Ionic conductivity in poly(di-poly(propylene glycol) itaconate)–salt mixtures

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A polymer, based on a poly(itaconic acid) backbone to which poly(propylene glycol) sidechains have been attached was synthesized. The material was mixed with several salts with which it formed homogeneous solutions and the glass transition temperature (T_g) and a.c. conductivity were measured for each solution. Addition of a salt tended to raise the T_g but the magnitude of this rise depended on the salt and increased in the order $LiCl < ZnCl_2 < LiClO_4 < NaClO_4$. This trend was also reflected in the conductivity levels achieved in these mixtures and this increased in the same order. Conductivity data were analysed using the Vogel–Tamman–Fulcher equation and the Adam–Gibbs configurational entropy approach. Values have been estimated for the activation energies of ion transport from these relationships and they lie in the range 45–125 kJ mol^{-1}. It is suggested that ion transport may occur via an associative exchange reaction.

(Keywords: ionic conductivity; glass transition temperature; polymer–salt mixtures; activation energies; poly(propylene glycol); comb-shaped polymer)

INTRODUCTION

The polyethers, in particular poly(ethylene oxide) PEO, and poly(propylene oxide) PPO, have been found to be capable of dissolving a wide range of inorganic salts. This encouraged studies of these materials as polymeric solid electrolytes for use in high energy density batteries after Wright *et al.*[1,2] reported that the conductivity levels achieved in PEO/salt solutions reached values which were considered suitable for such applications. In stereochemical terms the spacing of the oxygen atoms in the PEO and PPO chains appears to be especially suitable for complexing the metal cations of the salts thereby forming homogeneous polymer/salt solutions at low to medium salt concentrations and even specific stoichiometric complexes at higher salt concentrations[3–6]. As complexation appears to be less favoured in other poly ethers, such as poly(tetramethylene oxide)[7,8], perhaps because of the change in spacing of the oxygen atoms, attention has centred predominantly on PEO or PEO-containing structures as the most promising candidates for use as polymeric electrolytes. One feature which tends to detract from the performance of PEO is the presence of crystalline regions in the matrix and as ion mobility has been found to be greatest in the amorphous regions of a polymer, the conductivity in PEO/salt systems becomes most effective at temperatures above the polymer melting point which is normally in the range 330–350 K. While there are several ways of producing structures containing PEO which are unlikely to crystallize, it is also of interest to examine the related polymer PPO.

The investigation of PPO has not been neglected by other workers but the work reported[8–16] has been less intensive, probably because the polymer samples which are readily available are low molecular weight viscous liquids. These shorter polypropylene glycols can, however, be incorporated into other polymeric chains to improve the dimensional stability of the materials. Thus Watanabe *et al.*[8,11–13] have prepared PPO networks either by crosslinking a PPO triol with diisocyanates or by forming polyurethane alternating block copolymers structures using PPO blocks of different lengths. Cheradame *et al.*[14] have used similar strategies and have also prepared PEO–PPO block copolymers. Here we have used the alternative method of attaching short PPO side chains to a poly(itaconic acid) backbone. This leads to a comb branched polymer similar to those prepared using PEO oligomers attached to poly(methacrylic acid)[3,17], polyphosphazene[18], and poly(itaconic acid)[19] main chains.

EXPERIMENTAL

Sample preparation

Poly(propylene glycol) 1025 (BDH) was used as received. The number-average molecular weight (M_n), measured by vapour pressure osmometry, was 993 which represents an average of 17 propylene oxide units per chain. The itaconic acid diester was prepared by reacting the glycol and itaconic acid in toluene using *p*-toluene sulphonic acid as catalyst. Refluxing was continued for 4 days using a Dean and Stark trap and the monomer was isolated after removal of the toluene. Polymerization was effected using α,α′ azo bis isobutyronitrile as initiator and the reaction mixture was maintained at 340 K for 6 days. The polymer was precipitated in hexane and allowed to separate at 273 K overnight. The material was washed in petrol ether, filtered and dried in vacuum. The M_n was found to be 28 000 and the polymer was given the code PDPPGI. Polymer/salt mixtures were prepared from carefully dried materials as described elsewhere[19] and samples were handled under dry box conditions.

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A.c. conductivity

Measurements were made with a 1.59 kHz a.c. conductivity meter and a cell composed of two silver electrodes surrounded by a PTFE restraining ring. The complete assembly was housed in a dry box to ensure minimum contamination with water. The conductivities of the polymer/salt solutions were measured as a function of temperature, and the sample was allowed to equilibrate for one hour at each incremental temperature rise, before the conductivity was recorded.

