Macromolecules **1995,** *28,* 5063–5068

Fourier Transform Raman Spectroscopic Study of a Poly(propylene oxide)-Based Model Network Electrolyte

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Received December 20, 1994; Revised Manuscript Received April 19, 1995®

ABSTRACT: Raman spectroscopic studies of the model network derived from poly(propylene oxide) with tris(4-isocyanatophenyl) thiophosphate (triisocyanate) in the presence of salt, $LiClO_4$, have been carried out over a range of salt concentrations and molecular weights of poly(propylene oxide). The spectral analysis in the frequency region of 800 and 300–500 cm^{-1} representing characteristic vibrational modes of poly(propylene oxide) chains showed the salt to interact preferentially with the cross-link points, i.e. the urethane groups rather than the ether groups of the poly(propylene oxide) chain. Also, the relative intensity changes in the 1700 cm^{-1} carbonyl stretching region with increasing salt concentration provided a direct indication of the salt interaction with the urethane groups. Previously, an impedance spectroscopic study suggested that there are two ionic conduction mechanisms related to the ether units and the urethane groups, respectively. Our spectroscopic studies proved this hypothesis. Therefore ionic conductivity in this particular network-based polymer electrolyte is determined by the combination of two mechanisms, one coupled to the poly(propylene oxide) chains and the other to the urethane groups present at the cross-link points.

Introduction

Polymer-based electrolytes have generated great interest from both fundamental and applied points of view.[1] Particularly, linear polyether-based polymer electrolytes have been widely investigated to understand the relationship between polymer structure and ionic conductivity. Recently, network polymer-based electrolytes have been of interest because of their inherent advantages such as dimensional and thermal stability in spite of their lower ionic conductivity as compared to the corresponding linear polymer-based electrolytes.[1,2]

The network derived from poly(propylene oxide) (PPO) with multifunctional isocyanates has been used as a model network polymer because atactic poly(propylene oxide) has a narrow molecular weight distribution giving a homogeneous structure. The ionic conductivity of these network polymer electrolytes has been determined previously, and the temperature dependence of the ionic conductivity was described using the Williams–Landel–Ferry (WLF) equation.[1,3] This suggests that the ionic conductivity is mainly associated with local segmental motions of polymer chains. Furthermore, it has been shown that there are two distinct dielectric relaxation processes in this particular network polymer, one related to the ether units and the other associated with the urethane groups.[4] Also, in impedance measurements of poly(propylene oxide)-based network polymer containing $LiClO_4$, it has been suggested that both the ether units in the network chains and the urethane groups at the cross-link points contribute to the ionic conductivity of the system.[5] Further studies at the molecular level are needed, however, to differentiate ionic conduction processes coupled with urethane and ether groups.

In order to investigate the cross-linking effect on the ionic conduction mechanism in network-based polymer electrolytes, it is necessary to separate the ionic interactions with the cross-link points from those of the poly(propylene oxide) network chains and clarify the relationships between polymer structure and electrical properties of these systems. One of the best techniques for this is Raman spectroscopy. The Raman technique, especially in the low- to mid-frequency region, can be employed to investigate specific interactions between ions and polymer chains as well as the chain conformational distribution.[6–15] Previously, we characterized the chain conformational changes occurring in poly(propylene oxide) chains as a result of interactions with salt by analyzing the 800 cm^{-1} region of the Raman spectrum.[16] In addition to the changes observed in this region, characteristic bands which might be sensitive to the conformational and/or compositional changes were recognized in the low-frequency region of the Raman spectrum. The bands at ca. 360 and 500 cm^{-1} appear to be associated with conformational changes of poly(propylene oxide) as a result of complexation with the ions. In addition, several well-assigned localized vibrations exist which can provide information regarding interactions between specific functional groups and ions. For example, the characteristic carbonyl stretching region in the 1700 cm^{-1} region can provide information concerning changes in the carbonyl group in the urethane unit as a result of interaction with ions.

