Conductivity Behavior below and above the Critical Composition for Microphase Separation in Poly(propylene oxide)−Sodium Salt Electrolytes

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ABSTRACT: This study, performed on mixtures of $NaClO_4$ and $NaCF_3SO_3$ with atactic poly(propylene oxide) (PPO), confirms that a microphase separation phenomenon takes place in both low and high molecular weight PPO. Below a certain concentration, which corresponds to O/Na = 13 (O = ether oxygen) in a $M = 4 \times 10^3$ PPO and to O/Na = 11 in a $M = 2 \times 10^5$ PPO, optically clear mixtures exhibit two glass transition (T_g) features indicating that a salt-rich microphase separates from the polymer. A comparison with poly(ethylene oxide) (PEO) amorphous mixtures containing the same salts shows that this phenomenon has a dramatic effect on ion conduction. It also reveals that an ion-entrapping structure, similar to that in the salt-rich microphase, is present over a range of concentrations above the critical composition. Although chain length has a marginal effect on conductivity in PEO, it has a strong effect on conductivity in PPO. As evidenced by a sharper T_g splitting in the high molecular weight PPO, this effect is due to the formation of larger microdomains. From this feature and the change in the microdomain composition, it may be argued that solvating power of PPO decreases with increasing chain length or decreasing OH end-group density.

Introduction

Recently, we reported that conductivity of lithium salts in low molecular weight ($M = 4 \times 10^3$) atactic poly(propylene oxide) (PPO) is affected by a microphase separation phenomenon.[1] Below a certain concentration, which corresponds to a molar ratio O/Li = 9 (O = ether oxygen) for LiBr, O/Li = 10 for $LiClO_4$ and $LiCF_3SO_3$, and O/Li = 16 for $LiN(CF_3SO_2)_2$, optically clear mixtures of these systems exhibit two glass transition (T_g) features. Such a T_g splitting is in agreement with a thermomechanical study reported over 30 years ago by Moacanin and Cuddihy[2] on mixtures of $LiClO_4$ with a high molecular weight PPO. Just below the critical composition, a low-T_g feature comparable to that of the neat polymer becomes apparent and its amplitude increases with further dilution. At the same time, a high-T_g feature characteristic of a salt-rich microphase decreases in amplitude and asymmetrically broadens toward the low-T_g feature to finally disappear for O/Li > 24. From O/Li = 10 to O/Li = 70, the shear modulus of the high molecular weight materials shows a temperature dependence similar to that of a thermoplastic elastomer.[2] In this dependence, the amplitude of the rubbery plateau decreases markedly with decreasing salt content. This suggests a greater and greater dispersion of the salt-rich microphase.

Mixtures of sodium salts (NaSCN, NaI, or $NaClO_4$) with either high or low molecular weight PPO also exhibit a T_g splitting over the same range of compositions.[3,4] Furthermore, upon a long standing at room temperature, turbidity followed by a two-layer separation takes place in the subcritical mixtures of $NaClO_4$ with a $M = 4 \times 10^3$ PPO.[4] Above 40−50 °C, however, this macroscopic separation reversibly transforms into a microscopic separation. This suggests that there is a point where dilution leads to a critical balance between the cation−oxygen interactions, which favor salt dispersion, and the ion−ion, long-range Coulombic interactions, which oppose this dispersion. For most of the PPO−salt systems, the liquid−liquid separation remains microscopic because interface energy is small compared to thermal energy. This, together with the dynamical interactions at the microphase boundary, would account for the decrease in the size of the salt-rich microdomains with further dilution. These microdomains probably transform into more and more labile heterogeneities, which eventually fluctuate at rate high enough to become furtive in long-time-geared relaxation experiments.

Such a liquid−liquid separation does not take place in supercooled mixtures of the same salts with poly(ethylene oxide) (PEO), $[CH_2CH_2O]_n$, which has a greater density in oxygen atoms than PPO, $[CH(CH_3)CH_2O]_n$. A thermodynamical analysis of the solubility-temperature relationships constructed for $LiClO_4$ in $M = 4 \times 10^3$ PEO and PPO shows that the excess free energy of mixing of the liquid components is much more favorable to miscibility in the case of PEO.[4] In both cases, however, the magnitude of this quantity decreases markedly with increasing temperature due to a negative, excess entropy of mixing. Although this latter feature does not prevent $LiClO_4$ to be fully soluble in PEO and PPO at its melting point (251 °C), it probably accounts for the precipitation of some sodium salts above a certain temperature in PPO, as reported by Greenbaum *et al.*[3] for $NaClO_4$ and NaI, and by Teeters *et al.*[5] for NaSCN. Among these salts, only NaI exhibits a similar feature in PEO, and for a given composition it takes place at a much higher temperature than in PPO (e.g., 270 °C compared to 120 °C for O/Na = 16).[4] All these features indicate that solvating power of PPO is not as great as that of PEO. This difference probably accounts for the liquid−liquid separation observed in this polymer.

