Ionic conductivity in poly(ethylene oxide) modified poly(dimethylsiloxane) complexed with lithium salts

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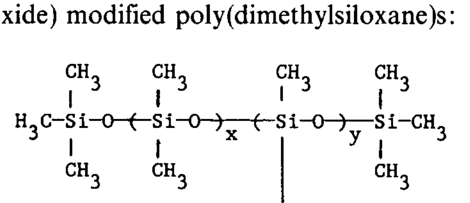
Poly(ethylene oxide) modified poly(dimethylsiloxane) has been complexed with $LiClO_4$ or $LiCF_3SO_3$. The configuration of these polymers enhances their flexibility. The ionic conductivity has been measured using complex impedance spectroscopy for different Li^+ ion concentrations. The temperature dependence of the conductivity has been measured for some of the samples. The ionic conductivity increases more rapidly with the addition of $LiClO_4$ than with $LiCF_3SO_3$ but the maximum conductivity is higher for complexes with $LiCF_3SO_3$. At room temperature the highest ionic conductivity values were of the order of $9 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ for $LiCF_3SO_3$ compounds with the polymer. Effects of viscosity and ethylene oxide chain length are discussed.

(Keywords: poly(ethylene oxide); poly(dimethylsiloxane); $LiClO_4$; $LiCF_3SO_3$; ionic conductivity; polymer electrolyte)

INTRODUCTION

It has been well-established by impedance spectroscopy[1], nuclear magnetic resonance (n.m.r.)[2,3] and light scattering[4,5] that structural relaxations in polyether chains are coupled to the motion of the ions. It is also generally contended that both the cation and the anion contribute to conductivity[6,7] unless polymer–salt complexes have been prepared where only the cation is mobile[8,9]. There is, however, considerable disagreement in the literature as to the role of cations, anions, cation clusters, solvated ion pairs, contact ion pairs, salt precipitates, ion pair aggregates, etc. in ion transport, especially with respect to the measurement of transference, transport and diffusion[10,11].

The polymers used in this study are poly(ethylene oxide) modified poly(dimethylsiloxane)s:



$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_x\left(\underset{CH_2-CH_2-CH_2-O(C_2H_4O)_m-R}{\overset{CH_3}{Si}}-O\right)_y\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

These polymers consist of a poly(ethylene oxide) chain terminated at one end by OH or CH_3 groups (*Table 1*) and at the other end by a poly(dimethylsiloxane) moiety. This enhances the chain flexibility since the glass transition temperature of poly(dimethylsiloxane) is ∼ −127°C, much lower than for the polyether chain (≈ −41°C). Our hope is that the coupling between structural relaxations and ion mobility will be improved.

When salts like $LiClO_4$ and $LiCF_3SO_3$ are complexed with these polyethers, the Li^+ co-ordinates with the ether oxygen atoms. At any one instant approximately four ether oxygens are linked to each Li^+ cation. These links are in dynamic equilibrium (breaking and reforming) permitting the cation to move in the complex in response to a very broad distribution of relaxation times. Studies on $CF_3SO_3^-$ show it to be a very poor ligand[12]; it is likely that it does not solvate (except if hydroxyl-terminated groups are present). Measurements of refractive index show that the free anion $CF_3SO_3^-$ and complexes containing the $CF_3SO_3^-$ anion are more effective in opening up structures than the corresponding moieties for ClO_4^-; so effective that the refractive index of the complex decreases with increasing concentration for $LiCF_3SO_3$ while the refractive index for $LiClO_4$ complexes increases with increasing concentration[13]. Compared to the polyether–$LiClO_4$ complexes the density of the polyether–$LiCF_3SO_3$ complexes increases much less than would be expected on the basis of the molecular weight of the salts for a given salt concentration[13].