In this study, we report Raman spectroscopic studies of model networks of atactic poly(propylene oxide) with different molecular weights end-linked with trifunctional isocyanate. By comparison with linear poly(propylene oxide)s complexed with $LiClO_4$, we investigated the cross-linking effect on the interaction between ions and the network and thus the mechanism of ionic conduction in the poly(propylene oxide)-based network polymer electrolytes.

Experimental Section

Hydroxy-terminated poly(propylene oxide) (HPPO) samples of molecular weight 1000 (HPPO1000) and 4000 (HPPO4000) were obtained from Aldrich Chemical. The salt containing HPPO solutions was prepared as described previously.[16] The hydroxy number was determined by titration (ASTM D4274). Lithium perchlorate/HPPO complexes were prepared with compositions of $[Li^+]/[\text{propylene oxide unit}] = 0.05, 0.10, 0.15,$ and 0.20.

® Abstract published in *Advance ACS Abstracts,* June 15, 1995.

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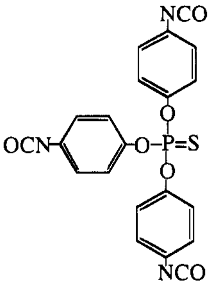

Figure 1. Chemical structure of tris(4-isocyanatophenyl) thiophosphate.

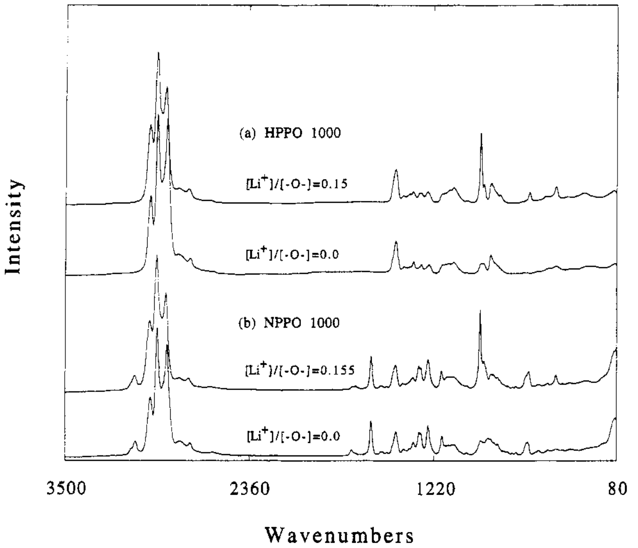

Figure 2. Raman spectra (3500–80 cm^{-1}) of HPPO1000 and NPPO1000 and their salt complexes.

The cross-linking agent, tris(4-isocyanatophenyl) thiophosphate (triisocyanate), is supplied as the ethyl acetate solution by Bayer Chemical Co. The triisocyanate was crystallized as described previously.[17] Figure 1 presents the chemical structure of the triisocyanate. Network films were prepared by dissolving $^{1}/_{3}$ mol of triisocyanate into $^{1}/_{2}$ mol of predried HPPO under vacuum at 90 °C until the solution became clear. The slightly yellow and transparent solution was poured onto a glass plate and then cured at 90 °C under vacuum for 3 days. Network samples prepared from HPPO1000 and HPPO4000 are designated as NPPO1000 and NPPO4000, respectively.

The salt-complexed network films are prepared by swelling the films in anhydrous THF solutions of lithium perchlorate with different concentrations for 1 day, drying at 60 °C under vacuum for 1 week, and further drying at 130 °C for 5 h. The concentration of lithium perchlorate in the films was determined by microanalysis and represented by the molar ratio of lithium cation to ether oxygen, i.e. [Li$^+$]/[−O−].

In these samples, particularly salt complexes, dispersive Raman studies using visible excitations were difficult to carry out because of the small amount of fluorescence that usually exists. This obstacle can be overcome by using the extremely long laser wavelength excitation usually only practicable in conjunction with the Fourier transform technique. In our laboratory, Fourier transform Raman spectra were obtained at room temperature using a Bruker FRA 106 spectrometer. A Nd:Yag laser (wavelength: 1064 nm) was used as excitation. Laser output power was maintained at 500 mW. A total of 1024 scans were coadded in order to obtain an acceptable signal to noise ratio. The excitation/collection geometry was 180° and spectral resolution maintained at 4 cm^{-1}. Raman spectra of HPPO1000 and NPPO1000 and their salt complexes are shown in Figure 2.