Since our first work[4] on this matter, Bergman *et al.*[6] have reported two relaxation features in a photon correlation study on mixtures of $NaCF_3SO_3$ with a $M =$

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4×10^3 PPO. Although they concluded that these mixtures were biphasic at the microscopic level, they did not reexamine the Raman data previously reported by Schantz and Torell[7,8] on this system and on the PPO−$LiClO_4$ system. These data, which had been interpreted in terms of ion association by assuming full homogeneity, reveal that the anion environment remains unchanged from O/Na = 16 to O/Na = 1000 for $NaCF_3SO_3$ and from O/Li = 10 to O/Li = 1000 for $LiClO_4$. As quoted in our previous works, this feature suggests that microphase separation persists down to high dilution. More recently, Angell and co-workers[9] have reported a T_g splitting for mixtures of $Mg(ClO_4)_2$ with a similar PPO. Shear modulus of these mixtures exhibited a rubbery plateau as in the work by Moacanin and Cuddihy.[2] Unaware of the literature, they claimed that this feature was due to a preferential coordination of the cations to the OH end groups (3 mol %) of their $M = 4 \times 10^3$ low molecular weight PPO. In a subsequent paper by McLin and Angell,[10] the same argument was offered to explain an anomaly in the viscosity−temperature relationships of subcritical mixtures of $NaClO_4$ with a similar polymer. Although they did not report any anomaly in the T_g behavior of this system, they had previously reported a T_g broadening[11] (and even suspected the presence of microheterogeneities)[12] for other alkali metal salts ($LiClO_4$ and $NaCF_3SO_3$) in such a PPO.

Until very recently, several studies have been reported on low molecular weight PPO−salt mixtures without any concern about the phase behavior of these materials.[13−19] This includes an infrared study by Bernson and Lindgren,[16,20] in which alkali metal ions were shown to exhibit a preferential coordination to the OH end groups of PPO. This infrared study also suggests that these groups form hydrogen bonds with certain anions, including ClO_4^- and $CF_3SO_3^-$. The aim of the present work, which deals with the PPO−$NaClO_4$ and PPO−$NaCF_3SO_3$ systems, was to further examine the structural features of these systems through a comparison with a high molecular weight PPO. For that purpose, DSC and conductivity data were also obtained for melted or supercooled mixtures of the same salts with a low and a high molecular weight PEO. As in the previous works,[1,4] we opted for a DSC study because this technique allows the characterization of the compositional features of the PPO−salt systems. Without this basic information, it would be difficult to interpret the other properties of these systems.

Experimental Section

Materials. Low molecular weight PEO ($M_n = 4.4 \times 10^3$, $M_w/M_n = 1.02$) and PPO ($M_n = 4.2 \times 10^3$, $M_w/M_n = 1.35$) were the same as those used in the previous works.[1,4] High molecular weight PEO ($M_{GPC} = 4 \times 10^6$) and PPO ($M_{GPC} = 2 \times 10^5$) were polydisperse materials. The latter polymer was a commercial rubber (Parel-C) containing a small fraction of allyl glycidyl ether units. Before utilization, all the polymers were dried under high vacuum for 48 h. The sodium salts ($NaClO_4$ and $NaCF_3SO_3$) were pumped for 24 h at 130 °C. Polymer−salt mixtures were prepared under a dry atmosphere by mixing weighed quantities of 1−5% methanol (or acetonitrile) solutions of each component. Solvent evaporation was carried out in ampules connected to a vacuum system. The solvent-free mixtures were transferred into 25-mm diameter glass vials (with screw caps) and dried under high vacuum for 24 h at 130 °C. The vials were stored under a dry atmosphere in a glovebox.

DSC Measurements. The calorimeter (Perkin-Elmer DSC-4) was flushed with dry helium, and sample pans were filled and sealed under a dry atmosphere in the glovebox. Glass transition features were recorded at a heating rate of 40 °C/min, and supercooled specimens (with PEO) were obtained by melt quenching at a cooling rate of 320 °C/min. Values of T_g were read at the intersection of the tangent drawn through the heat capacity jump with the base line recorded before the transition. For the $M = 4 \times 10^3$ PPO−$NaCF_3SO_3$ system, the high-T_g feature in the microphase-separated specimens could be defined through the derivatives of the DSC curves only. It was read as the second maximum on these derivatives.

