Ionic motions in network polymers containing lithium perchlorate

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Amorphous network polymer electrolytes were derived from poly(propylene oxide) and tris(4-isocyanatophenyl)thiophosphate complexed with lithium perchlorate. The complex impedance diagrams of the higher crosslink density samples were found to be a superposition of two semicircles having different relaxation times. On the other hand, the diagrams of the lowest crosslink density samples were a single semicircle. The Cole–Cole equation was employed to evaluate the relaxation parameters. The higher frequency process was assigned to ionic motions associated with segmental motions of the propylene oxide chain, and the lower frequency process was assigned to ionic motions associated with segmental motions of the urethane group. Dynamic mechanical thermal spectra show two relaxation peaks in the higher crosslink density samples and $T_{1\rho}$ as a function of temperature obtained by ^{7}Li n.m.r. study has a well defined minimum. These results indicate the correlation between the ionic mobility and the molecular motions of the network system.

(Keywords: network polymer electrolytes; complex impedance; ionic mobility; molecular motion)

INTRODUCTION

The ionic conducting behaviour of ion-containing polymers is of considerable interest as both a fundamental and an applied science[1,2]. Particularly, polyethers and polyesters with added alkali metal salts have been widely investigated because of their high ionic conductivity. Atactic poly(propylene oxide) (PPO) is known to be an amorphous polymer and dissolves alkali metal salts forming viscous polyelectrolyte solutions[3,4]. PPO-based polymers such as network polymers derived from the chain with di- or trifunctional isocyanates and segmented copolymers have been used for complex formation and their ionic conductivity mechanism has been studied[1,2,5]. The glass transition temperatures (T_gs) of these polymers increase upon the addition of alkali metal salts, and the temperature dependence of the ionic conductivity can be rationalized on the basis of free volume theory. The ionic conductivity of the network polymer electrolytes derived from PPO has been presented by Killis *et al.*[6] and the conductivity change as a function of temperature was expressed using the Williams–Landel–Ferry (WLF) equation[7]. This suggests that the ionic migrations are mainly associated with the segmental motions of the matrix. However, further studies are still needed to clarify the relationships of the ionic motions and the chain motions. WLF parameters, C_1 and C_2, of some PPO-based polyelectrolytes were found to deviate from the normal values at the high salt concentrations[8,9], therefore, the carrier generation process has been considered. It has been also reported that the segmented polyether/poly(urethane urea)s show two different time constants in the complex impedance spectrum and this was interpreted by an equivalent circuit based on the two-phase structure of the samples[10]. The distribution of the relaxation times in the complex impedance spectra can be represented by the Cole–Cole equation[11]. However, fewer studies have been made of these particular ion-containing polymers[12–14].

The molecular motions of network polymers derived from PPO with tris(4-isocyanatophenyl)thiophosphate have been used to investigate relationships between the structure and properties of these systems[15,16]. Particularly the narrow molecular weight distribution PPO could have advantages to obtain the homogeneous structure of the networks. Therefore, these networks could be considered as a model network system. It has been shown that there exist different relaxation processes in such networks on the basis of high resolution solid state n.m.r. The molecular motions in these networks have been also investigated by the dielectric relaxation technique[17], and it was found that the high frequency process is due to motions mainly involving the ether oxygen group and the low frequency process is due to motions mainly involving the urethane group.

In this study, the network polymers derived from different molecular weight PPO end linked with trifunction isocyanate were used and lithium perchlorate was dissolved in the network to obtain the solid electrolytes. In this particular system, both the ether oxygen and the urethane nitrogen could be expected to complex the

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lithium cation, and the concentration of each group changes as a function of the molecular weight between crosslinks. D.s.c. measurements were carried out to determine the T_gs of the samples and wide-angle X-ray diffraction (WAXD) patterns showed no evidence of crystalline structure. Ionic conductivity measurements, dynamic mechanical thermal analysis (d.m.t.a.) and ^{7}Li n.m.r. study were carried out, and the ionic motions are discussed in terms of the molecular motions of the system.

EXPERIMENTAL

The network polymers are similar to those described previously[15–17]. α,ω-Dihydroxypoly(propylene oxide)s of nominal molecular weights of 1000 (PPO1000), 2000 (PPO2000), 3000 (PPO3000), and 4000 (PPO4000) were obtained from Aldrich Chemical Co. The PPO was dried azeotropically in benzene and stored under dry nitrogen. Hydroxyl group functionality was determined by titration (ASTM D4274). Tris(4-isocyanatophenyl)thiophosphate, supplied by Mobay Chemical Co., was recrystallized twice from dry toluene solution and stored under dry nitrogen in a refrigerator.

