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Study on the Ionic Conductivity and Mobility of Liquid Polymer Electrolytes Containing Lithium Salts

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ABSTRACT: We report ionic conductivities and mobilities of the liquid polymer electrolytes formed by dissolving the lithium salts in poly(ethylene oxide) and poly(propylene oxide). A high resolution NMR (nuclear magnetic resonance) relaxation technique was used to study the dynamics of the ions in polymer electrolytes. The ^{7}Li NMR results revealed the coexistence of two separate lineshape components with substantially different spin–spin relaxation times (T_2). From the resolution of the two components, we could estimate the spin–spin relaxation time of the mobile free lithium ion and also the fraction of free lithium ions contributing to the ionic conductivity in polymer electrolyte.

KEY WORDS Polymer Electrolyte / Poly(propylene oxide) / Poly(ethylene oxide) / Ionic Conductivity / Ionic Mobility / ^{7}Li NMR / Spin–Spin Relaxation Time /

Polymer electrolytes are of growing importance in electrochemistry in view of their applications, the most important of which is for high-energy-density batteries.[1-3] Segmental motions of the amorphous polymer backbone in polymer electrolytes are liquid-like in character and are believed to be necessary for ionic migration to occur.[4,5] The presence of crystalline phase in high molecular weight PEO [poly(ethylene oxide)] provoked considerable problems in understanding of the mechanism of ionic migration. On the other hand, liquid polymer electrolytes are easy to prepare and the amorphous nature of these electrolyte solutions allows us to establish the useful model systems for studying the fundamentals of ion dynamics in polymer electrolytes. The low molecular weight PEO and PPO [poly(propylene oxide)] were thus chosen as the base polymers for the polymer electrolytes.

Nuclear magnetic resonance (NMR) spectroscopy has been a powerful technique for studying the structure, dynamics and morphology of polymers. Quite a few works on NMR studies of the polymer electrolyte have been reported.[6-11] The systematic study about the ionic mobility, the ion–polymer interaction and the number of carrier ions using the NMR relaxation in polymer electrolytes, however, appears to be rather unsettled. The present work focuses on the use of NMR relaxation technique for the measurement of ionic mobility and concentration of mobile species. We report the detailed ^{7}Li NMR relaxation results combined with ionic conductivity of the polymer electrolyte solutions containing lithium salts.

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EXPERIMENTAL

Materials

For pure PEO,[12] the limited molecular weight of maintaining the amorphous liquid-like structure at room temperature is known to be about 600, and so we used the low molecular weight PEO (MW: 400) in this study. PPO is an amorphous liquid throughout all the molecular weight ranges studied. Low molecular weight PEO (MW: 400) and PPO (MW: 425, 725, 1000, 2000, 4000) were supplied by Aldrich Chemicals Co. and the volatile compounds in these polymer samples were removed under vacuum at 80°C for 3 hours. Lithium salts ($LiClO_4$, LiSCN) were also purchased from Aldrich Chemicals Co. and dried at 120°C in a vacuum oven overnight.

Each electrolyte solution was prepared by dissolving both the pre-weighed amount of polymer and the lithium salt in methanol, followed by rotary evaporation to remove the residual methanol completely. The absence of methanol was checked by ^1H NMR spectroscopy. The concentration of salt in polymer electrolytes was represented in this report by the molar ratio of monomer units to inorganic salt, for example, PPO/LiSCN = 25 : 1 means [PO unit]/[LiSCN] = 25.

^7Li NMR

The ^7Li NMR measurement was performed in 10-mm diameter tube at a frequency of 120 MHz with Bruker-AM-300 NMR spectrometer. The pulse width of 15 μs was selected as a 90° pulse with an acquisition time of 0.39 s. After the termination of the pulse, the nuclei relax towards equilibrium by an exponential process which are characterized by the spin–spin relaxation time (T_2). During the acquisition period, they induce voltages in the receiver coil of the spectrometer yielding the time domain spectrum of the sample, which is refered to as the free induction decay (FID). An important feature common to all the NMR spectra of the polymer electrolyte systems was the presence of the two resolvable components. The intensities and spin–spin relaxation times of the two components were estimated from the FID, which was obtained by the inverse Fourier transform of the NMR spectrum. The sample temperature was maintained at 25°C.