Studies of a system similar to that studied here, poly(alkane oxide) modified poly(hydromethylsiloxane) polymer–salt complexes, have been conducted pre-

Table 1 Sample specification according to the manufacturer

Polymer	Molecular weight	*x*	*y*	*m*	R	Viscosity at 25°C ($m^2\ s^{-1}$)
1	600	0	1	7.5	CH_3	20×10^{-6}
2	3000	19	3	7.5	CH_3	100×10^{-6}
3	4000	16	6	7.5	H	350×10^{-6}

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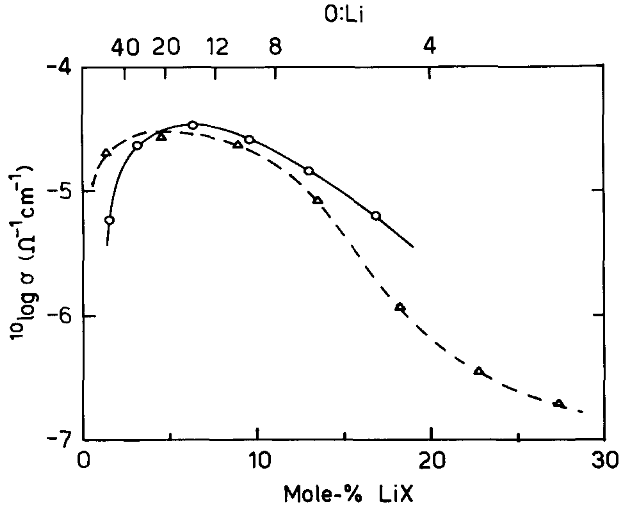

Figure 1 Ionic conductivity at 25°C of polymer 2 (*Table 1*) complexed with LiX where X = CF_3SO_3 (○) or ClO_4 (Δ). O:Li indicates the polyether oxygen to lithium ratio

viously[14,15]. In these systems, the linkage between the silicon atom and the polyether side chain or polyether crosslink is through an oxygen atom instead of a direct silicon–carbon linkage as in this system which is more stable at higher temperatures[14] and easier to shield against moisture and other sources of degradation. For these similar systems, the conductivities at 25°C are reported to be 2×10^{-4} ($LiClO_4$, O:Li = 24:1)[14] and 7×10^{-5} S cm^{-1} ($LiClO_4$, O:Li = 25:1)[15]. Polymethacrylates with pendant oligooxyethylene chains could be considered as another similar system and the conductivity at 25°C has been reported as 2×10^{-5} S cm^{-1} ($LiClO_4$, O:Li = 15:1)[16]. In these studies of polyether network–salt complexes, a solvent such as acetonitrile or tetrahydrofuran was used to dissolve the salt into the network. The solvent was subsequently evaporated from the thin films produced. It is found that solvents and especially water are extremely difficult to remove from such complexes. Water bound to polyether oxygen sites influences the cation mobility. Further, the lithium salts are known for their ability to retain water of hydration. From n.m.r. and neutron diffraction studies[17], it is concluded that small cations such as Li^+ remain hydrated. The presence of solvents or low molecular weight plasticizers used to dissolve the salts would enhance the conductivity; possibly by as much as an order of magnitude and certainly much more in the cases of propylene carbonate[18], tetraethylene glycol[9] and crown ethers[6].

In this study, we find that stringent drying of the polyether–siloxane polymer allows the $LiCF_3SO_3$ and $LiClO_4$ salts in anhydrous form to dissolve directly without the use of solvents. Our objective is to work with pure components which are as free of water as possible.

EXPERIMENTAL

The poly(ethylene oxide) modified poly(dimethylsiloxane) samples were obtained from Union Carbide. The properties of the various samples are listed in *Table 1*. The synthesis and properties of these polymers are discussed elsewhere by Khan *et al.*[19]. Under a vacuum of $< 1.33 \times 10^{-3}$ Pa these liquids were stringently freeze-dried using freeze–pump–thaw cycles. While still under vacuum the samples were transferred to an argon atmosphere where newly purchased $LiClO_4$ (Ventron Division, Alpha Products) or $LiCF_3SO_3$ (Aldrich) was dissolved directly into the liquids without a volatile solvent intermediary. The doped samples were stored in a dry atmosphere. Without this stringent drying procedure it is very much more difficult, if not impossible, to dissolve the salts in the temperature range of 70–90°C used here. Using Fourier transform infra-red and Raman spectroscopy we looked for the water bending mode at 1635 cm^{-1} or the stretch mode in the region 3600–3700 cm^{-1}. There is no evidence of water or OH. In the region 3600–3700 cm^{-1} the background was ~2 counts s^{-1} cm in the Raman spectra. The nearest polymer modes (2900–3000 cm^{-1}) had intensities 30 times this value. Further, using ^{1}H n.m.r. we have been unable to detect the presence of water. We suggest our samples have a maximum of 0.01 wt% water.