Band deconvolution to separate the multiple components observed was carried out using a commercial package *Lab Calc* purchased from Galactic Industries. The band shape used was a mixture of Gaussian and Lorentz functions. This program provides the capability to fix, if necessary, any parameter used to describe the band position, shape, or intensity. Relative intensity was then measured as the integrated area of individual deconvoluted peaks.

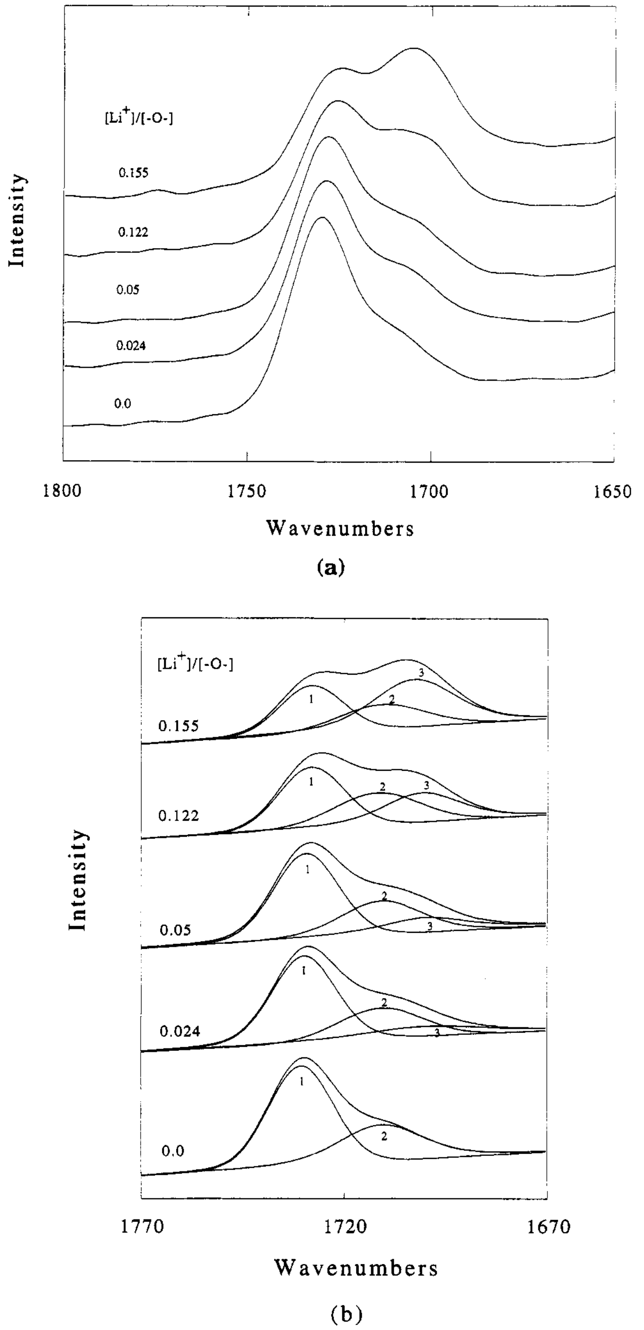

Figure 3. (a) Raman spectra of NPPO1000 in the carbonyl stretching region as a function of salt concentration. (b) Deconvoluted results for the 1700 cm^{-1} region for NPPO1000.

