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Influence of Hydroxyl Terminal Groups on the Ionic Speciation and Ionic Conductivity in Complexes of Poly(propylene glycol)(4000) and $LiCF_3SO_3$ Salt

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Introduction

Pioneering work by Armand[1] on ionically conducting polyether−alkali metal salt complexes, i.e., polymer electrolytes, has motivated extensive research on such systems during the past 2 decades.[2] The observation that ionic transport mainly occurs in amorphous liquid-like regions of these complexes[3] is the rationale for using low molecular weight liquid polymers as model systems in fundamental studies of microscopic properties and transport processes. However, in order to extrapolate trends observed in such model electrolytes to higher molecular weight analogue systems, it is essential that specific interactions associated with polymer terminal groups are eliminated.

Poly(propylene glycol) of molecular weight 4000, PPO(4000), has frequently been used in studies on the temperature and concentration dependency of the ionic conductivity[4] and also in vibrational spectroscopic studies of ion−ion interactions.[5−7] Still, it is questionable whether PPO(4000) is a suitable model host polymer. For instance, Bernson and Lindgren have pointed out that characteristic infrared vibrational bands of the hydroxyl end groups are affected upon complexation with alkali metal salts.[8] Furthermore, Prud'homme and co-workers[9,10] have suggested that the dramatic concentration dependency of the ionic conductivity[4] can be attributed to a microphase separation occurring in electrolytes based on PPO(4000).

In the present study, the influence of large densities of polar end groups on the ionic conductivity, σ, and the ionic speciation is investigated by directly comparing Raman and conductivity data recorded on the normal hydroxyl-terminated and endo-methylated complexes, respectively.

Experimental Section

Methyl-terminated PPO(4000) was obtained by treating PPO (Aldrich, MW = 4000) with dimethyl sulfate (Aldrich) at 0 °C in an ethylene glycol dimethyl ether (glyme) solution. Typically, 50 g of PPO(4000) was mixed with 100 mL of glyme in an inert atmosphere, and 20 g of finely ground KOH was charged. End group substitution was accomplished by adding 25 g of dimethyl sulfate dropwise under vigorous stirring. The reaction was kept overnight for completion; the resulting mixture was washed in deionized water, and methyl-capped PPO was extracted in methylene chloride of high purity. After several wash and extraction cycles, the resulting polymer was dried under high vacuum at elevated temperature. Before use the polymers were carefully freeze-dried using repeated pump−thaw cycles. Comparisons of infrared spectra of the modified PPO and the original hydroxyl-capped polymer indicated an efficiency of the end-capping process better than 90%, as determined from the relative intensity of the characteristic hydroxyl infrared band envelope at ~3500 cm^{-1}. AC impedance measurements on the pure methyl-capped polymer showed that the ionic conductivity at 80 °C was approximately ~10^{-9} S·cm^{-1}. Lithium triflate, $LiCF_3SO_3$ (Aldrich Chemical Co., Inc.), was dried under vacuum at 80 °C for 24 h and at 120 °C for another 24 h.

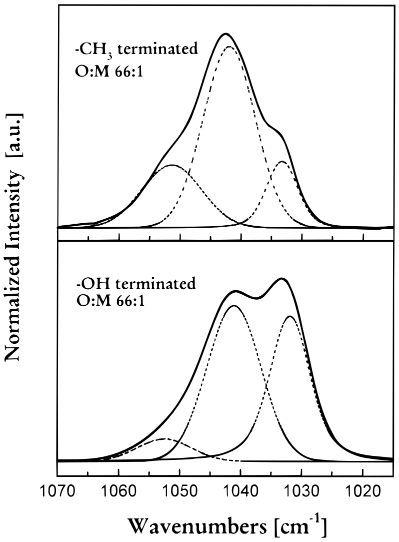

Figure 1. Raman spectra of the $\nu_S(SO_3)$ region of the triflate anion for PPO_M−LiTf and PPO−LiTf electrolytes of composition O:M = 66:1 (~0.25 mol/kg), corrected for the polymer background. Dotted lines indicate a curve fit with components at ~1032, 1042, and 1052 cm^{-1}, respectively.

Polymer-salt complexes were prepared in a dry helium atmosphere, the oxygen level being less than 10 ppm, by complexing PPO(4000) with $LiCF_3SO_3$. Methyl- and hydroxyl-terminated electrolytes will be referred to as PPO_M−LiTf and PPO−LiTf, respectively.

FT-Raman spectra were recorded at 23 °C using a Bruker IFS 66 spectrometer with a Raman module FRA 106. Ionic conductivity was measured as a function of salt concentration at 25 °C using the complex impedance method.

Results and Discussion

Figure 1 shows the $\nu_s(SO_3)$ region of the Raman spectra of the PPO_M−LiTf and PPO−LiTf electrolytes for the ether oxygen to alkali metal cation ratio (O:M) 66:1 along with typical three-component curve fits. According to the literature,[11] the component observed at ~1033 cm^{-1} has been assigned to "free" anions not interacting directly with lithium cations; components at ~1042 and ~1052 cm^{-1} have been attributed to contact ion pairs and $Li_2CF_3SO_3$ triplets, respectively.