The complex impedance was measured using a computer-controlled HP4274A LCR meter over a frequency range of 100–100 × 10^3 Hz with an applied signal of 20 mV. Silver or stainless steel electrodes were used. The sample temperature was measured using a Platinel II thermocouple. The complex impedance measurements were performed in a dry atmosphere.

RESULTS AND DISCUSSION

The ionic conductivity as a function of Li^+ ion concentration for polymers 2 and 3 complexed with $LiClO_4$ and $LiCF_3SO_3$ are shown in *Figures 1* and *2*. The ionic conductivity increases more rapidly with the addition of $LiClO_4$ than with $LiCF_3SO_3$ but the maximum conductivity is higher for complexes with $LiCF_3SO_3$. In *Figure 3* the ionic conductivities for complexes of $LiCF_3SO_3$ with the three polymers are shown. The maximum ionic conductivity is obtained for about the same $LiCF_3SO_3$ concentration for all polymers. The lower molecular weight polymer 2 complexed with $LiCF_3SO_3$ has a poorer conductivity than the polymer 3 complex. This is probably due to double the ethylene oxide units on polymer 3 compared to polymer 2 and to the OH terminations on polymer 3 which

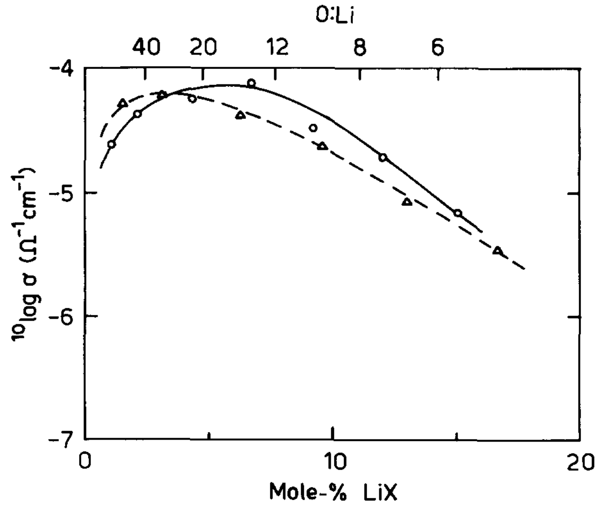

Figure 2 Ionic conductivity at 25°C of polymer 3 complexed with LiX where X = CF_3SO_3 (○) or ClO_4 (Δ)

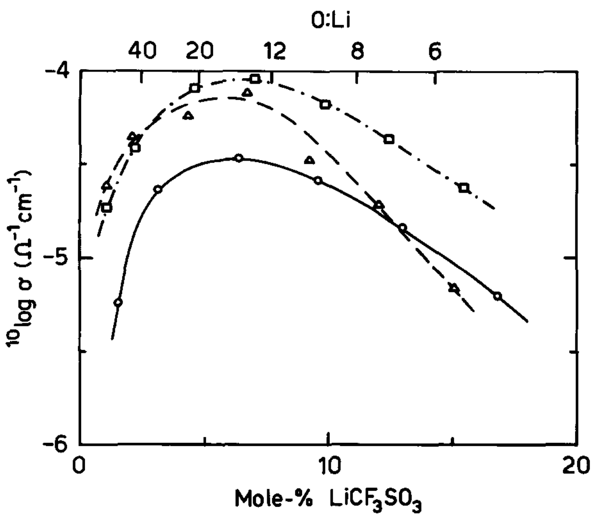

Figure 3 Ionic conductivity at 25°C of LiCF$_3$SO$_3$ complexed with polymer 1 (□), polymer 2 (○) and polymer 3 (△)

can bind CF$_3$SO$_3^-$ anions. In the polymer 3 complex the anions which bind to the OH groups would not be available for ion pairing thus contributing to a higher conductivity. In agreement with observations in other systems[20] the maximum conductivity is obtained for the sample containing the polymer with the lowest viscosity (*Table 1*). The highest conductivity at room temperature ($9 \times 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) was obtained for polymer 1 complexed with 7 mol% LiCF$_3$SO$_3$ (O:Li = 13.4:1).