Conductivity and Viscosity Measurements

The conductivity of each electrolyte solution was measured with a Cole–Parmer digital solution analyzer (L-5800-05 model). Conductivity cells have a cell constant 10 cm^{-1} and the analyzer was calibrated using a standard 718 $\mu\Omega$ KCl aqueous solution. The temperature of the solution was maintained constant by a thermoregulator with circulator. And viscosity of each electrolyte solution was determined with a Cannon–Fenske capillary viscometer at 25 $\pm$ 0.1°C.

DSC

The differential scanning calorimetry studies were carried out to determine the glass transition or melting temperature of the polymer electrolytes using a du Pont 9900 instrument. Samples were loaded in hermetically-sealed aluminum pans and heated at 10 K min^{-1} in a stream of liquid nitrogen.

RESULTS AND DISCUSSION

NMR Relaxation and Conductivity

If I (spin quantum number) > 1/2, the nucleus possesses an electric quadrupole moment and thus electric field gradients at the nucleus also lead to relaxation. For several alkali nuclei such as ^{23}Na, ^{39}K, and ^{87}Rb, the quadrupole moments are big enough to produce quadrupole effects, which can dominate the NMR spectra for most systems, while for a ^7Li nucleus, the quadrupole effects can be often neglected due to a highly symmetric environment of the Li^+ ion.[8,13] Thus the quadrupole relaxation effect of ^7Li is assumed

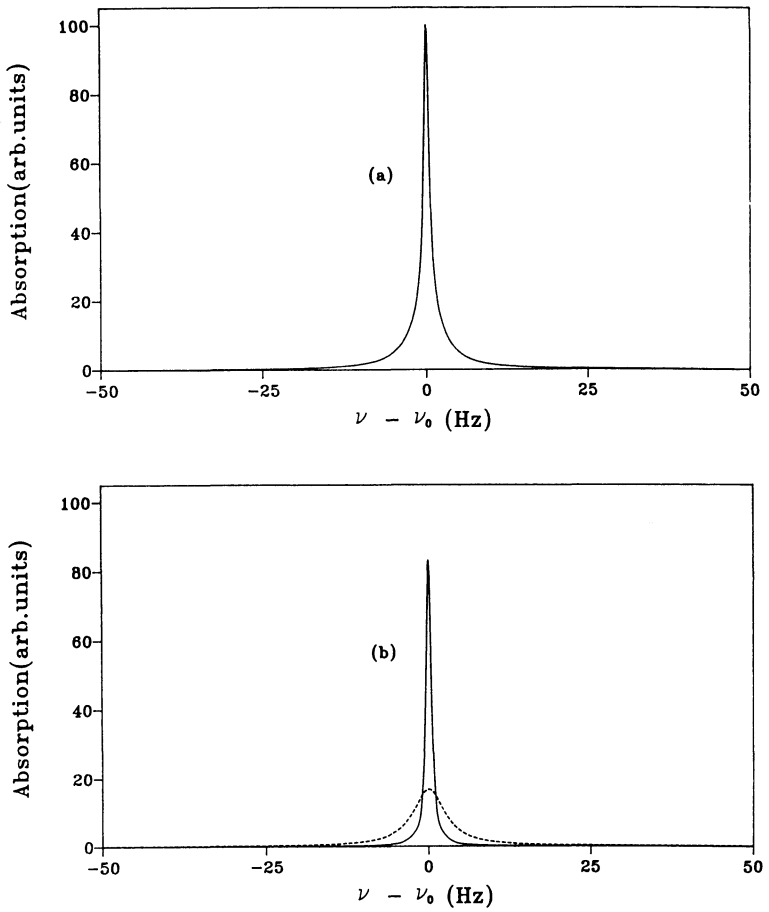

Figure 1. The ^{7}Li NMR spectrum of PPO 425/LiSCN (25 : 1) complex: (a) without resolution; (b) with resolution at 25°C. (ν_0 is the resonance frequency at the maximum absorption and ν is the resonance frequency.)

to be relatively inefficient in our experiments.

