-fit (using a commercial program, Grams 386) to a straight base line and one Gaussian−Lorentzian product function for each band using a nonlinear least-squares method. It is assumed that the relative concentrations of the various triflate species are directly proportional to their relative intensities. The results are summarized in Table 1. With increasing plasticizer content, the relative concentration of the more highly associated species, indicated by the bands at 763 and 767 cm^{-1}, are seen to increase. However, the relative amount of the compound $(PEO)_3$-$LiCF_3SO_3$ decreases with increasing plasticizer content. Figure 7 shows the spectra for the $[(PEO)_{1-x}(TEG)_x]_9$-$LiCF_3SO_3$ in the region 775−745 cm^{-1}. As in the TEGDME case, the PEO:TEG ratios were varied as 3:1, 1:1, and 1:3. The spectral data in Figure 7 were curve-fit using the same methods as for the TEGDME-plasticized samples, and the results are shown in Table 1. The concentration of less associated species as evidenced by intensity of the ion pair band at 757 cm^{-1} increases while that of the “free” ion band decreases with increasing plasticizer content. As before, the relative amount of the compound $(PEO)_3LiCF_3SO_3$ decreases with increasing amounts of plasticizer. It is evident from the data that when TEGDME is used as a plasticizer, more highly associated ionic species are present than when TEG is used as a plasticizer. Thus, the end group can play a significant role in a compound used as a plasticizer.

The effect of end group on ionic association in complexes of oligomers with $LiCF_3SO_3$ has been previously reported.[28,40] In these studies it has been observed that, for an O:M ratio of 20:1, the concentration of the “free” ions relative to the associated species is greater in the OH-capped oligomers, while the opposite is observed in the CH_3-capped oligomers. However, with an increase in salt concentration, the more associated species (aggregates) dominate in the glymes while ion pairs become predominant in the glycols. This difference in behavior of the glymes and glycols has been attributed to the differences in their solvating abilities. The hydroxyl groups of the glycols solvate the cations through a Lewis

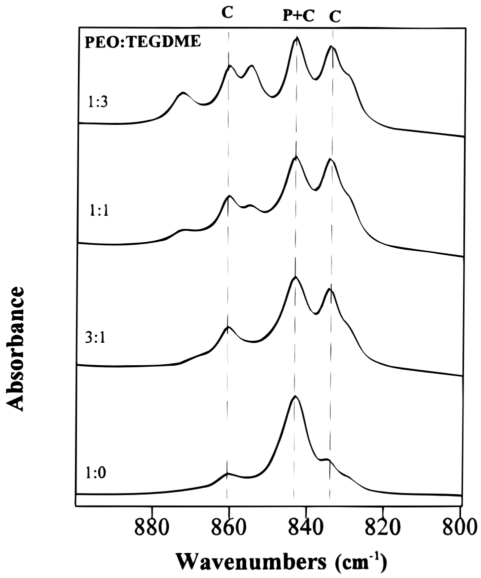

Figure 8. IR spectra of $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ in the 880−800 cm^{-1} spectral region. C = crystalline compound; P = crystalline PEO.

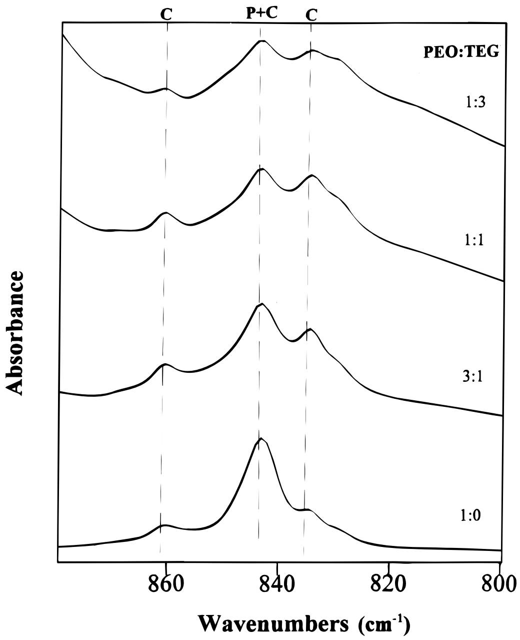

Figure 9. IR spectra of $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$ in the 880−800 cm^{-1} spectral region. C = crystalline compound; P = crystalline PEO.