For a styrene–polyester network incorporating 40% poly(ethylene oxide) ($M_w = 400$) conductivities of 1×10^{-5} (LiClO$_4$, O:Li = 20:1) and $3 \times 10^{-5}\,\mathrm{S\,cm}^{-1}$ (LiClO$_4$, O:Li = 50:1) at ambient temperatures have been reported[21]. For polymer 1 with about the same number of ethylene oxide units our best value for the polymer 1-LiClO$_4$ complex is $9.4 \times 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for 6 mol% LiClO$_4$ (O:Li = 16:1). We conclude that the large poly(dimethylsiloxane) end groups are very effective in increasing flexibility and thus ionic conductivity.

For lithium complexes with poly(ethylene oxide) it has been found that ionic conductivity increases with increasing size of the anion, at least up to a certain limit[22]. Since the CF$_3$SO$_3^-$ ion is larger than the ClO$_4^-$ ion this is in agreement with the results of the present investigation. There is little difference between the polarizability of polypropylene glycol (PPG)–LiClO$_4$ (10:1) and PPG–LiCF$_3$SO$_3$ (10:1) complexes[13], and thus we expect that the influence of different polarizabilities on conductivity is also small for our samples.

As has been shown from ^{7}Li n.m.r. studies[23,24] the local viscosity has the greatest effect on the ionic mobility. Bulk viscosity is not as important as we see from this study where a polymer with a molecular weight of 4000 and a viscosity of $3.5 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$ (at 25°C) has a higher conductivity than a similar polymer with a molecular weight of 3000 and a viscosity of $1.0 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$ (at 25°C). When, however, the bulk viscosity is lowered by an order of magnitude at about the same weight per cent of ether oxygens then the conductivity is increased.

For amorphous materials the ionic conductivity can often be described by the Vogel–Tammann–Fulcher (VTF) equation[25–27]:

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

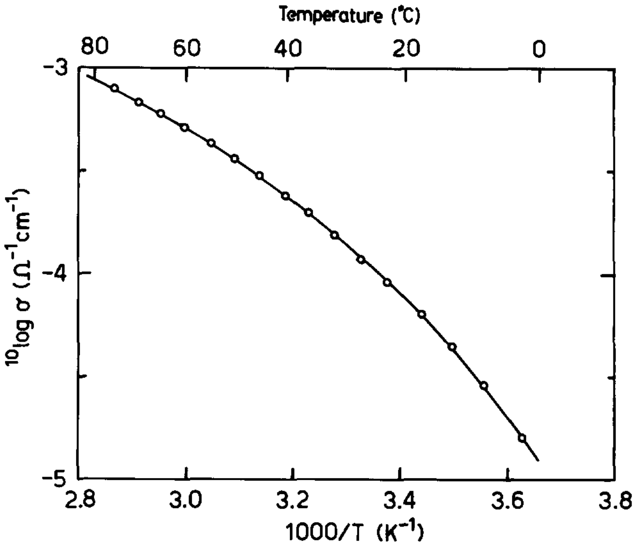

Figure 4 Temperature dependence of the ionic conductivity of polymer 1 complexed with 10 mol% LiCF$_3$SO$_3$. The solid line shows a least squares fit to the VTF equation using fit parameters: $A = 0.69\,\mathrm{K}^{1/2}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, $E = 0.048$ eV and $T_0 = 205$ K

where A is a pre-exponential factor, E is a pseudo-activation energy and T_0 is the ideal glass transition temperature. For polymer 1 complexed with 10 mol% LiCF$_3$SO$_3$ (O:Li = 9:1) the result of a least squares fit to the conductivity VTF equation is shown by the solid line in *Figure 4*.