Networks were prepared by dissolving under dry nitrogen 0.33 mol of crosslinker with 0.50 mol of PPO using dry tetrahydrofuran (THF, Aldrich) as a solvent. Solutions were evaporated *in vacuo* to remove THF and poured into a Teflon-lined aluminium mould and then heated to 90°C *in vacuo* for 3 days. The thickness of the samples was 0.3 mm. Network samples prepared from PPO1000, PPO2000, PPO3000 and PPO4000 are designated as N1000, N2000, N3000 and N4000, respectively.

Lithium perchlorate (Aldrich) was dried at 150°C for 20 h *in vacuo*. The network films were swollen in the dry THF solutions of lithium perchlorate with different concentrations for 20 h and dried at 50°C for 6–10 days until the sample weights reached constant values. The concentration of lithium perchlorate in the samples was determined by atomic absorption analysis which was carried out at the Microanalysis Laboratory in the University of Massachusetts, and the concentration was represented by the molar ratio of lithium perchlorate to the repeating unit of PPO ([LiClO$_4$]/[PO unit]).

Impedance measurements were performed as follows. A 13 mm diameter sample was sandwiched between two platinum electrodes in a sealed cell under dry argon. The frequency dependence of the complex impedance was measured with a Yokogawa-Hewlett-Packard 4192A LF-impedance analyser in a frequency range of 5 Hz to 13 MHz at an oscillation level of 500 mV.

D.s.c. measurements were carried out with a Perkin-Elmer DSC-4 over the temperature range of −100 to 50°C at a heating rate of 20°C min^{-1}. The T_g was defined as the midpoint of the heat capacity change. WAXD patterns were obtained using a Siemens two-dimensional area detector with CuKα radiation, and air scattering in the diffraction angles up to 18° was subtracted.

Dynamic mechanical measurements were carried out with a Polymer Laboratories DMTA at 1 Hz with a heating rate of 2°C min^{-1}.

An IBM 200 AF spectrometer with solids accessory was used with ^{7}Li observed at 77.8 MHz. The samples were cut into discs and packed in the sample tube. All spectra were obtained without spinning and with high power proton decoupling. T_1 was determined by the standard π–τ–$\pi/2$ sequence. $T_{1\rho}$ was measured as the decay of ^{7}Li magnetization during spin lock of length 0.1–15 ms after a single $\pi/2$ preparation pulse. A $\pi/2$ pulse was set to 5 μs.

Table 1 Thermal properties of network polymer electrolytes

Network	Code	[LiClO$_4$]/ [PO unit]	T_g (°C)	ΔT_g (°C)
N1000	N1000–0.030	0.030	−4	25
	N1000–0.070	0.070	17	38
	N1000–0.090	0.090	16	25
N2000	N2000–0.016	0.016	−40	25
	N2000–0.054	0.054	−7	40
	N2000–0.104	0.104	7	32
N3000	N3000–0.014	0.014	−46	30
	N3000–0.058	0.058	−18	49
	N3000–0.105	0.105	3	22
N4000	N4000–0.028	0.028	1	27
	N4000–0.127	0.127	4	29

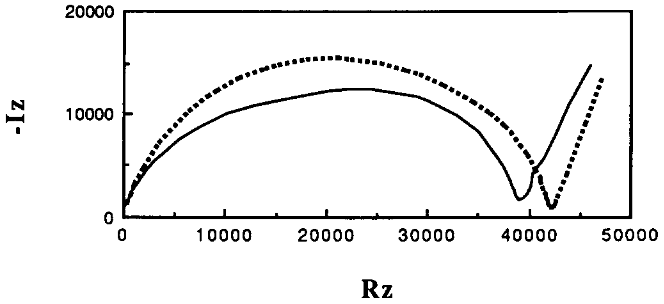

Figure 1 Cole–Cole plots of complex impedance for network electrolytes: (——) N1000–0.030 at 69°C; (– – –) N4000–0.028 at 40°C. I$_Z$, Imaginary part of complex impedance; R$_Z$, real part of complex impedance

The sample code, the salt concentration, the observed T_g and the transition region of each sample are listed in *Table 1*.