Results and Discussion

The network derived from the reaction of the hydroxy groups of poly(propylene oxide) and the isocyanate contains urethane groups at the cross-link points. Figure 3a shows the Raman spectrum in the carbonyl stretching band region of the urethane group as a function of salt concentration for NPPO1000. Without salt, the strongest band is assigned to the free carbonyl stretching mode at 1730 cm^{-1} and the weak shoulder to the hydrogen-bonded one at ~1710 cm^{-1}.[18-20]

In the salt−network complexes, a specific interaction between the salt and urethane is evidenced by the

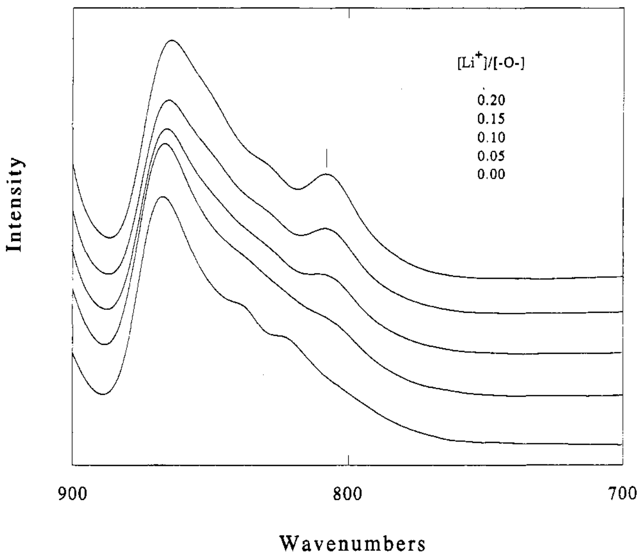

Figure 4. Raman spectra of HPPO1000 in the 700−900 cm^{-1} region as a function of salt concentration.

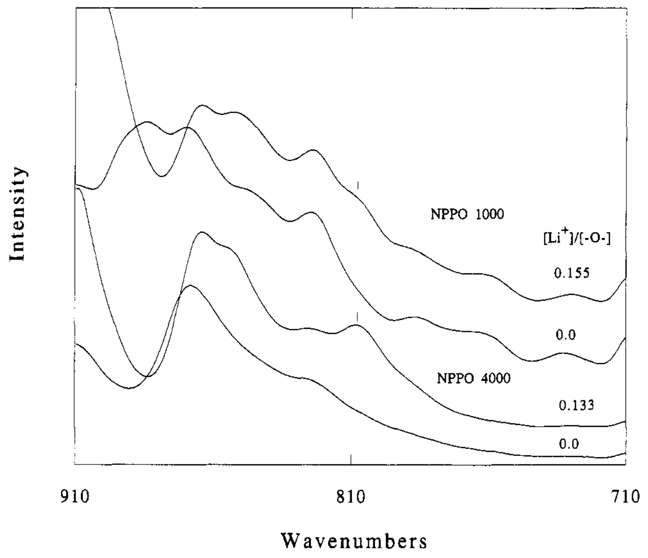

Figure 5. Raman intensity of the bands in the 800 cm^{-1} region for NPPO1000 and NPPO4000.

increased intensity in the 1700−1710 cm^{-1} region with increased salt concentration while the intensity of the free carbonyl stretching band at 1730 cm^{-1} decreases. Further quantitative analysis has been performed by utilizing the band deconvolution technique for the multiple components observed in the 1700−1730 cm^{-1} region. Three peaks are considered for salt−NPPO complexes, and two, for NPPO without salt. Without fixing any fitting parameter, we have deconvoluted the spectrum into the bands at 1731 (band 1) and 1711 cm^{-1} (band 2) for NPPO1000 without salt. The series of band deconvolution results for spectra obtained as a function of salt concentration are shown in Figure 3b. In the presence of salt, we have deconvoluted the various components by fixing only the band position at 1711 cm^{-1} with a width of ∼25 cm^{-1} for the hydrogen-bonded carbonyl stretching component. A best fit can only be achieved by adding a third component at 1700−1703 cm^{-1}. It can be clearly seen in Figure 3b that the intensity of this third component increases with a corresponding decrease in intensity of band 1 as a function of increasing salt concentration. No significant change was observed in the intensity of band 2 as compared with changes found for bands 1 and 3. We therefore conclude that lithium cations interact mostly with free carbonyl groups and that interaction is characterized by the new carbonyl stretching component at 1700 cm^{-1}.