CONCLUSIONS

Three poly(ethylene oxide) polymers terminated at one end by a large poly(dimethylsiloxane) moiety and at the other by OH or CH$_3$ have been complexed with LiClO$_4$ and LiCF$_3$SO$_3$ salts. The molecular configuration enhances the chain flexibility. Ionic conductivities have been measured for ether oxygen to Li$^+$ ratios of 5:1–100:1. For the low molecular weight polymer the temperature dependence of the conductivity is found to fit a VTF relationship over the range 0–70°C. It is found that the lithium salt with the larger anion has a higher conductivity. Such factors as the terminal group and the length of the ethylene oxide chains affect the conductivity; the bulk viscosity has a secondary effect. The large poly(dimethylsiloxane) end groups appear to be very effective in increasing the flexibility to give a higher conductivity than a network polymer incorporating a similar poly(ethylene oxide) chain.

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REFERENCES

1 Fontanella, J. J., Wintersgill, M. C., Smith, M. K., Semancik, J. and Andeen, C. G. *J. Appl. Phys.* 1986, **60**, 2665
2 Chadwick, A. V. and Worboys, M. R. in 'Polymer Electrolyte Reviews 1' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1987, p. 275

3 Spindler, R. and Shriver, D. F. *J. Am. Chem. Soc.* 1988, **110**, 3036
4 Sandahl, J., Schantz, S., Börjesson, L., Torell, L. and Stevens, J. R. *J. Chem. Phys.* 1989, **91**, 655
5 Sandahl, J., Börjesson, L., Stevens, J. R. and Torell, L. *Macromolecules* 1990, **23**, 163
6 Kaplan, M. L., Reitman, E. A. and Cava, R. J. *Polymer* 1989, **30**, 504
7 Bhattacharja, S., Smoot, S. W. and Whitmore, D. H. *Solid State Ionics* 1986, **18/19**, 306
8 Hardy, L. C. and Shriver, D. F. *J. Am. Chem. Soc.* 1985, **107**, 3823
9 Zhou, G., Khan, I. M. and Smid, J. *Polym. Commun.* 1989, **30**, 52
10 Cowie, J. M. G. and Cree, S. H. *Ann. Rev. Phys. Chem.* 1989, **40**, 85
11 Cameron, C. G. and Ingram, M. D. in 'Polymer Electrolyte Reviews 2' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1989, p. 157
12 Scott, A. and Taube, H. *Inorg. Chem.* 1971, **10**, 62
13 Wixwat, W., Fu, Y. and Stevens, J. R. *Polymer* 1991, **32**, 1181
14 Hall, P. G., Davies, G. R., McIntyre, J. E., Ward, I. M., Bannister, D. J. and Le Brocq, K. M. F. *Polym. Commun.* 1986, **27**, 98
15 Fish, D., Khan, I. M. and Smid, J. *Macromol. Chem. Rapid Commun.* 1986, **7**, 115
16 Fish, D., Xia, D. W. and Smid, J. *Macromol. Chem. Rapid Commun.* 1985, **6**, 761
17 van der Maarel, J. R. C., Powell, D. H., Jawachier, A. K., Leyte-Zuiderweg, L. H., Neilson, G. W. and Bellissent-Funel, M. C. *J. Chem. Phys.* 1989, **90**, 6709
18 Xia, D. W., Soltz, D. and Smid, J. *Solid State Ionics* 1984, **14**, 221
19 Khan, I. M., Yuan, Y., Fish, D., Wu, E. and Smid, J. *Macromolecules* 1988, **21**, 2684
20 Watanabe, M. and Ogata, N. in 'Polymer Electrolyte Reviews 1' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1987, p. 39
21 Hu, C. P. and Wright, P. V. *Br. Polym. J.* 1989, **21**, 421
22 Munshi, M. Z. A. and Owens, B. B. *Polym. J.* 1988, **20**, 577
23 Wintersgill, M. C., Fontanella, J. J., Calame, J. P., Greenbaum, S. G. and Andeen, C. G. *J. Electrochem. Soc.* 1984, **131**, 2208
24 Wintersgill, M. C., Fontanella, J. J., Calame, J. P., Smith, M. K., Jones, T. B., Greenbaum, S. G., Adamic, K. J., Shetty, A. N. and Andeen, C. G. *Solid State Ionics* 1986, **18/19**, 326
25 Vogel, H. *Phys. Z.* 1921, **22**, 645
26 Tammann, V. G. and Hesse, W. *Z. Anorg. Allg. Chem.* 1926, **156**, 245
27 Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **8**, 339