RESULTS

Figure 1 shows typical results of the complex impedance plots (Cole–Cole plot) of N1000 and N4000 complexes at various temperatures. The spectra obtained are interpreted by the appropriate equivalent circuit including an interfacial impedance and a bulk impedance. The impedance locus as a spike at the low frequency region corresponds to the interfacial impedance, and the locus centred at ~R$_z$/2 in the high frequency region corresponds to the bulk impedance[1]. As is seen, the complex impedance diagrams of the higher crosslink density samples were found to be a skewed arc or a superposition of two semicircles having different time constants. On the other hand, the diagrams of the lowest crosslink density samples were a single semicircle. In order to define the change in shape, the normalized curve of the imaginary part of the complex impedance was employed. In *Figure 2*, the normalized curves are shown in the case of the N1000 complex sample at various temperatures. It is obvious that the shape of this relaxation does not depend on the temperature.

The Cole–Cole distribution function can be applied to evaluate the relaxation parameters such as relaxation strength, and this parameter is expected to relate to the concentration of segments which can facilitate the ionic motions in the system. The Cole–Cole function is given by:

$$Z^* = Z + \Delta Z/[1 + (i\omega\tau)^{\beta}] \qquad (0 < \beta \leqslant 1) \qquad (1)$$

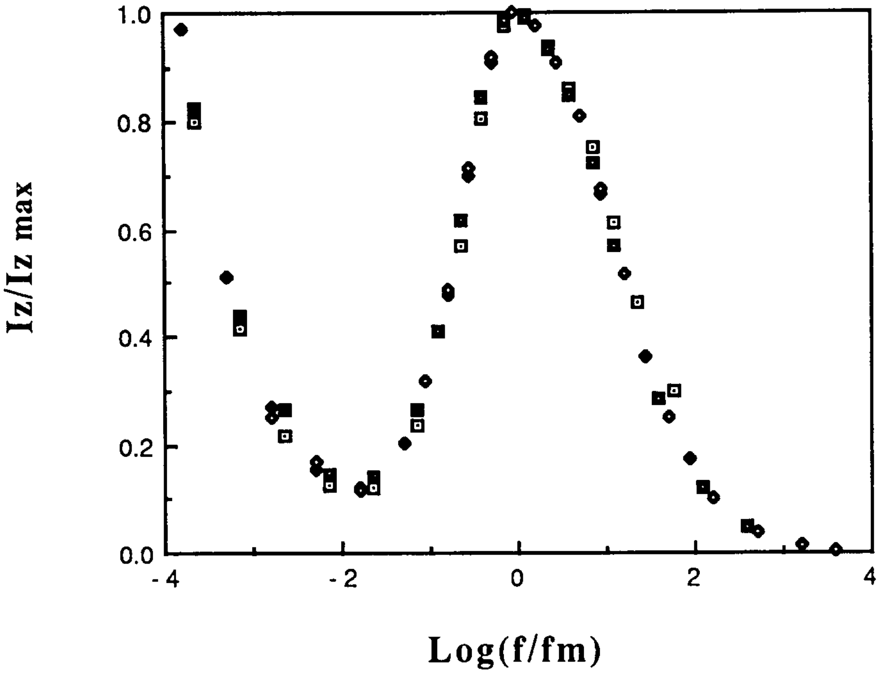

Figure 2 Normalized impedance spectra observed at various temperatures for N1000–0.030: (□) 97.2°C; (◆) 79.2°C; (■) 59.6°C; (◇) 40.0°C

where Z^* is the complex impedance, $\Delta Z = Z_0 - Z_\infty$, Z_0 and Z_∞ are the low- and high-frequency limits of the real part, respectively, ω is the angular frequency, τ is the relaxation time and β is a shape factor. It was found in the present study that the plots of the imaginary part of Z^* against the frequency show a symmetrical distribution. Therefore, it is reasonable to assume the presence of two relaxation processes having the same β value. Appropriate values of the parameters were chosen to describe the observed data.

Some of the analysed results are shown in *Figure 3*. In this analysis, the observed data, both real and imaginary parts, were found to be well fitted by assuming that the value of β is 0.83 ± 0.01. As is seen in this figure, the relative relaxation strength of the lower frequency process decreases with decreasing crosslink density, and in the N4000 complexes this contribution was estimated to be <5% of the higher frequency process. The relative relaxation strength of the higher frequency process decreased with increasing salt concentration as shown in *Figure 4*. The plots of the peak positions against the inverse of the absolute temperature show WLF-type dependences, and the difference of the peak positions of the two processes was 0.5 decades in N4000 complexes and 1.8 decades in N1000 complexes. The relative relaxation strength of the higher frequency process showed no significant dependence on the temperature. The relaxation which corresponds to the interfacial transition could be ignored in this analysis because of its small contribution to the lower frequency side of the main relaxation.