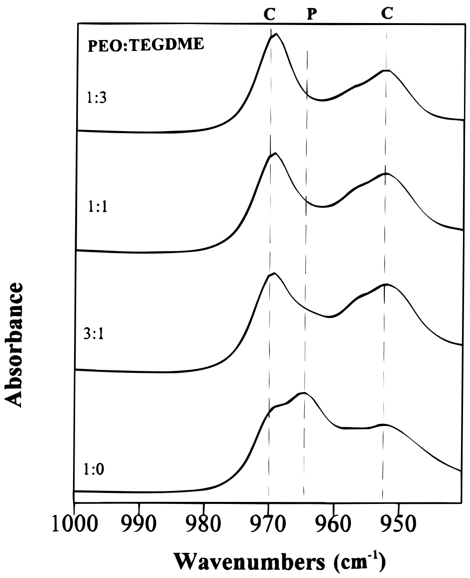

Figure 10. IR spectra of $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ in the 1000−940 cm^{-1} spectral region. C = crystalline compound; P = crystalline PEO.

acid−base interaction (in this case, $HO\cdots Li^+$) and also stabilize the triflate anion through hydrogen bonding ($CF_3SO_3\cdots HO$). "Wrapping" of the Li^+ by the polyether oxygen atoms of the plasticizer, as seen in the TEGDME case in the CH_2 rocking mode, is not observed spectroscopically in TEG (compare Figures 8 and 9), and this can be attributed to the competing end group interaction.

3.2.2. Conformational Effects of TEGDME and TEG. Figure 8 shows the spectra for TEGDME case in the 900−800 cm^{-1} region. As mentioned before, the peak at 844 cm^{-1} is due to the CH_2 rocking of PEO, and the bands at 860 and 834 cm^{-1} are due to the compound. Two peaks at 853 and 872 cm^{-1} grow in intensity with increasing TEGDME concentration. The band at 853 cm^{-1} is assigned to the CH_2 rocking motion (and some C−O stretching) of the TGT conformer (with some contribution from the TGG conformer) of TEGDME. The peak at 872 cm^{-1} is assigned to a CH_2 rocking mode of a new conformation of TEGDME, which is not observed in the pure liquid but is stabilized by the interaction of the ether oxygen atoms with lithium ion.[27] The IR spectra reveal that TEGDME, when used as a plasticizer, also interacts with the Li^+ ion although not to as great an extent as PEO. This follows from the fact that the peak at 872 cm^{-1}, which results from the TEGDME coordinating a lithium ion, is less intense compared to the peak at 860 cm^{-1}, which is characteristic of PEO−Li^+ coordination, even at a PEO:TEGDME ratio of 1:3.

Figure 9 shows the corresponding plots for the TEG system. The significant changes noticeable are the variation in the relative intensities of the bands and the growth of a peak at 830 cm^{-1}, which may be assigned to the CH_2 rocking motion of TEG. From this plot it is apparent that there is no noticeable change in the conformation bands of TEG nor the growth of an additional band due to a new conformation as in the case of TEGDME. When TEG is added, Li^+ ion interacts with the −OH end, and consequently the ion pair species dominate as noted earlier in the $\delta_s(CF_3)$ region.

We have previously observed that EC appears to preferentially interact with the pure crystalline PEO phase rather than the 3:1 compound. It is important to consider whether this also occurs in TEG and TEGDME. Figure 10 shows spectra for the TEGDME system in the region 1000−940 cm^{-1}. With increased addition of TEGDME, the peak at 964 cm^{-1}, which is due to the CH_2 rocking motion mixed with the COC stretching vibration of crystalline PEO, decreases in intensity and then disappears. However, the peaks at 969, 957, and 952 cm^{-1} due to the 3:1 compound still persist. Two other spectral regions where this effect is clearly observed are 1100−1000 and 1380−1330 cm^{-1}. In the former, the band at 1060 cm^{-1} due to a combination of COC stretching and CH_2 rocking modes [symbolized as $\nu_a(COC) + r_s(CH_2)$] disappears, and in the latter, the peak at 1360 cm^{-1} due to the CH_2 wagging motion (and some C−C stretching) [symbolized as $w_s(CH_2) + \nu(CC)$] also disappears. Identical results are also observed in these spectral regions for PEO−$LiCF_3SO_3$ complexes plasticized with TEG. This behavior was also previously noted in the 9:1 complex plasticized with EC