Figure 1(a) shows the ^{7}Li NMR spectrum of PPO 425/LiSCN (25 : 1) complex. A proper resolution of this spectrum as shown in Figure 1(b) indicates that the ^{7}Li absorption line is not a single Lorentzian curve, but is consisted of a relatively broad Lorentzian curve (dotted curve) superimposed on a narrow Lorentzian line (solid curve). This result suggests the presence of two lithium configurations in which differ in their relative motions. In a rigidly bonded configuration where there is no relative motion of nuclei, the local magnetic field arising from the randomly aligned nuclear magnetic dipoles vary from site to site within the lattice, giving rise to a distribution of resonance frequencies, and thus its resonance line becomes broader. In a mobile configuration, these local fields tend to cancel because the nuclei causing them are in rapid, and its resonance line is thus narrow. The narrow component is thus corresponding to a highly mobile lithium ion, while the broad component is attributed to lithium species with tightly bound configuration. This identification is consistent with those of other works showing the presence of both mobile and bound sodium species from the tempera-

ture dependence of the ^{23}Na spin–lattice relaxation time (T_1) in polymer electrolyte containing sodium salts.[9-11]

The presence of two lineshape components in NMR spectrum indicates the existence of two separate relaxation processes which differ in spin–spin relaxation (T_2) by an order of magnitude. The nuclear magnetization $M(t)$ could be thus represented as the sum of contributions from both mobile and bound lithium species

$$M(t) = M_{01} \exp(-t/T_{21}) + M_{02} \exp(-t/T_{22}) \quad (1)$$

where M_{01} and M_{02} stand for the initial magnetization intensity of the mobile lithium nucleus and the tightly bound lithium nucleus, reprectively, and T_{21} and T_{22} are spin–spin relaxation times of each lithium nucleus. It is therefore possible to evaluate the portion of mobile free cations contributing to the ionic conductivity using the parameters in eq 1

$$x_F = \frac{M_{01}}{M_{01} + M_{02}} \quad (2)$$

where x_F is the fraction of mobile free cations in polymer electrolyte.

It is well understood that the spin–spin relaxation time and the linewidth of the NMR signal having Lorentzian shape are related *via*

$$T_2 = \frac{1}{\pi \Delta \nu_{1/2}} \quad (3)$$

where $\Delta \nu_{1/2}$ is the NMR line width at half-height. From eq 3, it is noted that the T_2 value increase as the motion of nuclei becomes faster. We can thus obtain the information about ionic motion from the spin–spin relaxation time of the mobile free cation (T_{21}) in eq 1.

In polymer electrolytes, the ionic conductivity is given by

$$\sigma = \sum n_i z_i e \mu_i \quad (4)$$

where n_i is the number of the carrier ions, z_i is the valency of the carrier ions, and μ_i is the ionic mobility. The number of carrier ions is proportional to x_F at a given salt concentration since x_F of the incorporated salts dissociates to the free ions. And the mobility

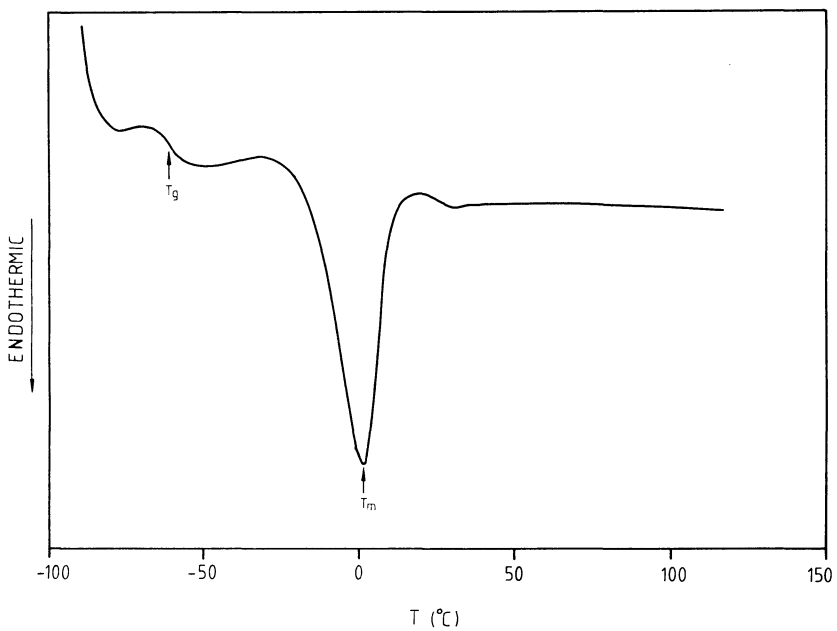

Figure 2. DSC thermogram of PEO 400/LiSCN (25 : 1).

of free cation is proportional to its spin–spin relaxation time (T_{21}). The NMR experiments can thus be employed to evaluate the fraction of mobile free ions and their mobility in polymer electrolytes.