Because conformationally sensitive backbone skeletal modes in the mid to low-frequency region all exhibit changes in polarizability, Raman spectroscopy has been particularly useful in providing polymer microstructural information.[16,21,22] Figure 4 shows the 700−900 cm^{-1} region of the Raman spectrum of HPPO1000 with changing salt concentration, [Li$^+$]/[−O−] = 0.0−0.2. The intensity of the 810 cm^{-1} band increases with increasing salt concentration. This band at 810 cm^{-1} has been assigned to the TGT conformation of the propylene oxide unit. The intensity increase indicates an increase in the TGT conformation population of the poly(propylene oxide) chain induced by the interaction between the lithium cation and the ether units.[16] We do not, however, suggest the presence of long range order due to this increase in the TGT conformation. In the same frequency region, Raman spectra of NPPO1000, NPPO4000, and their salt complexes are shown in Figure 5. Compared with HPPO1000, a relatively smaller intensity change of the 810 cm^{-1} band occurs in NPPO1000. In contrast with NPPO1000, NPPO4000, which has a lower cross-link density, shows an intensity change in the 810 cm^{-1} band comparable to that of the corresponding linear poly(propylene oxide), HPPO4000.[16]

In addition, characteristic differences between linear and network polymers are observed at ca. 360 and 500 cm^{-1}. The bands in the 300−500 cm^{-1} region are assigned to the COC/CCO bending vibrational mode.[22] HPPO1000 (Figure 6a) has broad features at around 364 and 503 cm^{-1} while NPPO1000 (Figure 6b) shows narrower bands at higher frequencies centered at 370 and 510 cm^{-1}, respectively. The sharpening of the bands for the network indicates a better defined chain conformational distribution. The higher frequency observed in the network polymer indicates a change in the conformational distribution.[22] It should be mentioned that the sizes of these cross-linking groups are as large, if not larger, than the molecular dimensions of these low molecular weight poly(propylene oxide) chains. Therefore, the presence of cross-linking groups can influence the conformational distribution of the connecting poly(propylene oxide) chains.[4,23] As expected, the smaller the molecular weight of the poly(propylene oxide) chain, the greater the effects.

With increasing salt concentration, a relative intensity increase at ca. 388 and 526 cm^{-1} is observed in linear poly(propylene oxide) and these new growing bands dominate in the high salt concentration range, as shown in Figure 6a. However, the Raman bands of NPPO1000 in this region show almost no change at low salt content. With increasing salt content, only moderate changes in intensity at ca. 380 and 520 cm^{-1} are observed but the bands at ca. 371 and 512 cm^{-1} remain dominant (Figure 6b). The frequency shift represents a change in the conformational distribution. The normal coordinate calculation for methyl isopropyl ether by Snyder et al.[22] shows a conformational dependence on frequencies in the 300−500 cm^{-1} region. The calculated frequencies for the C_1 species (TT) are 372 and 492 cm^{-1} and 385 and 569 cm^{-1} for the C_s species (GT). These bands were assigned to the vibrational modes of COC bending and asymmetric skeletal bending of the isopropyl group.[22]