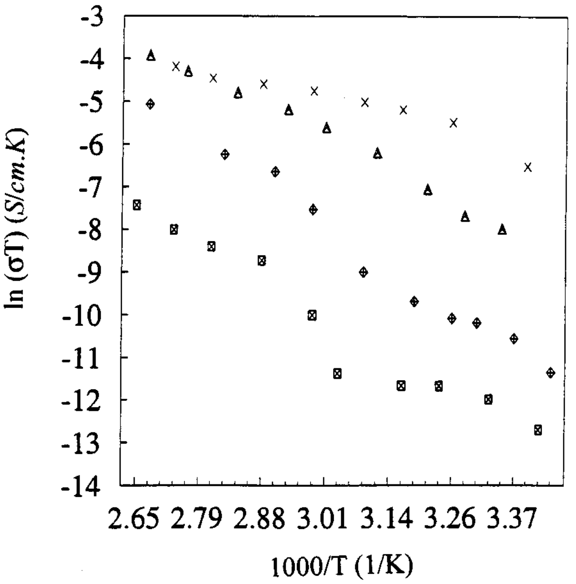

Figure 11. Plot of ln(σT) vs 1000/T for the system $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$. Values of x are 0 □, 0.25 ◊, 0.50 △, and 0.75 ×.

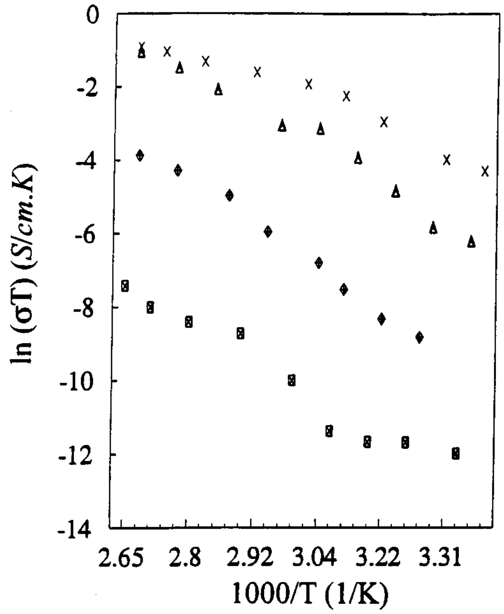

Figure 12. Plot of ln(σT) vs 1000/T for the system $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$. Values of x are 0 □, 0.25 ◊, 0.50 △, and 0.75 ×.

(section 3.1.2) where the peaks at 1060 and 1360 cm^{-1} also disappeared at ~90 wt % EC. Therefore, it can be concluded that the additives EC, TEG, and TEGDME preferentially interact with crystalline PEO relative to the 3:1 compound. In other words, the plasticizer modifies the polymer electrolyte by decreasing the crystallinity of the PEO phase.

4. Conductivity Studies

Conductivity studies can provide additional insight into the nature of the plasticizer interaction with the host matrix. Figures 11 and 12 show plots of ln(σT) vs 1000/T for the systems $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ and $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$, respectively. With increasing amounts of plasticizer, the conductivity behavior of plasticized systems follows the VTF (Vogel–Tamman–Fulcher)-like curves which are typical for amorphous polymers.[2,20,41] In each case the conductivity is enhanced with the progressive addition of plasticizer by several orders of magnitude. The polymer complex with the composition $[(PEO)(TEG)_3]_9LiCF_3SO_3$ has a conductivity value of 6.5×10^{-5} S/cm at 30 °C, which is more than 3 orders of magnitude higher than that of $(PEO)_9LiCF_3SO_3$. In the ln(σT) vs 1000/T plot of each system, the knee corresponding to the melting of the crystalline PEO at ~60 °C disappears with increasing concentration of plasticizer, indicating a decrease in the amount of crystalline PEO. This is consistent with the observations of Wang et al.[16] and the conclusions drawn from the IR studies that the plasticizer preferentially interacts with the crystalline PEO phase rather than the 3:1 compound.