The Effect of Host Polymer Structure

Figure 2 shows the DSC thermogram for PEO 400/LiSCN (25:1). It is found that the melting temperature is 2°C and, thus the sample has the amorphous liquid-like structure at the temperature above this melting point, which is the temperature range considered in this experiment.

Figure 3 shows the plot of $\log\sigma$ *versus* $1/T$ for PEO 400/LiSCN, PPO 425/LiSCN and their blend. The data on temperature dependence of the conductivities of these polymer electrolytes seem to reasonably follow a Vogel–Tamman–Fulcher (VTF) equation

$$\sigma = AT^{-1/2}\exp[-E_a/R(T-T_0)] \quad (5)$$

where A is a constant proportional to the number of charge carriers, E_a is the apparent activation energy, and T_0 is the temperature at which configurational entropy becomes zero.

The relaxation parameters estimated from eq 1 using the FID data on the above three polymer electrolytes are listed in Table I. This shows that the value of x_F in PEO complex is

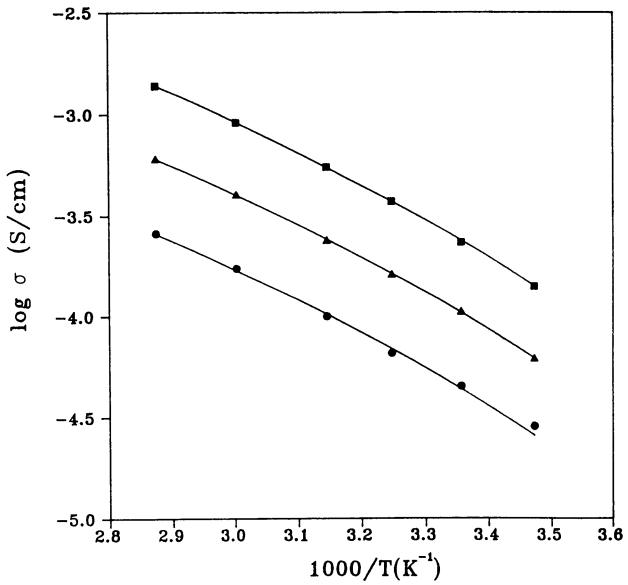

Figure 3. Temperature dependence of ionic conductivity of PEO/LiSCN, PPO/LiSCN, and their blend. The symbols represent data points and the solid line is the best fit of VTF equation (eq 5). (■, PEO 400/LiSCN (25:1); ▲, PEO 400/PPO 425/LiSCN (25:25:2); ●, PPO 425/LiSCN (25:1).)

Table I. The glass transition temperatures and NMR relaxation parameters for PEO/LiSCN, PPO/LiSCN, and their blend

Polymer electrolyte system	T_g/°C	x_F	T_{21}/s	T_{22}/s
PEO 400/LiSCN (25:1)	−63.8 (−73.2)[a]	0.94	0.208	0.027
PPO 425/LiSCN (25:1)	−67.3 (−71.1)[a]	0.45	0.328	0.054
PEO/PPO/LiSCN (25:25:2)	−65.8 (−71.6)[a]	0.65	0.322	0.047

[a] The value in ( ) stands for the glass transition temperature of the uncomplexed polymer.