Figure 5 shows the temperature dependence of the loss factor obtained from d.m.t.a. for N1000 and N3000 complexes. The transition at −7°C for the N1000 pure network and at −43°C for the N3000 pure network is associated with the segmental glass transition, and in the N3000–0.014 complex this transition peak still remains. In both network complexes, this transition temperature increased with increasing salt concentration. However, in the case of the N1000–0.070 complex a splitting of this peak was observed. This split was also observed in the N2000–0.054 complex and no split was observed in the N3000 and N4000 complexes.

Spin-lattice relaxation times (T_1 values) of ^{7}Li for N1000–0.090 and N3000–0.103 complexes at various temperatures were obtained from the semilog plots of the magnetization *versus* spin lock time. The plots were well characterized by a single exponential decay, and the temperature dependence of the relaxation times is shown in *Figure 6a*. The offset between the T_1 curve for the two samples is ~15–20°C and this corresponds to the difference in the T_g observed by d.s.c. On the other hand, the decay curves of the magnetization in the rotating frame were biphasic and two components were characterized by the least square methods. The temperature dependences of these relaxation times ($T_{1\rho}$) is shown in *Figure 6b*. Each component of $T_{1\rho}$ showed a well defined minimum at 50°C for the N3000 complex and 70°C for the N1000 complex, respectively. This temperature difference is the same as the offset between T_1 curves. This result strongly suggests the interaction of the lithium cation with surrounding chains. In this study, the spin-lock/rotating frame frequency is 50 kHz for the $T_{1\rho}$ measurements and the frequency is 50 MHz for the T_1 measurements. Although the plotted curves of T_1 have shown no minimum, it would be expected to occur at higher temperatures. The slow decay phase is about one-half of the total in both samples and no significant change of this ratio as a function of temperature was observed.

DISCUSSION

It has been shown that there exist different relaxation processes in this particular network system on the basis of high resolution solid state n.m.r.[15,16], and dielectric measurements have shown that the lower frequency process is due to the motions involving the urethane