Figure 1 shows that triflate anions interact directly with lithium ions to a greater extent in the endo-methylated electrolyte. The observed difference is more pronounced at low salt concentrations.[12] This shows that the polar hydroxyl end groups greatly influence the microscopic properties of dilute electrolytes based on PPO(4000).

The $\delta_S(CF_3)$ mode of the triflate anion in the region ~750−765 cm^{-1} has also been used to estimate the relative fraction of various ionic species in other polymer−triflate salt systems.[11,13,14] The interpretation of observed shifts for this mode is analogous to the analysis of the $\nu_S(SO_3)$ mode, and components at ~753, ~758, and ~763 cm^{-1} have been attributed to "free" anions, ion pairs, and $Li_2CF_3SO_3$ triple ions, respectively.[11] Figure 2 shows this region for the same PPO_M−LiTf and PPO−LiTf electrolytes as in Figure 1. The finer band

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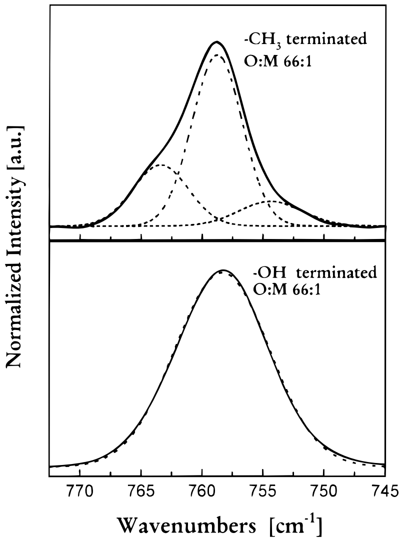

Figure 2. Raman spectra of the $\delta_S(CF_3)$ band envelope for the same complexes as in Figure 1, corrected for the polymer background. Dotted lines indicate a curve fit with components at ~753, 758, and 763 cm^{-1}, respectively. For the PPO−LiTf complex, a single Gaussian band centered at ~758 cm^{-1} satisfactorily fits the data.

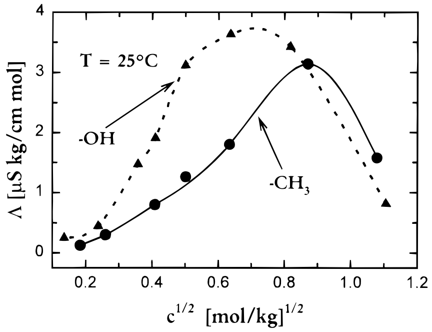

Figure 3. Molar conductivity at 25 °C as a function of concentration. Filled circles and triangles correspond to the methyl- and hydroxyl-terminated electrolytes, respectively. Values for the hydroxyl-terminated complexes have been calculated from ref 4. Lines are drawn as a guide to the eye.

structure seen in the methyl-capped system is not observed in the normal PPO−LiTf complex. We attribute this observation to a specific anion−solvent interaction, involving the hydroxyl terminal groups, which masks shifts due to cation−anion interactions.[13]

We now turn to the conductivity results. Figure 3 shows the concentration behavior of the molar conductivity Λ (=σ/c) at 25 °C for the PPO and PPO$_M$ electrolytes, respectively. Notably, Λ increases rapidly with increasing salt concentration in both systems, though the characteristic maximum is considerably sharper in the PPO$_M$−LiTf electrolyte and is shifted to higher concentration; the ratio $\Lambda_{max}/\Lambda_{min}$ is also greater for the methyl-terminated electrolyte. For the PPO−LiTf system, a previous Raman study[7] showed that the distribution of local anionic environments was essentially independent of salt concentration in the concentration region corresponding to an increase in Λ by a factor of ~14.[4] To account for this observation, a concentration dependent enhancement of the ionic mobility, attributed to an increasing rate of ionic exchange in combination with a potential saturation of preferred coordination sites, was put forward as a possible explanation.[6,7]

In this context, we note that Prud'homme and coworkers have interpreted at T_g splitting in various PPO−LiX complexes in terms of a liquid−liquid microphase separation, where salt rich regions of a uniform composition are dispersed in a salt free polymer matrix.[9,10] Referring to studies on high molecular weight systems, they argue that the observed T_g splitting is not resulting from the finite content of hydroxyl end groups in PPO(4000)[10] and also conclude that the concentration behavior of the conductivity is dominated by the coexistence of liquid phases of different composition.

Clearly, if conduction is confined to microscopic droplets of a fixed composition which fluctuate at a relatively slow rate, the electrolyte is essentially heterogeneous and percolation phenomena may occur.[15] Still, in view of the differences observed in the conductivity and Raman data in the present study, it is evident that the large density of polar terminal groups (O:OH ~ 35:1) strongly must influence the composition of any conceivable liquid microphases coexisting in polymer−salt complexes based on PPO(4000).

Concluding Remarks

From FT-Raman measurements on methyl- and hydroxyl-terminated PPO(4000) complexed with $LiCF_3SO_3$ salt, we conclude that large densities of polar end groups contribute significantly to the ability of PPO(4000) to dissolve salt. Differences observed in the $\delta_S(CF_3)$ band envelope are interpreted in terms of a specific interaction between the triflate anion and terminal hydroxyl groups. We also conclude that the dramatic concentration behavior of Λ, generally found in the PPO(4000)-based electrolytes,[4] is not governed by a saturation of preferred coordination sites associated with the polar hydroxyl end groups.

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