larger than that in PPO complex, indicating that the number of free mobile cations which contributes to the ionic conductivity is considerably larger in PEO complex than in PPO complex. This result suggests that the ionic dissociation should be relatively restrained in PPO electrolyte. Polyether owns its capacity for dissolving the alkali metal salts in consequence of the interaction of the lone pairs of electrons on the oxygen atoms with the metal cation. The weaker solvating property of PPO is conjectured to be due to the fact that the bulky methyl groups in the PPO hamper the donor power of the oxygen atoms to salts. The relatively lower ionic dissociation in PPO may also be explained by the fact that the dielectric constant of PPO ($\varepsilon_{PPO,425}=8.8$) is lower than that of PEO ($\varepsilon_{PEO,400}=13.7$).[14] When we compare the spin–spin relaxation times of free mobile lithium ions in each polymer solution, it is found that the value of T_{21} (0.208 s) in PEO solution is smaller than that (0.328 s) in PPO solution. This means that the free lithium cation is less mobile in PEO than in PPO solution. The interaction between the polar oxygen atoms and the cations of the salt is stronger in the PEO complex and thus the segmental mobility of the polymer main chain is suppressed due to such a strong interaction. This speculation is also confirmed with the T_g and viscosity data of each electrolyte. The larger increase of T_g of PEO complex compared to the uncomplexed PEO than in the case of PPO complex ($\Delta T_{g,PEO}=9.4°C$, $\Delta T_{g,PPO}=3.8°C$) and also the larger viscosity of PEO solution ($\eta_{PEO/LiSCN}=176$ cP, $\eta_{PPO/LiSCN}=132$ cP at 25°C) may be due to the abundance of transient crosslinking points between polymer segments through the interaction between the oxygen atoms and the cations. From the results disscussed above, we can suggest that the larger concentration of mobile free ions in PEO electrolyte than in PPO electrolyte gives rise to a larger conductivity, while the strong polymer–ion interaction promoting the salt solubility tends to reduce the motion of free mobile cations.

From the relaxation parameters estimated from FID measurements on the blend, it is found that the value of x_F (0.65) of the polymer blend is less than the one (0.70) which averaged x_F of each component sample. This result probably indicates that the bulky methyl groups in PPO also hinder the solvation of the salts in PEO which is the other component of the blend.

The Effect of the Molecular Weight

Figure 4 shows the ionic conductivities for PPO/$LiClO_4$ complexes with the different polymer molecular weights (MW: 425, 1000, 2000, 4000). The ionic conductivity decreased with increasing the molecular weight of host polymer over the temperature range studied as the previous work had already shown.[15] The relaxation parameters estimated by FID measurements of the ^7Li NMR are given in Table II. From this data, it is found that there are little differences in the amount of free mobile cations, but the spin–spin relaxation time of the mobile free cations decreases as the molecular weight of PPO increases. The decrease in cationic mobility with increasing the molecular weight of host polymer is considered to be due to the reduction of segmental motion on account of the chain entanglements, which can be shown by the viscosity increase with molecular weight ($\eta_{PPO\,425/LiClO_4}=307$ cP, $\eta_{PPO\,1000/LiClO_4}=765$ cP, $\eta_{PPO\,2000/LiClO_4}=2514$ cP, $\eta_{PPO\,4000/LiClO_4}=23320$ cP at 25°C). Thus the difference in the ionic conductivity with changing the molecular weight of the polymer orginates in the ionic migration process rather than in the generation process of the free ions.

The Effect of Salt Concentration and Temperature

It was well known that the maximum conductivity was observed as the salt concentration was changed in polymer electrolytes.[15,16] We analyzed the previous work[15] on the conductivity behavior of PPO 1000/$LiClO_4$

complexes by performing ^{7}Li NMR experiment. A summary for the NMR relaxation parameters is given in Table III. The spin–spin relaxation time of free molile lithium ion (T_{21}) was decreased with increasing $LiClO_4$ concentration. The decrease in T_{21} at higher salt concentration may be related to the reduction of segmental motion due to abundance of transient crosslinks at higher concentration. On the other hand, the number of free cations calculated by multiplying the salt concentration by x_F value increased as the salt concentration increased. Thus, the existence of the maximum conductivity can be attributed to the oppositely competing contributions from the two effects considered above on the ionic conductivity.