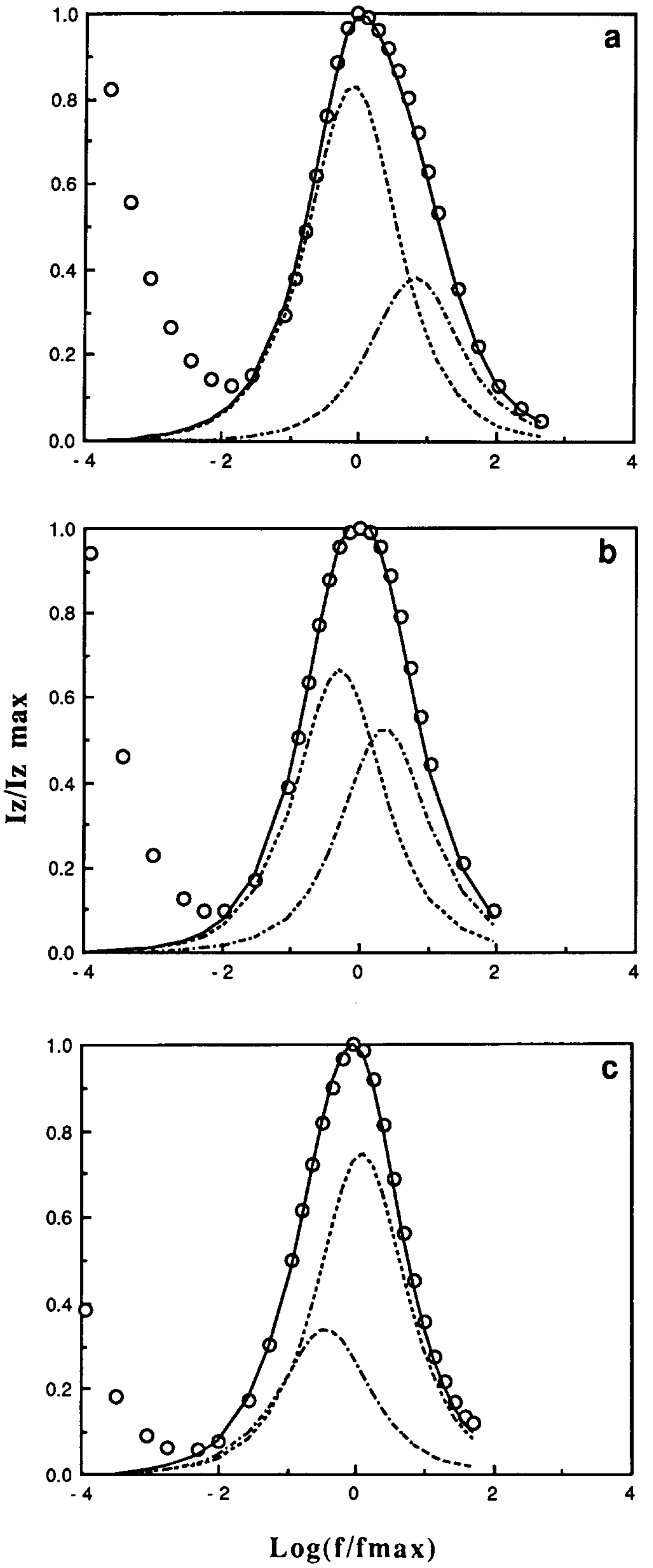

Figure 3 Observed and calculated impedance spectra for (a) N1000–0.030, (b) N2000–0.016 and (c) N3000–0.014 complexes. Open circles represent observed data; solid and broken lines are calculated using equation (1)

groups and the higher frequency process is due to motions involving the ether oxygen atoms[17]. Lithium cations could be complexed by both the ether oxygen and the urethane nitrogen. The concentration of the ether oxygen group increases and that of the urethane group decreases with decreasing crosslink density, respectively. In the present analysis, it has been found that the relative intensity of the higher frequency process decreases with decreasing crosslink density for the low salt concentration complexes as shown in *Figure 3*. It is obvious from this consideration that the ionic relaxation strength of each process corresponds to the concentration of the ether oxygen and the urethane nitrogen, respectively.

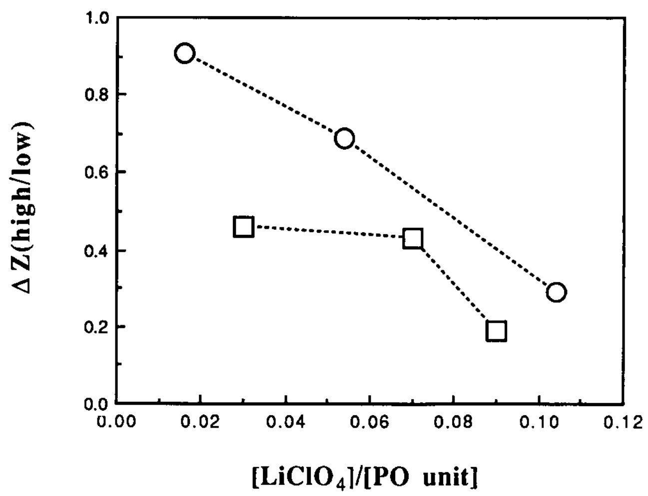

Figure 4 Dependence of relative relaxation strength of the higher frequency process on the salt concentration: (□) N1000 complexes; (○) N2000 complexes