The conductivities of the $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$ complexes are found to be higher than the corresponding $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ complexes. In general, ionic conduction in polymer complexes depends on the number of carriers and the ionic mobility. The conductivity can be understood better when the trends are compared within each series of plasticized samples. Panels a and b of Figure 13 show plots of conductivity (solid lines) versus mol % of plasticizer. In addition, the relative intensities of the triflate species obtained from curve-fitting results of IR data are plotted. The dashed lines in these figures are to serve as visual guides for the various ionic species. In the $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$ series, the % fraction of "free" ions decreases with the increase in TEG content and the ion pair fraction grows at the expense of the compound (Table 1 and Figure 13b). Despite this fact, the conductivity of the plasticized samples increases with increasing TEG content. In the $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$ series, there is a 2–3 order conductivity increase, although only aggregates are present to an appreciable extent in addition to the compound (Table 1 and Figure 13a). These observations suggest that the formation of an amorphous matrix is more crucial than the ionic species present. Temperature-dependent IR studies have been carried out on $(PEO)_9LiCF_3SO_3$ and $(PEO+P)_9LiCF_3SO_3$ complexes. The data have been curve-fitted, and some of the results are presented in Table 2. With increasing temperature, the relative concentration of the ion pairs increases in the $(3PEO+TEGDME)_9LiCF_3SO_3$ complexes, while the relative concentration of aggregate (II) at 767 cm^{-1} increases in the $(PEO+3TEGDME)_9LiCF_3SO_3$ complexes. The intensities of these peaks grow at the expense of the compound peak intensity. Some of the compound therefore seems to break up into ionically associated charge-carrying species which are assumed to be not as mobile as "free" ions. The conductivity increases when the matrix is amorphous in nature.

5. Conclusions

The effect of plasticizers such as EC, TEG, and TEGDME have been studied in the PEO–$LiCF_3SO_3$ system using infrared spectroscopy augmented with measurements of conductivity. Plasticizers affect the ionic association in the polymer–salt complexes, although this effect is small in the more salt-rich polymer–salt complexes. This study shows that EC and TEG tend to increase the concentration of the less associated species while TEGDME increases the concentration of more associated species relative to the $(PEO)_9LiCF_3SO_3$ complex with no plasticizer. A quantitative study of the TEGDME plasticized complexes establishes that with the addition of plasticizer some of the 3:1 compound disappears, with a concomitant increase in ion pair