Table II. The fraction of free Li^+ ions and their spin–spin relaxation times in PPO/$LiClO_4$ complexes with different molecular weights

Polymer electrolyte system	x_F	T_{21}/s
PPO 425/$LiClO_4$ (25 : 1)	0.62	0.276
PPO 1000/$LiClO_4$ (25 : 1)	0.63	0.250
PPO 2000/$LiClO_4$ (25 : 1)	0.62	0.078
PPO 4000/$LiClO_4$ (25 : 1)	0.59	0.008

The plot of $\log\eta$ *versus* $\log T_2$ is shown in Figure 5 in order to analyze the relation between ionic mobility and viscosity. It was

Table III. The NMR relaxation parameters and physical properties of PPO 1000/$LiClO_4$ with different salt concentrations

$LiClO_4$/PO unit	T_{21}/s	x_F	n_+ (ions/PO unit)	T_g/°C	η/cP
0.02	0.564	0.77	0.931×10^{22}	−62.9	590
0.04	0.250	0.63	1.507×10^{22}	−59.4	1350
0.06	0.114	0.57	2.055×10^{22}	−48.3	4340
0.08	0.050	0.54	2.586×10^{22}	−37.1	12860
0.10	0.005	0.52	3.118×10^{22}	−28.2	101500

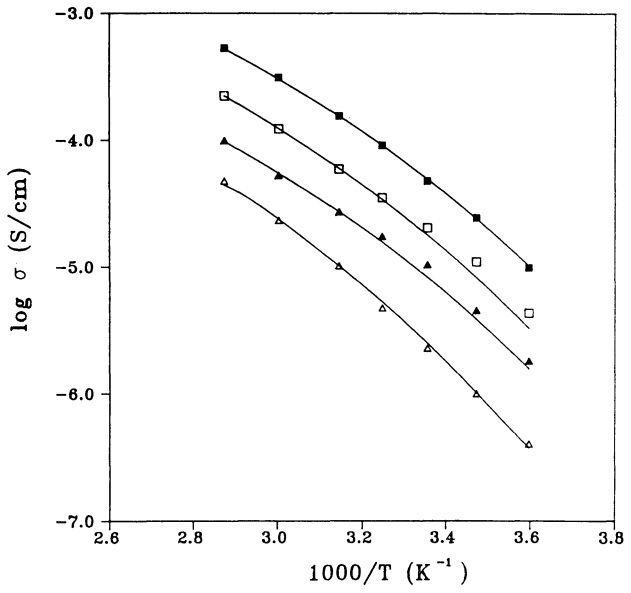

Figure 4. Molecular weight dependence of ionic conductivity of PPO/$LiClO_4$ complexes. (■, PPO 425/$LiClO_4$ (25 : 1); □, PPO 1000/$LiClO_4$ (25 : 1); ▲, PPO 2000/$LiClO_4$ (25 : 1); △, PPO 4000/$LiClO_4$ (25 : 1).)

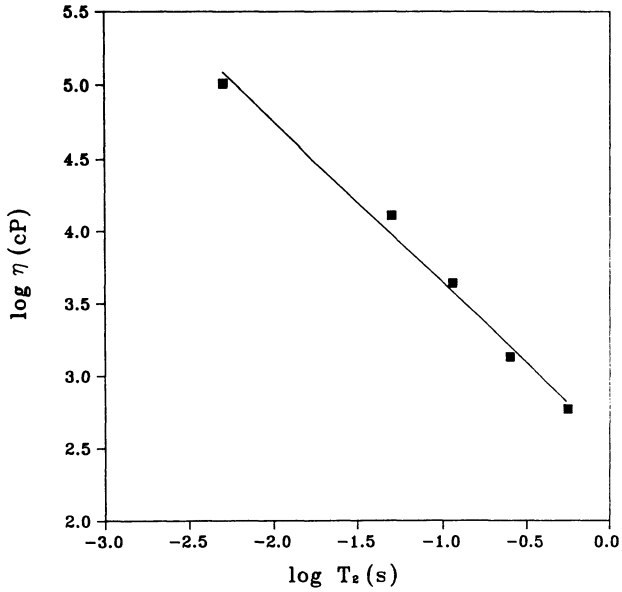

Figure 5. Relation between T_2 and viscosity in PPO 1000/$LiClO_4$ solution at 25°C.