Differential scanning calorimetry

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to measure the glass transition temperature T_g of each polymer/salt sample. This was taken to be the mid-point temperature of the base line shift measured during the transition. The change in heat capacity on moving from the glass to the rubbery state, ΔC_p, was measured as described in previous publications[20].

RESULTS

The glass transition temperatures of the PDPPGI/salt mixtures have been reported previously[21], and T_g values were observed to increase monotonically with added salt. The extent of the increase ΔT_g depends on the type of salt used and was found to increase in the order $LiCl < ZnCl_2 < LiClO_4 < NaClO_4$, as seen in *Figure 1*. The extent of solvation of the salt by the polymer to form free ions rather than ion pairs was reflected in ΔT_g, and an analysis of the data showed that the dependence of T_g on the added salt could be described by a simple equilibrium of the type:

$$P + MX \rightleftharpoons PM^+ + X^- \qquad (1)$$

where P is the polyether, MX is the salt and PM^+ the polymer/cation complex. The extent of this ionization was greatest for large ΔT_g values, and it was also found to decrease as the salt concentration increased.

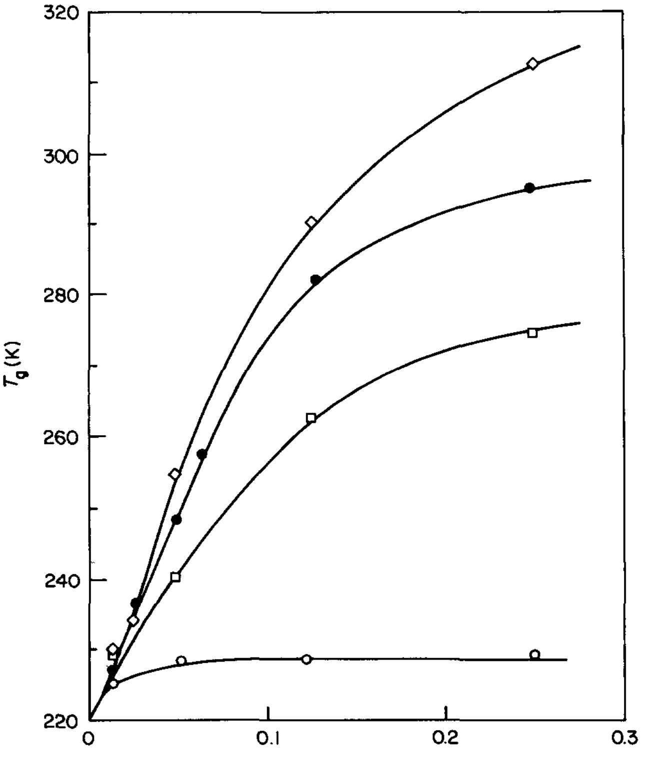

Figure 1 Variation of glass transition temperature with salt concentration for $NaClO_4$ –◇–; $LiClO_4$ –●–; $ZnCl_2$ –□–; and LiCl –○– dissolved in PDPPGI

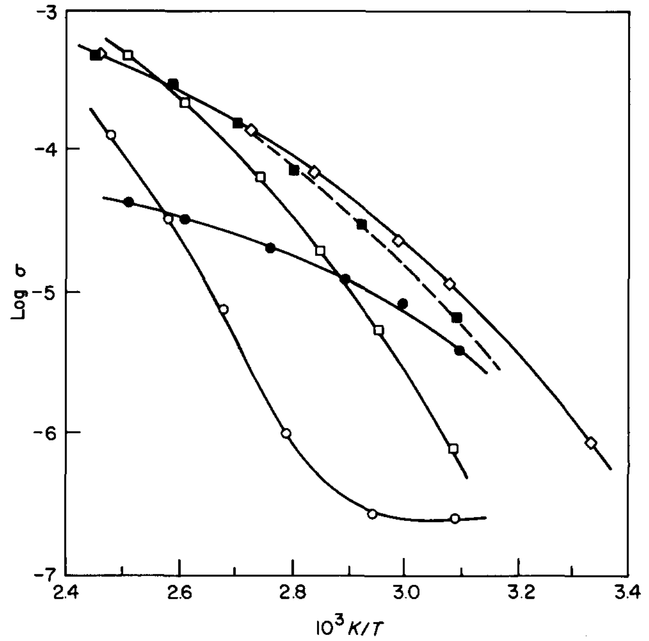

Figure 2 Log conductivity against reciprocal temperature plots for $PDPPGI/LiClO_4$ mixtures with $[Li^+]/[O]$ ratios of 0.0125 –●–; 0.05 –◇–; 0.066 –■–; 0.125 –□–; and 0.25 –○–

The $NaClO_4$ and $LiClO_4$ systems exhibit the greatest degree of salt dissociation in PDPPGI and so should produce the largest number of potential charge carriers. Thus polymer/salt systems in which ΔT_g is large should also have a correspondingly high conductivity. This appears to be the case.