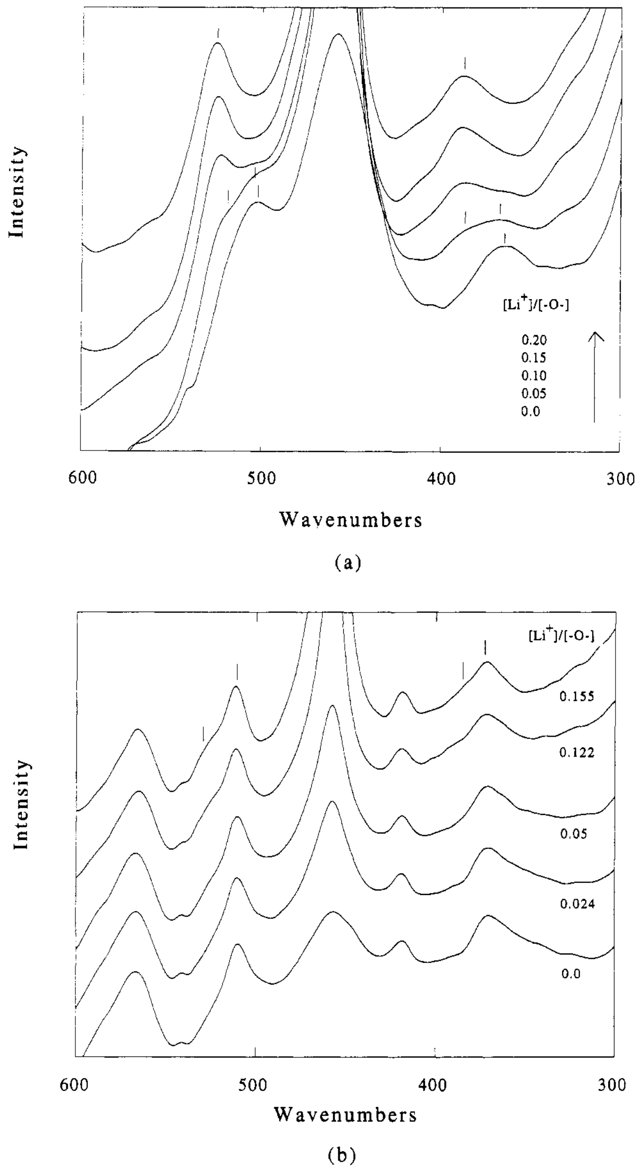

Figure 6. Raman spectra (600–300 cm^{-1} region) as a function of salt concentration: (a) HPPO1000; (b) NPPO1000.

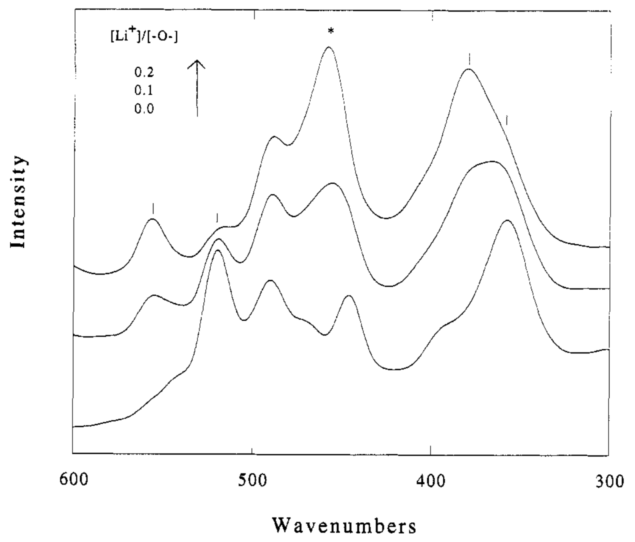

Figure 7. Raman bands of DMP in the 600–300 cm^{-1} range as a function of salt concentration. * designates the anion (ClO_4^-) band.

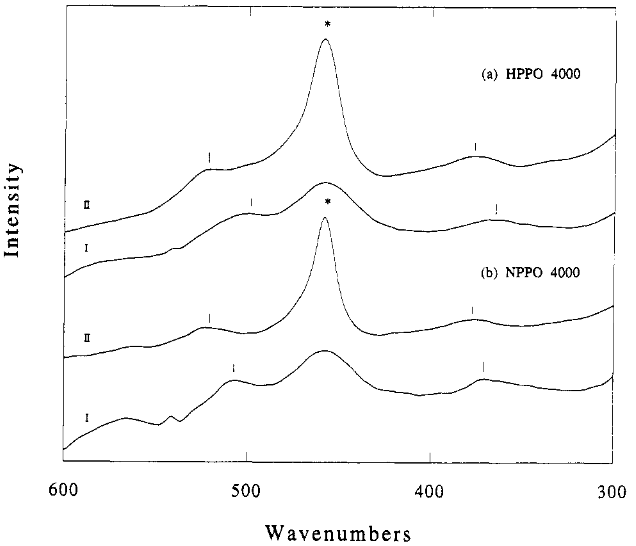

Figure 8. Raman spectra of HPPO4000 and NPPO4000 in the range 600–300 cm^{-1}. [Li$^+$]/[–O–] = 0.0 (I), 0.133 (II) for NPPO; 0.0 (I), 0.10 (II) for HPPO. * designates the anion (ClO_4^-) band.