Conductivity Measurements. The bulk electrolytes were contained in airtight cells consisting of two stainless steel solid cylinders encapsulated at both ends of a Teflon ring. A 1-cm diameter disk-shape electrode−electrolyte contact surface was imposed by Teflon sleeves. The gap between the electrodes (3 mm) was measured with an accuracy better than 1% and no correction was made for the thermal expansion of the cells. The conductivity measurements were performed in a Instron temperature chamber equipped with a computer-driven controller. The temperature of the electrolytes was measured with an accuracy better than ±0.2 °C by means of a thermocouple inserted in a well dug in the body of the cells. The real part, Z', and the imaginary part, Z'', of the complex impedance of the cells were measured over the frequency range 5 Hz to 13 MHz by using a Model 4192A Hewlett-Packard impedance analyzer. The impedance data were collected at intervals of 5 °C by means of a HP-IB interface. The temperature range was 30−130 °C for PPO and 50−130 °C for PEO (with a cycle from the highest temperature). As usual, the bulk dc resistance of the electrolyte was determined as the point where the high-frequency semicircle in the plot of Z'' as a function of Z' cuts the Z' axis.

Results and Discussion

1. Physical Behavior. Figure 1 shows DSC curves recorded on subcritical mixtures (O/Na = 16 and 20) of $NaClO_4$ and $NaCF_3SO_3$ with the present PPO ($M = 4 \times 10^3$) and with a high molecular weight PPO ($M = 2 \times 10^5$). For $NaClO_4$ in the present PPO, macroscopic homogeneity was obtained by a preheating to 50 °C. The other mixtures, including those of $NaClO_4$ with the high molecular weight PPO, were optically clear even after a long standing at room temperature. It may be seen that high molecular weight PPO yields a sharper T_g splitting than the present PPO. T_g of the salt-rich microphase is also higher in that polymer than in the present one. As revealed by a more extensive comparison (not shown) dealing with $NaClO_4$ in both polymers, this latter feature is due to a change in the critical composition for microphase separation (O/Na = 11 in the high molecular weight PPO compared to O/Na = 13 in the present PPO). This suggests that chain ends (or chain length) have a sizable effect on the interactional features that govern microphase separation.

Since a lower salt content is required to obtain microscopic homogeneity in the present PPO, its solvating power must be greater than that of the high molecular weight PPO. A lower salt content in the complexed microdomains of this polymer also means a lower interface tension at the microphase boundary.[4] As will be shown later, this expectation is in agreement with the broadening of the high-T_g feature in the present PPO. This broadening suggests smaller and more labile microdomains than in the high molecular weight PPO. Since a broadening of the high-T_g feature is still present for $NaCF_3SO_3$ in the high molecular weight PPO, and since a T_g splitting is barely distinguishable for this salt in the present PPO, the microdomain size also depends on the nature of the salts. Note that in agreement with the photon correlation

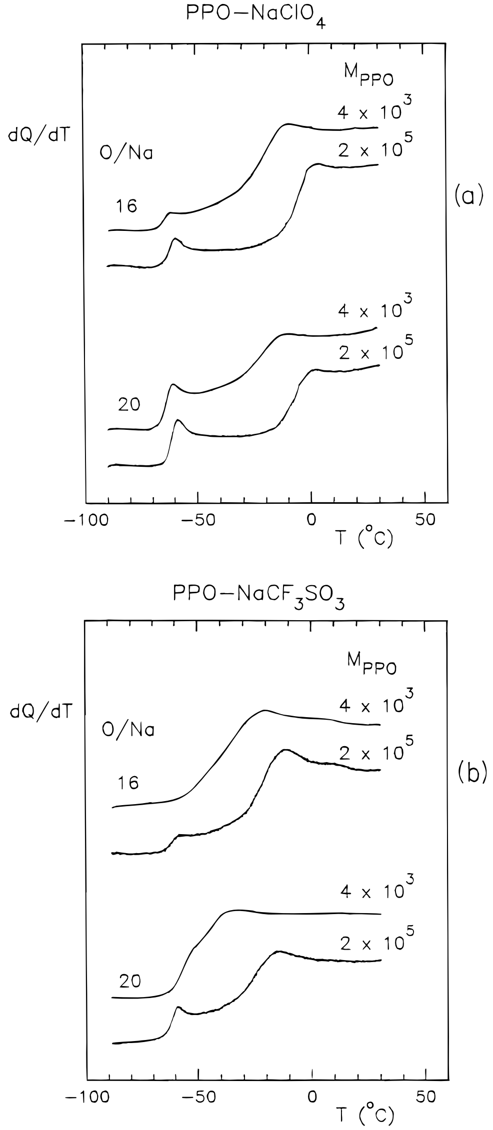

Figure 1. DSC heating curves recorded at 40 °C/min on subcritical mixtures of $NaClO_4$ (a) and $NaCF_3SO_3$ (b) with the present PPO ($M = 4 \times 10^3$) and with its high molecular weight counterpart.

study of Bergman *et al.*,[6] two distinct relaxations are clearly seen in the derivatives of the DSC curves of this salt in the present PPO (Figure 2). These derivatives show that its critical composition for microphase separation is comparable to that of $NaClO_4$ in the same polymer (O/Na = 13).