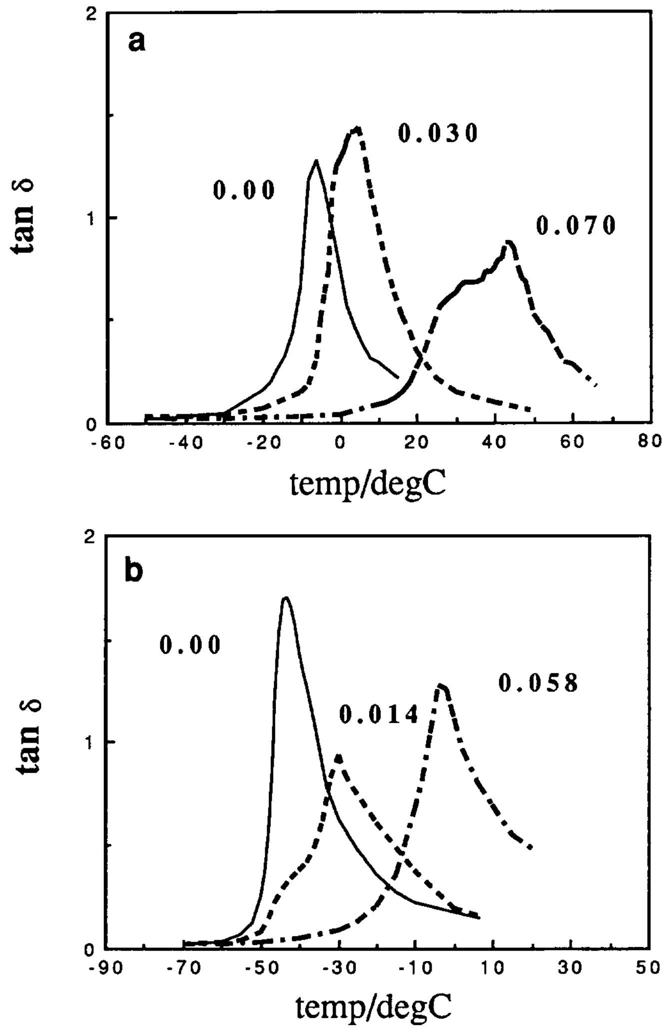

Figure 5 Dynamic mechanical spectra of (a) N1000 and (b) N3000 complexes obtained at 1 Hz

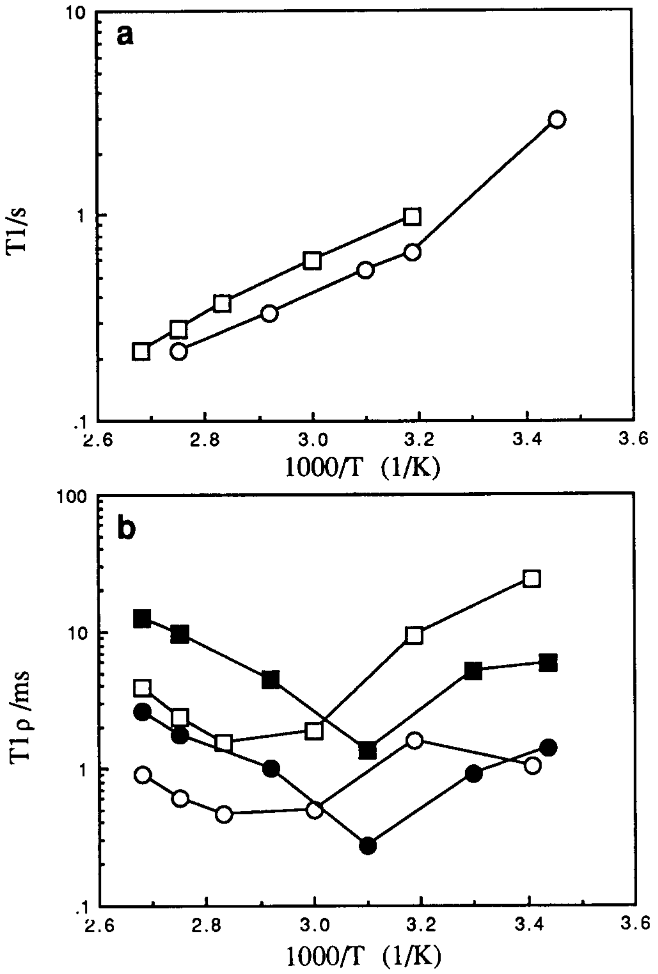

Figure 6 (a) Temperature dependence of T_1: (□) N1000–0.090; (○) N3000–0.105. (b) Temperature dependence of $T_{1\rho}$ slow (squares) and fast (circles) components for N1000–0.090 (open symbols) and N3000–0.105 (closed symbols)

The relative relaxation strength of the higher frequency process was found to decrease with increasing salt concentration as shown in *Figure 4*. In this case, the relaxation strength of the lower frequency process was observed to increase more rapidly than that of the higher frequency process with increasing salt concentration, and this might suggest a strong interaction between the lithium cation and the urethane nitrogen. The relaxation strength could be proportional to, at least, the number of ions by analogy with dielectric theories. The number of propylene units is the ratio of the ether oxygen concentration to the urethane nitrogen concentration in the present network. Therefore, the relative relaxation strength should be proportional to this ratio. In the present study, the relative relaxation strength at a given salt concentration (0.030) was plotted against the number of propylene units for N1000, N2000 and N3000 complexes. A good correlation between these two parameters was found and this supports the assignment of the ionic motions. For the N4000 network the result was available only for N4000–0.014, and the relative relaxation strength was ~20 and this value could not be explained by the correlation described above. It would be possible to assume an orientational correlation factor of ionic motions by analogy with dielectric theory. The correlation factor g is given by