The Raman spectrum of 1,2-dimethoxypropane (DMP), which has one isopropyl group, as a model compound for poly(propylene oxide) has been utilized in this study. As shown in Figure 7, Raman bands for 1,2-dimethoxypropane were observed at 358 and 520 cm^{-1} at room temperature. With increasing salt concentration, intensity increases occur at 380 and 557 cm^{-1}. On the basis of Snyder's assignment,[22] this spectral change might be related to conformational changes of the –O–C–C–O– backbone caused by interaction with lithium cations. Our previous study which showed an increase of the TGT conformation population of the –O–C–C–O– backbone with increasing salt concentration supports this interpretation.[16] Although there is a frequency difference among the molecules, this interpretation can be extended to a poly(propylene oxide) chain having the same chemical structure as DMP. Therefore the higher frequency shift of bands at ca. 360 and 500 cm^{-1} in the presence of salt can be attributed to conformational changes of poly(propylene oxide) chains interacting with salt. The discrepancy in the spectroscopic changes between HPPO1000 and NPPO1000 indicates the difference in the degree of chain conformational change of poly(propylene oxide) in the two systems.

The Raman spectrum of NPPO4000 in this region (Figure 8) shows bands at 371 and 507 cm^{-1}, which are a few wavenumbers higher than the bands at 367 and 500 cm^{-1} in HPPO4000. This difference is also observed in NPPO1000 as compared to HPPO1000, indicating changes in the chain conformational distribution of poly(propylene oxide) or restraint by network formation. On the other hand, unlike NPPO100 chains, NPPO4000 with added salt shows almost no difference from that of HPPO4000 in this region.

This result is in good agreement with the spectral change observed at 810 cm^{-1} for these systems. It was found in our previous study that the intensity change of the 810 cm^{-1} band is proportional to the salt concentration in HPPO-based polymer electrolytes.[16] Also, the spectral change in the 300–500 cm^{-1} region is dependent upon salt concentration. Since both Raman scattering band regions represent characteristic vibrational modes of poly(propylene oxide) chains, the relative intensity changes of those bands indicate the proportion of poly(propylene oxide) chains interacting with the ions through changes in chain conformation by solvation of ions. Therefore the smaller intensity changes observed in the networks based on the short chain length (mol wt 1000) of poly(propylene oxide) indicates a low local concentration of lithium cations interacting with ether oxygen although the total salt concentration based on the number of ether units is the same as that in linear poly(propylene oxide)-based polymer electrolytes. From the cross-link density dependence of the spectral change in the 800 and 300–500 cm^{-1} region, depletion of salt associated with ether units in the network of low molecular weight poly(propylene oxide) chains can be attributed to the interaction of the lithium cation with the urethane group of the cross-link point. As mentioned earlier, additional evidence for this is found in the intensity increase in the 1700 cm^{-1} region.

All spectroscopic evidence suggests that Li^+ ions interact preferentially with the urethane cross-links. The molar ratio of the ether units to urethane groups, including the NPPO1000 sample, is at least 8:1. If lithium cations are distributed between urethane and ether units only on the basis of the statistical weight of the two components, the local content of lithium cations should be much higher along the poly(propylene oxide) chains and thus should be reflected in changes of the skeletal modes.[16] As mentioned above, this is contrary to our observations. Despite the large changes observed for the C=O bands in the 1700 cm^{-1} region for all the network samples independent of molecular weight (Figure 3), the changes in the skeletal region for the network samples are identical to those found for the linear polymers (Figures 6 and 8). These observations lend support to the greater solvation ability of the urethane group for the lithium cation than that of the ether unit. It is true, however, because of the large size of the junction points, that the chain conformation between network junction points may not be the same as for linear polymers. This change may restrict interaction between Li^+ ions and ether oxygens. We have, however, no quantitative evidence indicating a change in the chain conformation distribution.