Although the DSC curve recorded for the composition O/Na = 16 of $NaCF_3SO_3$ in the present PPO does not show a clear T_g splitting, the global transition extends over 40 °C. This broadening is much larger than that (over 12 °C) reported by McLin and Angell[11] for a similar mixture. More puzzling, however, is the failure of these authors[10,11] to record a T_g splitting for mixtures of this composition with either $LiClO_4$ or $NaClO_4$. Though we did not further study $NaCF_3SO_3$ in the high molecular weight PPO, the data in Figure 1 also suggest a higher concentration in the complexed microphase of this system. From this comparison with a high molecular weight PPO, it is clear that microphase separation is not induced by the OH end groups in the present PPO. On the contrary, if these groups have an effect on the interactional balance (and they should), they would produce a lowering in the critical composition, which in turn would contribute to depress the interface tension.

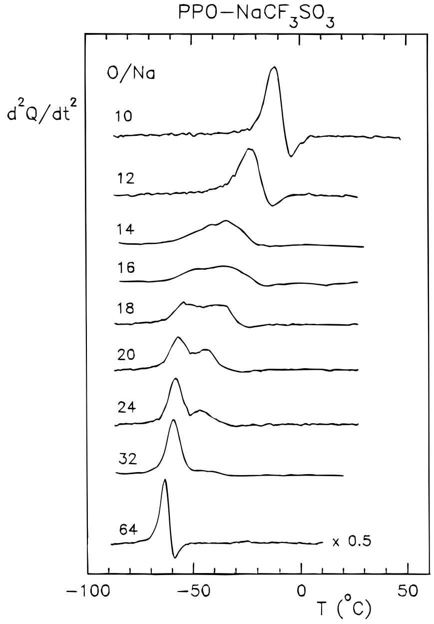

Figure 2. Derivatives of the DSC curves recorded on mixtures of $NaCF_3SO_3$ with the present PPO ($M = 4 \times 10^3$).

Interface tension, which appears to be greater for $NaClO_4$ than for $NaCF_3SO_3$ in either low or high molecular weight PPO, should increase with decreasing temperature. This, together with the low viscosity of the present PPO, probably accounts for the macroscopic separation observed for $NaClO_4$ in this polymer. This separation is a long-time process because it is governed by the diffusion of PPO segments out of the complexed microphase. This explains why it does not take place in high molecular weight PPO where chain entanglements, as well as physical cross-links resulting from complexation and segregation, severely hinder long-range chain displacement.

The two-layer separation observed for $NaClO_4$ in the present PPO is best illustrated by considering the composition O/Na = 32. Just after their heating to 50 °C, mixtures of this composition exhibited a single T_g comparable to that of the neat polymer. Over a few weeks, however, they became turbid, and a clear layer of low viscosity slowly separated from the turbid material. After 2 months, this upper layer was thick enough to allow its characterization by ^{23}Na NMR and GPC. It was salt-free PPO with a molecular weight distribution comparable to that of the original polymer. This indicates that the dispersion of the complexed phase had become coarse enough to allow an effective percolation of the PPO chains under the effect of buoyancy. Although the lower layer remained turbid, it contained a decreasing amount of salt-free PPO with increasing time. After 2 months, its DSC curve was comparable to that in Figure 1 for the composition O/Na = 16.

Since any given cation is coordinate to more than one ether oxygen, diffusion of polymer segments out of the complexed microdomains should depend on the magnitude of the cation–oxygen interactions. It is well known that magnesium cations have a rate of exchange much slower than alkali metal cations in amorphous PEO electrolytes.[21] It is also well documented that alkaline earth salts produce a T_g elevation about twice as large as that produced by alkali metal salts in such materials.[22] Both these features probably account for the rubbery plateau reported by Angell and co-workers[9] for subcritical mixtures of $Mg(ClO_4)_2$ with a $M = 4 \times 10^3$ PPO. For the composition O/salt = 20, which is well below the critical composition of this system (O/Mg = 10), T_g of the salt-rich microphase is 40 °C higher than that of the PPO−$NaClO_4$ system. This yields an interval of 70 °C over which the mixture containing $Mg(ClO_4)_2$ consists of both a soft and a rigid microphase. In comparison, this interval does not exceed 30 °C for $NaClO_4$. In either case, the material probably consists of salt-rich microdomains providing physical cross-links to a PPO matrix. Although preferential coordination to the OH end groups may contribute to enhance this feature, the physical situation is essentially the same as that in the PPO-$LiClO_4$ system studied by Moacanin and Cuddihy.[2]