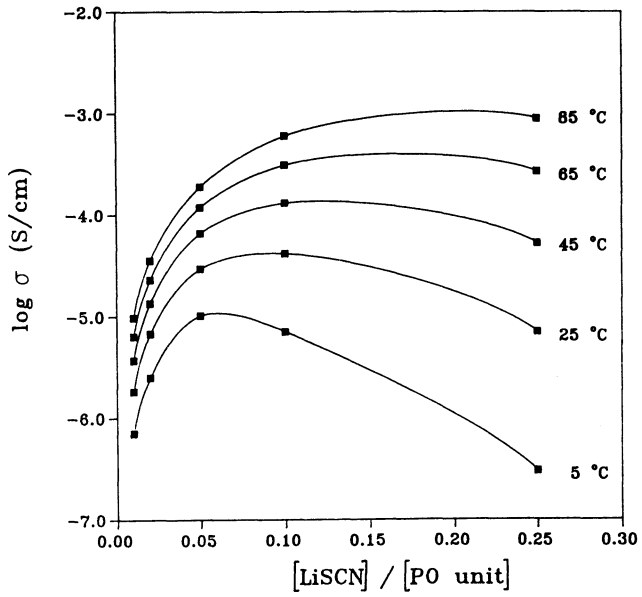

Figure 6. Isothermal variation of ionic conductivity with LiSCN concentration for PPO (MW: 725) complexes.

already noted that the spin–spin relaxation time of the mobile free lithium ion represented the ionic mobility. The observed relation is nearly linear and the value of slope is about -1, indicating that T_2 is proportional to the reciprocal of η. This result suggests that the relation between a spin–spin relaxation time and a viscosity obeys the empirical Walden's

Table IV. Best-fit VTF parameters (eq 5) of PPO 725/LiSCN with different salt concentrations

[LiSCN]/[PO unit]	$A/S \cdot K^{0.5} cm^{-1}$	$E_a/J\ mol^{-1}$	T_0/K	RMS deviation[a]	T_g/K	$T_g - T_0/K$
0.01	0.0087	6143.4	166.5	0.026	204.2	37.7
0.02	0.0322	6160.9	166.8	0.020	206.0	39.2
0.05	0.2085	6274.0	172.4	0.015	211.4	39.0
0.10	2.1551	7609.2	183.6	0.017	221.1	37.5
0.25	15.4990	9343.6	202.4	0.021	244.9	42.5

[a] An RMS deviation means the root mean square deviation in $\log_{10} \sigma$.

rule at a given temperature.

$$T_2(\mu) \cdot \eta = \text{constant} \quad (6)$$

We measured the ionic conductivities of PPO 725/LiSCN complexes with different salt concentrations. The influence of salt concentration on the ionic conductivity at a given temperature is shown in Figure 6. It is found that we have a certain salt concentration at which the conductivity passes through a maximum for each temperature just as other workers have already reported.[17-19] This maximum is displaced to higher concentrations as the temperature increases. At lower temperature (*e.g.*, 5°C or 25°C), the salt-polymer interactions predominate in the sample with higher salt concentration, thus inducing a reduction of free volume and resulting in a decrease in ionic conductivity with increasing salt concentration. The increase in the number of free ions, however, predominates on the conductivity with increasing salt concentration for the sample with lower salt concentration. Especially at higher temperature (*e.g.*, 85°C), on the other hand, the increase of free volume due to the weaker salt–polymer interactions leads to an easier ionic diffusion. As a result, the conductivity increases through the salt concentrations studied. A nonlinear least-square fits of eq 5 with the conductivity data are given in Table IV. It is found that T_0 is about 40°C lower than the onset T_g that was determined by DSC, which is reasonably consistent with the results reported recently for PPO containing sodium perchlorate.[11] From the data in Table IV, it is also found that the apparent activation energies are increased with increasing the salt concentration. This result means that the potential energy barrier for displacement of the polymer segments associated with ions increases due to the reduction of free volume as the salt concentration increases.

CONCLUSION

The study of the ionic mobility by measuring the NMR spin–spin relaxation time in liquid polymer electrolytes seemed to be especially fruitful for understanding of the fundamental dynamics of ions in polymer electrolytes. We have derived the relative ionic mobility and also the fraction of free mobile ions contributing to the ionic conductivity by using the ^7Li NMR relaxation technique.

From the ^7Li relaxation data (T_{21} and x_F) for PEO and PPO, it was found that the controlling parameter in ionic conductivities of these polymer electrolytes was the concentration of free mobile ions, but not the mobility of free ion itself. The combination of the ionic conductivity and NMR data of the polymer electrolytes with different molecular weights provided the evidence that the difference in conductivity was caused by the ionic migration process rather than the carrier generation process.

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