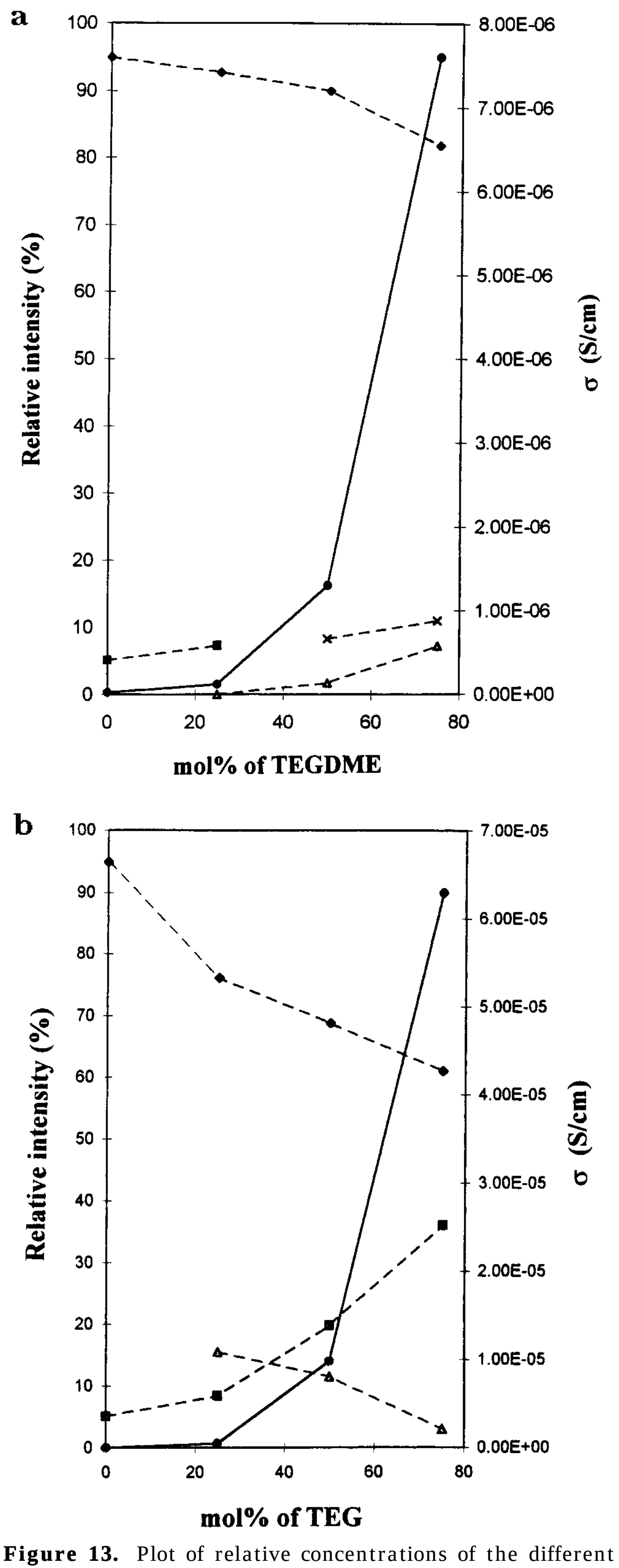

Figure 13. Plot of relative concentrations of the different triflate species and $\sigma_{30\ ^\circ C}$ for (a) $[(PEO)_{1-x}(TEGDME)_x]_9LiCF_3SO_3$: ion pair ■, compound ♦; aggregate I ▲, aggregate II ×, conductivity ●; and (b) $[(PEO)_{1-x}(TEG)_x]_9LiCF_3SO_3$ complexes: "free" ion ▲, ion pair ■, compound ♦, conductivity ●.

concentration and, at higher levels of TEGDME substitution, the formation of more highly associated ionic aggregates. The most significant data are obtained from an analysis of the TEG system. Here Table 1 shows that the relative concentration of the "free" ions markedly decreases with increasing amounts of TEG; yet the conductivity increases, as the data of Figure 12 indicate. The conductivity data show that the sharp crystalline to amorphous phase transition at 60 °C in the pure PEO fraction is suppressed with the addition of increasing amounts of plasticizer. The spectroscopic data establish that the plasticizer interacts preferentially with the crystalline PEO phase in the polymer−salt complexes. Therefore, the effect of the plasticizer appears to be twofold: (1) interaction with the crystalline PEO phase to produce an amorphous phase and (2) a partial breakup of the crystalline 3:1 compound to produce highly associated ionic species. Because both the crystalline PEO and the 3:1 compound have low ionic conductivities, we further conclude that the net effect of the plasticizer is to create regions of faster segmental motion and as a result an increase in ionic conductivity. The creation of these plasticized regions appears to be more important than the small changes in the degree of ionic association which accompanies the addition of plasticizer. This argument is underscored by two observations: (1) the addition of TEGDME increases the number of more highly associated ionic species, yet the conductivity still dramatically increases, and (2) the addition of TEG decreases the relative number of "free" ions.

Table 2. Results of Curve-Fitting in the $\delta_s(CF_3)$ Region for the $(PEO+P)_9LiCF_3SO_3$ Complexes at Room Temperature, 65 °C, and 90 °C

T (°C)	767 cm^{-1}	763 cm^{-1}	760 cm^{-1}	757 cm^{-1}
	$(3PEO+TEGDME)_9LiCF_3SO_3$			
RT			92.7	7.3
65			89.0	11.0
90			86.6	13.4
	$(PEO+3TEGDME)_9LiCF_3SO_3$			
RT	11.0	7.2	81.8	
65	18.3	6.8	74.9	
90	22.5	6.1	71.4	

Acknowledgment. This work was partially supported by funds from the U.S. Army Research Office (Grant DAAH04-94-G-0250) and the NSF EPSCOR program under Cooperative Agreement #OSR-9550478.

References and Notes

(1) Scrosati, B. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman and Hall: London, 1993; p 251.
(2) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH: New York, 1991.
(3) Hooper, A.; Gauthier, M.; Belanger, A. In *Electrochemical Science and Technology of Polymers*; Linford, R. G., Ed.; Elsevier Applied Science: London, 1990; Vol. 2, p 375.
(4) Armand, M.; Sanchez, J. Y.; Gauthier, M.; Choquette, Y. In *Polymeric Materials for Lithium Batteries*, in *The Electrochemistry of Novel Materials*; Liplowski, J., Ross, P. N., Eds.; VCH: New York, 1994; p 65.
(5) Scrosati, B.; Neat, R. J. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman and Hall: London, 1993; p 182.
(6) Armand, M. B.; Chabagno, J. M.; Duclot, M. In *Fast Ion Transport in Solids*; Vashista, P., Mundy, J. N., Shenoy, G. K., Eds.; Elsevier Applied Science: North Holland and New York, 1979; p 131.
(7) Le Nest, J.-P.; Gandini, A. *Proc. 2nd International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: Amsterdam, 1990; p 129.
(8) Schantz, S.; Torell, L. M.; Stevens, J. R. *J. Chem. Phys.* **1991**, *94*, 6862.
(9) Manning, J.; Frech, R.; Hwang, E. *Polymer* **1990**, *31*, 2245.
(10) Schantz, S.; Sandahl, J.; Borjesson, L.; Torell, L. M.; Stevens, J. R. *Solid State Ionics* **1988**, *128−30*, 1047.
(11) Gauthier, M.; Belanger, A.; Kapfer, B.; Vassort, G.; Armand, M. In *Polymer Electrolyte Reviews*; MacCallum, J. R., & Vincent, C. A., Eds.; Elsevier Applied Science: London, 1989; Vol. 2, p 285.
(12) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.