Figure 3 depicts the T_g-composition relationships of the present systems ($M = 4 \times 10^3$). In the case of the PPO materials, onsets of the low- and high-T_g features (when observed) are denoted by $T_{g,L}$ and $T_{g,H}$, respectively. Although $T_{g,L}$ does not vary with increasing salt content for the PPO−$NaClO_4$ system, it increases from −67 °C (neat PPO) to −54 °C (O/Na = 14) for the PPO−$NaCF_3SO_3$ system. This change in $T_{g,L}$ might be interpreted in terms of a small but increasing amount of salt in the low-T_g microphase of this system. However, in the high molecular weight PPO where the complexed microdomains are larger, $T_{g,L}$ remains invariant for both $NaClO_4$ and $NaCF_3SO_3$ (Figure 1). This suggests that an interface effect could also play a part in this feature. Note that an inversion in the nature of the dispersed microphase should take place above a certain salt content in all those systems. Thus, as in the case of the complexed microdomains at low salt contents, interface tension must govern the size of the salt-free (or salt-poor) microdomains at large salt contents. Though interface tension appears to be minimal for $NaCF_3SO_3$ in the present PPO, it is positively maximal for $NaClO_4$ in the high molecular weight PPO. In the study of the latter system, not only $T_{g,L}$ and $T_{g,H}$ remained invariant, but $T_{g,H}$ (−15 °C) could be recorded down to O/Na = 64.

Figure 3 shows that the T_g elevation produced by the present salts is much greater in PPO than in PEO. It is also much greater for $NaClO_4$ than for $NaCF_3SO_3$ in both polymers. These features, which are deduced from the data over the range above microphase separation in PPO, are comparable to those reported for $LiClO_4$ and $LiCF_3SO_3$.[1] The data related to PEO concern fully amorphous mixtures only. Rapid crystallization, even under melt-quenching, explains the lack of data below O/Na = 30 for both salts, and above O/Na = 10 for $NaCF_3SO_3$. In the phase diagrams of these systems,[4,23] PEO partakes in a eutectic equilibrium with an intermediate compound. The eutectic composition is O/Na = 8 for $NaClO_4$ and O/Na = 12 for $NaCF_3SO_3$. Below this composition, the highest-temperature, liquid−solid equilibrium is the PEO liquidus curve. Thus, in either case, a conductivity study could be performed at moderate temperatures (down to 50−55 °C under supercooling) over a range of compositions well suited for a comparison with PPO.

2. Conductivity Behavior. When conductivity (σ) isotherms of PPO electrolytes are compared to those of PEO amorphous electrolytes (see Figure 4 for the present salts at 60 °C), there is no evidence for any anomaly resulting from microphase separation in PPO. In such isotherms, however, conductivity is lower in PPO than in PEO and the difference between the two polymers increases markedly with decreasing salt content. It may be seen that this change is much greater in the high molecular weight materials than in the present ones. It may also be seen that chain length has a small effect on conductivity in PEO. This proves that this polymer provides a good background to quantify the effects observed in PPO. From the concentration dependence of $\sigma_{PPO}/\sigma_{PEO}$ (Figure 5), it is clear that $NaClO_4$ yields smaller and more labile microdomains in the present PPO than in the high molecular weight PPO. Over the range where a comparison is possible (from O/Na = 10 to O/Na = 64), this ratio decreases by a factor of 10 in the former polymer compared to a factor of 60 in the latter. Figure 5 also confirms that $NaCF_3SO_3$ yields more labile microdomains than $NaClO_4$ in either of these polymers.