Ichikawa et al. studied ionic motions in the same network-based polymer electrolytes.[5] They found that the complex impedance diagram of NPPO1000 having a higher cross-link density was a superposition of two semicircles having different relaxation times. On the other hand, the diagram of NPPO4000 was found to be a single semicircle. By applying normalization of the imaginary part of the complex impedance and the Cole–Cole distribution function, we analyzed the two relaxation processes observed in NPPO1000. The higher frequency process was found to be related to the ether units, and the lower frequency process was assigned to relaxation involving the urethane groups.

The salt dependence of the relative relaxation strength of the higher frequency process showed a difference between NPPO1000 and NPPO2000. While NPPO2000 showed a decrease in the relative relaxation strength with increasing salt concentration, there was no change up to salt concentration $[Li^+]/[-O-] = 0.07$ for NPPO1000. Since the relaxation strength is proportional to both the number and strength of the dipoles, the relaxation strength change of the higher frequency process is related to the changes in the ether dipoles due to interaction with lithium cations. Therefore no change in the relaxation strength below $[Li^+]/[-O-] = 0.07$ for NPPO1000 indicates no significant influence on the ether units by lithium cations, which reflects a depletion of lithium cations associated with the poly(propylene oxide) chain of NPPO1000. These results are in good agreement with our vibrational spectroscopic studies, indicating preferred interactions of the lithium cation with the urethane group.

Until now, it has been concluded that the lower ionic conductivity in network-based polymer electrolytes is due to their reduced chain segmental motion compared to that of the linear polymer.[1] This may be true for the case of networks having sufficiently long chains (≥MW 3000) between cross-link points so that the effect of cross-linking agent can be ignored.[23] However, for short chains, a cross-linking agent consisting of polar groups which can interact with ions can play an important part in ionic conduction, as shown in the isocyanate-based network used in our study.

Since urethane groups have a different interaction strength with lithium cations compared to ether groups, the number of carrier ions and the ionic mobility which determine ionic conductivity must be dependent upon cross-link density. Based on the equation derived by Barker et al.,[24] the number of carrier ions (n) for a monovalent salt in a polymer is determined by the lattice energy of the salt (U) and the relative dielectric constant (ϵ) of a polymer at the temperature T by eq 1,[25] where N_o is a constant and k is the Boltzmann constant.

$$n = N_o \exp(-U/2\epsilon kT) \qquad (1)$$

The dielectric relaxation measurements previously carried out showed that urethane groups contribute to increasing the dielectric constant of the system.[4] Therefore urethane groups can generate more carrier ions than ether groups because of a higher ϵ. Even though the urethane group can generate more carriers than the ether group, the higher binding energy between the urethane group and the lithium cation can cause reduced ionic mobility. The contribution of the urethane group to ionic conductivity is determined by the balance of forces between the lattice energy of the salt and the binding energy of the salt to the urethane group. Therefore the lower ionic conductivity in NPPOs than HPPOs complexed with $LiClO_4$ should be interpreted as arising from the higher binding energy of the urethane group with the lithium cation in addition to any restrictions on chain mobility as a result of network formation in this particular system.

Conclusions

Vibrational spectroscopy results correlate well with the dielectric relaxation behavior of oligomeric poly(propylene oxide) chains and their corresponding networks formed by end linking them with triisocyanate. When lithium perchlorate is dissolved in these linear and network species, ionic conductivity is observed and is generally lower in the networks than in the linear oligomers. The complex impedance behavior of these systems exhibits two conductivity regions for the network. Fourier transform Raman results confirm that these are associated with the complexation of the lithium cation with the ether group of the chains on the one hand and with the urethane group of the cross-link points on the other. The lithium cations interact more strongly with the urethane than the ether oxygen groups.

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MA9463021