(13) Armand, M. B. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987; Vol. 1, p 1.

(14) Fauteux, D.; Prud'homme, J.; Harvey, P. E. *Solid State Ionics* **1988**, *28−30*, 923.

(15) Sheldon, M. H.; Glasse, M. D.; Latham, R. J.; Linford, R. G. *Solid State Ionics* **1989**, *34*, 135.

(16) Wang, C.; Liu, Q.; Cao, Q.; Meng, Q.; Yang, L. *Solid State Ionics* **1992**, *53−56*, 1106.

(17) Kelly, I.; Owen, J. R.; Steele, B. C. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *168*, 467.

(18) Kelly, I.; Owen, J. R.; Steele, B. C. H. *J. Power Sources* **1985**, *14*, 13.

(19) Watanabe, M.; Kanba, M.; Matsuda, H.; Tsunemi, K.; Mizoguchi, K.; Tsuchida, E.; Shinohara, I. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 741.

(20) Paulmer, R. D. A.; Kulkarni, A. R. *Solid State Ionics* **1994**, *68*, 243.

(21) Huq, R.; Koksbang, R.; Tonder, P. E.; Farrington, G. C. *Electrochim. Acta* **1992**, *37*, 1681.

(22) Yang, L.; Lin, J.; Wang, Z.; Wang, C.; Zhou, R.; Liu, Q. *Solid State Ionics* **1990**, *40/41*, 616.

(23) Fish, D.; Smid, J. *Electrochim. Acta* **1992**, *37*, 2043.

(24) Cameron, G. G.; Ingram, M. D.; Sarmouk, K. *Eur. Polym. J.* **1990**, *26*, 1097.

(25) Hyodo, S.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1557.

(26) Frech, R.; Huang, W.; Johansson, P.; Lindgren, J. *Electrochem. Acta* **1995**, *40*, 2147.

(27) Frech, R.; Huang, W. *Solid State Ionics* **1993**, *66*, 183.

(28) Huang, W. Ph.D. Thesis, The University of Oklahoma, 1994.

(29) Huang, W.; Frech, R.; Wheeler, R. A. *J. Phys. Chem.* **1994**, *98*, 100.

(30) Huang, W.; Wheeler, R. A.; Frech, R. *Spectrochim. Acta* **1994**, *50A*, 985.

(31) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. Solids* **1981**, *42*, 493.

(32) Dissanayake, M. A. K. L.; Frech, R. *Macromolecules* **1995**, *28*, 5312.

(33) Frech, R.; Huang, W.; Dissanayake, M. A. K. L. *Proc. Mater. Res. Symp.* **1995**, *369*, 523.

(34) Angell, C. L. *Trans. Faraday Soc.* **1956**, *52*, 1178.

(35) Durig, J. R.; Coulter, G. L.; Wertz, D. W. *J. Mol. Spectrosc.* **1968**, *27*, 285.

(36) Wawrzyniak, G.; Warnke, Z.; Chmurzynski, L. *Spectrosc. Lett.* **1993**, *26*, 103.

(37) Hyodo, S.; Okabayashi, K. *Electrochim. Acta* **1989**, *34*, 1551.

(38) Battisti, D.; Nazri, G. A.; Klassen, B.; Aroca, R. *J. Phys. Chem.* **1993**, *97*, 5826.

(39) Stevens, J. R.; Jacobsson, P. *Can. J. Chem.* **1991**, *69*, 1980.

(40) Bernson, A.; Lindgren, J. *Polymer* **1994**, *35*, 4842.

(41) Ratner, M. A. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1989; Vol. 1, p 173.

MA9515644