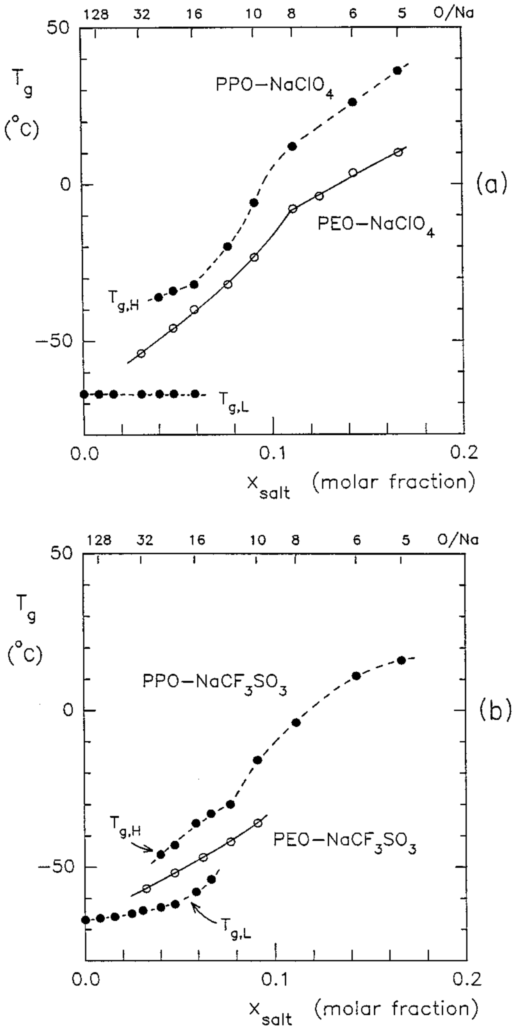

Figure 3. Plots of T_g as a function of the salt molar fraction for mixtures of $NaClO_4$ (a) and $NaCF_3SO_3$ (b) with the present PPO and PEO ($M = 4 \times 10^3$). $T_{g,L}$ and $T_{g,H}$ denote the low- and high-T_g features recorded below the critical composition in PPO. The data related to PEO concern melt-quenched amorphous mixtures only.

As in other glass forming electrolytes, ion mobility in homogeneous polyether electrolytes decreases exponentially with decreasing temperature toward T_g. Since T_g increases with salt content, this feature partly accounts

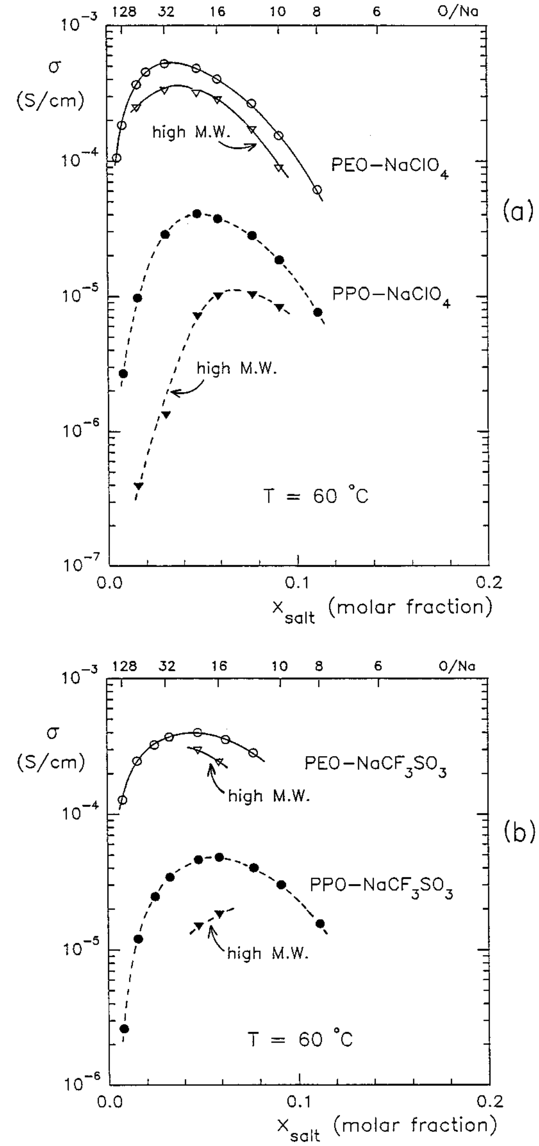

Figure 4. Conductivity isotherms at 60 °C of $NaClO_4$ (a) and $NaCF_3SO_3$ (b) in the present PPO and PEO ($M = 4 \times 10^3$) and in their high molecular weight counterparts.