$$g = 1 + \sum_{k \neq j} \cos \gamma_{jk} \qquad (2)$$

where $\cos \gamma_{jk}$ is the average of the cosine of the angle γ_{jk} made between the reference ionic motion j and an ionic motion k. The relaxation strength could be a function of both concentration and the correlation factor. It is likely that hydrogen bonding exists between the urethane groups[17], and the g value for the ionic motions associated with the urethane groups could be > 1. If the correlation of this ionic motion in the N4000 complex is weak because of the low crosslink density, the relaxation strength of this process could be smaller than that expected from the concentration alone. The ionic relaxation strength could be explained by taking into account both the concentration and the correlation factor.

The difference between the peak positions of the two ionic processes is 0.5–1.8 decades, and that of the dielectric relaxation processes obtained for the pure networks was ~3 decades[17]. The apparent activation energy of the lower frequency process in the pure networks was found to be slightly smaller than that of the higher frequency process in the transition temperature region[17]. The difference of the peak positions observed in the impedance spectra is reasonable if it is considered to reflect the difference in activation energy of the two processes. Therefore, it is reasonable to consider that the higher frequency process is due to the ionic motions coupled to the segmental motion of the ether group and the lower frequency process is due to the ionic motions coupled to the segmental motion of the urethane group.

D.m.t.a. gives detailed information about the segmental motions, and the increase of transition temperatures can be interpreted on the basis of the interaction between lithium perchlorate and the ether oxygen group, since the samples are amorphous. The broadening and/or the splitting of the transition region was also observed in the d.s.c. results, and similar results have been reported for the PPO complex[4], the PEO-based network electrolytes[18] and the segmented polyurethane complex[8]. The complexed urethane units could be randomly located in the network as well as the randomly distributed complexed propylene units along the PPO chain. This kind of inhomogeneous structure could be responsible for the broadening.

Comparing the d.m.t.a. results of N1000–0.070 with that of N3000–0.058, it can be seen that the broadening might correspond to the crosslink density, i.e. the broad transition peak might suggest larger contributions from the relaxation which is due to the motion involving the urethane groups. The complex impedance study suggests the existence of two molecular motions and this is consistent with the dynamic mechanical results.

The present ^{7}Li n.m.r. analysis strongly suggests that the motion of lithium cations is dominated by the motion of the network chains. This could be taken into account by different interactions between not only the cation and network chains but also the cation and the anion because of the quadrupolar nature of the lithium nuclei. In the present case, however, the former interaction seems to play an important role, because the temperature differences of the relaxation times (T_1 and $T_{1\rho}$) correspond to those of the d.s.c. T_gs. It is of interest to compare the relaxation times obtained from complex impedance analysis and ^{7}Li n.m.r. measurements shown in *Figure 7*. The Arrhenius plots show some relationship between the ^{7}Li n.m.r. results and the complex impedance results with the [frequency, $(1/T)^{-1}$] point from the $T_{1\rho,\min}$ falling near the complex impedance domain data. The $T_{1\rho}$

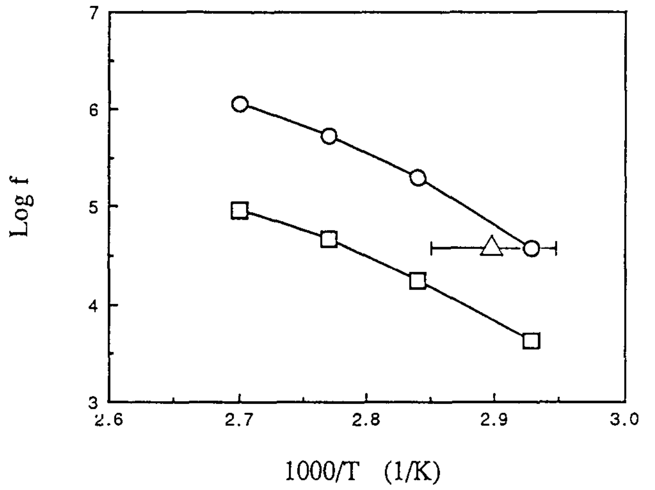

Figure 7 Arrhenius plots of the peak frequency of ionic relaxation processes for the N1000–0.090 complex: (△) relaxation time obtained by $T_{1\rho}$ measurements; (○) high frequency process; (□) low frequency process