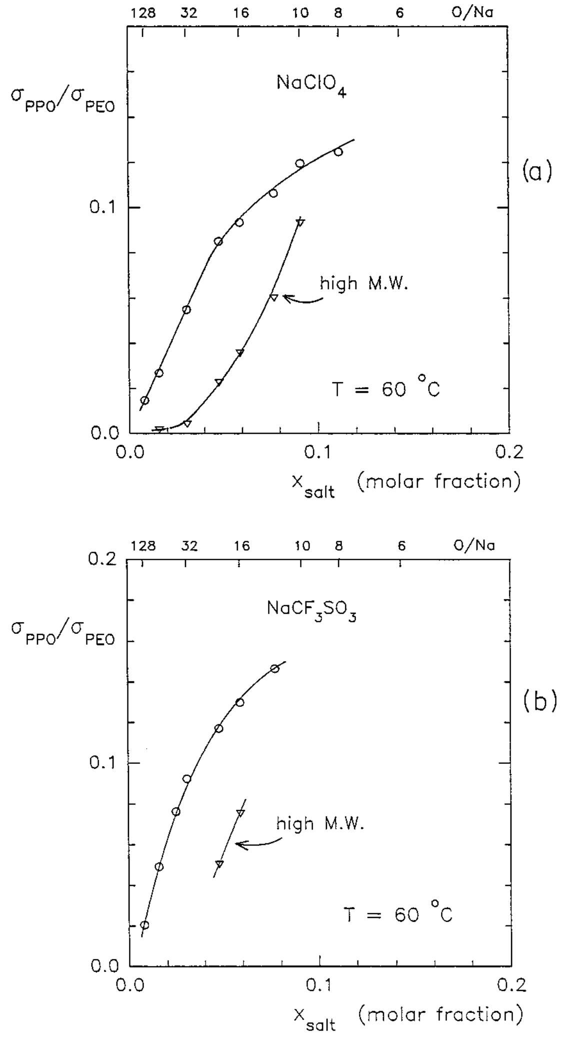

Figure 5. Conductivity ratio $\sigma_{PPO}/\sigma_{PEO}$ at 60 °C of $NaClO_4$ (a) and $NaCF_3SO_3$ (b) in the present PPO and PEO ($M = 4 \times 10^3$), and in their high molecular weight counterparts.

for the maximum in the conductivity isotherms of Figure 4. Furthermore, since PPO homogeneous electrolytes exhibit a greater T_g than their PEO counterparts, this feature also affects the magnitude of the ratio $\sigma_{PPO}/\sigma_{PEO}$ in Figure 5. In either case, it contributes to mask the effect due to the structural change in PPO. This is particularly true in the present PPO where this change is not as marked as in the high molecular weight PPO.

Figure 6 shows a new comparison of the $M = 4 \times 10^3$ materials based on reduced conductivity σ_R, i.e., conductivity at a fixed value of $T - T_g$ (110 °C). For the mixtures exhibiting two T_g's, values of σ_R were established for $T_{g,L}$ and $T_{g,H}$, respectively. This blind procedure allows the definition of the lowest and highest values of σ_R that can be extracted from the raw data. It may be seen that either of these values are roughly in agreement with the global pattern that emerges from the data related to the other mixtures. With increasing salt content, σ_R first increases very slowly up to the critical composition (O/Na = 13) and then exhibits a marked rise above this point. This pattern, which suggests a percolation threshold for ion conduction, is identical to that reported for LiBr, $LiClO_4$, and $LiN(CF_3SO_2)_2$ in the former work.[1]

Thus, in all the $M = 4 \times 10^3$ PPO−salt systems studied until now, ion conduction at a fixed value of $T - T_g$ appears to increase abruptly just above the critical composition for microphase separation. We noted that this feature also applies to $NaClO_4$ in the high molecular weight PPO. In the former work on $LiN(CF_3SO_2)_2$ in the present PPO,[1] the comparison with PEO could be made over a wide range of concentrations (up to O/Li = 2). This salt, which is highly soluble in PEO and PPO, exhibited a maximum of σ_R near the composition O/Li = 6 in both polymers. Furthermore, above the maximum (lower by 30% in PPO), σ_R was essentially independent of the nature of the polymers. This, together with the trends observed in Figure 6, indicate that the PPO systems converge toward a structure similar to that of the PEO systems at high salt contents. Although this change is an accelerated one, it takes place above the critical composition only. This suggests that a local structure, comparable to that in the salt-rich microdomains, remains present over a range of concentrations above this point.

Since this structure is not favorable to an exchange of solvation sites, it must be highly ordered (i.e., with a maximum of interactions and a minimum of tension). Above the critical point, its stability must be affected

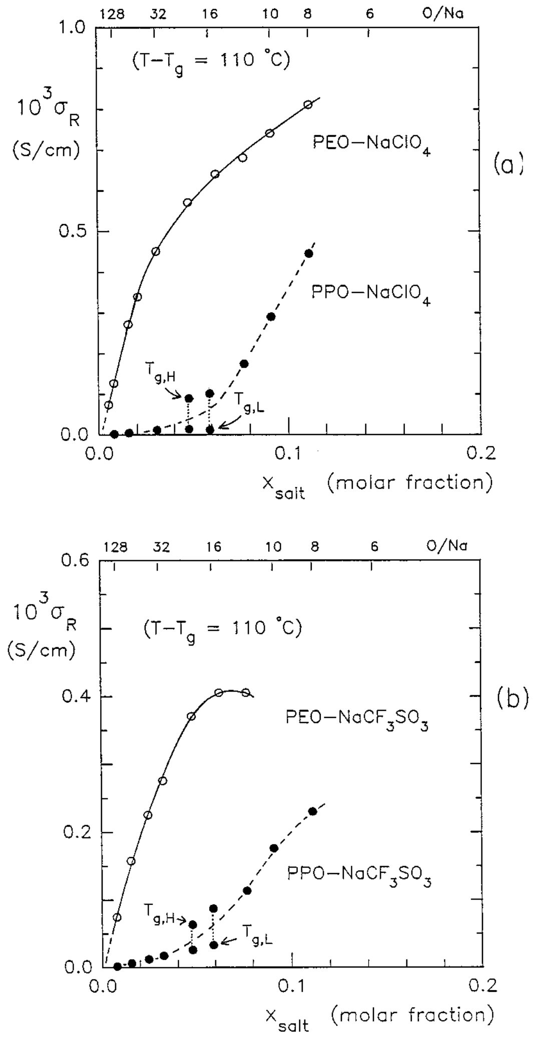

Figure 6. Reduced conductivity σ_R at $T - T_g = 110$ °C of NaClO$_4$ (a) and NaCF$_3$SO$_3$ (b) in the present PPO and PEO ($M = 4 \times 10^3$).