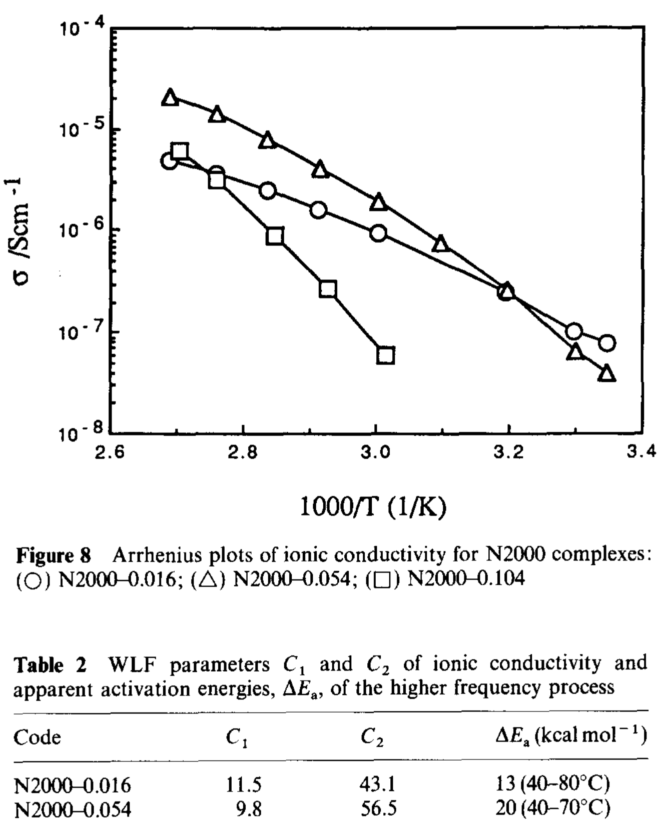

Figure 8 Arrhenius plots of ionic conductivity for N2000 complexes: (○) N2000–0.016; (△) N2000–0.054; (□) N2000–0.104

Table 2 WLF parameters C_1 and C_2 of ionic conductivity and apparent activation energies, ΔE_a, of the higher frequency process

Code	C_1	C_2	ΔE_a (kcal mol^{-1})
N2000–0.016	11.5	43.1	13 (40–80°C)
N2000–0.054	9.8	56.5	20 (40–70°C)
N2000–0.104	14.6	58.6	34 (60–90°C)

minimum is broad, therefore, the estimated error is large. The decay profiles in the rotating frame were represented by two processes with different $T_{1\rho,\mathrm{min}}$ occurring at the same temperature and this might indicate different Li sites[19]. One possibility would be separate $T_{1\rho}$s for the ^{7}Li on the ether or perchlorate sites (or urethane sites).

Figure 8 shows the temperature dependence of ionic conductivity for N2000 complexes with various salt concentrations and a WLF-type dependence is seen. All the other samples in the present study showed this type of temperature dependence. It is obvious that the ionic conductivity of the N2000–0.016 sample does not depend strongly on the temperature compared with the N2000–0.054 and –0.104 samples. The WLF parameters C_1 and C_2 are listed in *Table 2* and the values are almost constant. There are two processes in the ionic relaxation spectra as mentioned above. The apparent activation energy was obtained by assuming linear Arrhenius behaviour of the peak frequency for both processes. There was no significant difference of the apparent activation energy between the two processes and the values for the higher frequency process are listed in *Table 2*. The higher frequency process is assigned to the ionic relaxation process coupled to the segmental motion of the ether group. The potential barrier height[20] of this segmental motion is thought to be 2–3 kcal mol^{-1}. However, the value of the activation energy could be largely determined by viscous effects. On this basis, the results indicate that the local viscosity increases with increasing salt concentration and this viscosity change dominates the temperature dependence of the ionic conductivity. The same tendency was seen in the temperature dependence of the ionic conductivity for the other network polyelectrolyte samples. The WLF parameters C_1 and C_2 have been found to deviate from the standard values with increasing salt concentration[8,9]. However, no significant deviation was observed in the present study.

CONCLUSIONS

Two ionic motions are clearly observable in the networks studied and their origins are interpreted in terms of molecular motions from the results of a complex impedance study, a dynamic mechanical study and a ^{7}Li n.m.r. study.

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