by the local asymmetry produced by the solvation of the new cations. Furthermore, the presence of a disordered domain in one region must favor a greater disordering of this region. Such a cooperative change, which is characteristic of any order–disorder transition, probably accounts for the abrupt rise in σ_R.

In some aspects, this interpretation is similar to that recently proposed by Ferry *et al.*[19] to account for the abrupt increase in the molar conductivity (Λ) of the $M = 4 \times 10^3$ PPO–LiCF$_3$SO$_3$ system above the composition O/Li = 300 (at 20 °C). Unaware of the phase behavior of this system, they nevertheless considered the possibility that ion mobility could suddenly change above a critical point. By assuming that this point corresponds to the saturation of preferred solvation sites, they suggested that the remaining sites (less stable than the former ones) could rapidly exchange their cations with other species such as free anions, ion pairs, and ion triplets (identified as a minor species from O/Li = 300 to O/Li = 11 in their infrared study). In our former work,[1] a plot of σ_R based on their conductivity data[13] was marginal when compared to that obtained for PEO. For instance, at the composition where they reported a maximum of Λ (O/Li = 40), σ_R was 40 times lower in PPO than in PEO. Also note that their spectroscopic data show some difference with respect to those reported by Schantz and Torell[7,8] for LiClO$_4$ and NaCF$_3$SO$_3$ in a similar PPO. They indicate that the anion environment remains unchanged from high dilution (O/Li = 3000) to O/Li = 50 only, that is, up to a limit well below the critical composition for microphase separation.

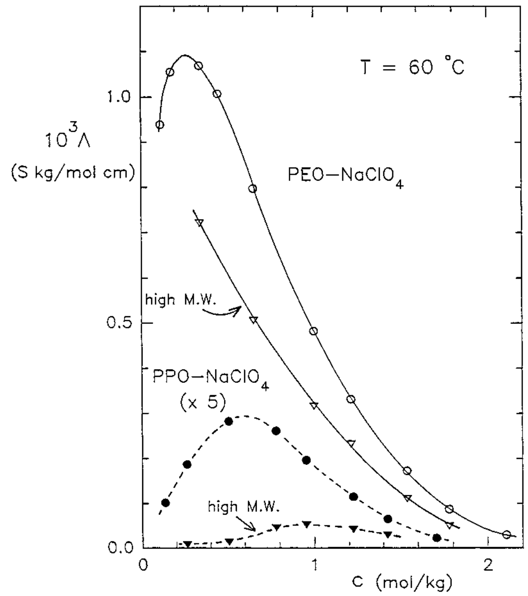

Figure 7. Molar conductivity Λ at 60 °C of NaClO$_4$ in the present PPO and PEO ($M = 4 \times 10^3$) and in their high molecular weight counterparts.

Unfortunately, LiCF$_3$SO$_3$ is not well suited for a comparison with PEO. The liquidus curve of the 3/1 compound related to this system precludes any conductivity study at moderate temperatures over the range above O/Li = 32.[1] Figure 7 shows the concentration dependence of Λ for NaClO$_4$ in PEO and PPO. This comparison, which is based on the conductivity isotherms of Figure 4, includes the high molecular weight materials. From the Λ data related to these materials, it may be argued that the maximum observed for PPO is associated with the change in the size (and lability) of the complexed microdomains with salt content. This maximum, which is near O/Na = 16 in the high molecular weight PPO, is shifted to a lower concentration (O/Na = 30) in the present PPO. Such a feature is not observed for PEO. In that case, the maximum is located at a much lower concentration (below O/Na = 85) in either the low or high molecular weight PEO.

Conclusion

PPO–alkali metal salt systems exhibit a peculiar phase behavior resulting from the low solvating power of PPO. Below a certain concentration, which depends on the nature of the salts, complexed microdomains separate from the polymer and the size of these microdomains decreases upon further dilution. Although a $M = 4 \times 10^3$ PPO yields smaller and more labile microdomains than a high molecular weight PPO, the comparison with a $M = 4 \times 10^3$ PEO shows that any basic study performed which such a polymer is destined to yield erratic or problematic results due to this separation phenomenon.

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