Conductivities

$LiClO_4$ systems. The log conductivities (σ) of the PDPPGI sample containing varying amounts of salt are shown in *Figure 2* plotted against reciprocal temperature. The behaviour is not Arrhenius and curvature is observed in all cases. For $[Li^+]/[O]$ ratios of <0.07 the conductivities range between 5×10^{-4} S cm^{-1} at 400 K to 10^{-6} S cm^{-1} at 300 K. At higher salt concentrations the conductivities tend to be lower and an isothermal plot of log σ passes through a maximum which changes with temperature from a $[Li^+]/[O]$ ratio of 0.04 at 303 K to the higher salt concentration ratio of 0.08 at 393 K. This is illustrated in *Figure 3(a)* but if the data are replotted in terms of a reduced temperature $(T - T_g)$, as shown in *Figure* 3(*b*), then the maximum conductivity is observed at a constant $[Li^+]/[O]$ ratio of 0.125. This latter plot compares the conductivity of each polymer/salt solution at the same temperature above its T_g and implies that at equivalent levels of free volume in the system there is a maximum conductivity when there are eight oxygen atoms per lithium ion in the matrix.

Angell and Bressel[22] have shown that the maximum in conductivity can be predicted from an isothermal transport equation of the form:

$$\sigma = AX \exp\{-B/Q(X_0 - X)\} \qquad (2)$$

where X is the mole fraction of salt in the system, Q is the dependence of T_g on salt concentration, X_0 is the mole fraction at which $T = T_g$, and A and B are constants. This

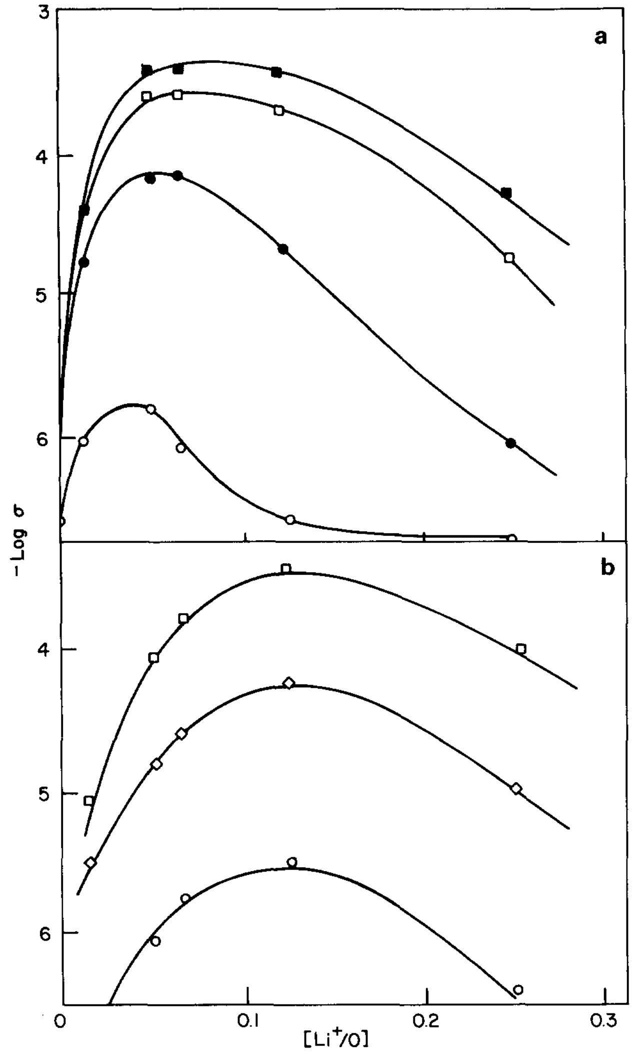

Figure 3 (a) Upper diagram: Isothermal plots of log conductivity against $[Li^+]/[O]$ ratio for PDPPGI/$LiClO_4$ systems. The temperatures for each curve are 303 K -○-; 353 K -●-; 373 K -□- and 393 K -■-. (b) Lower diagram: Data plotted at fixed values of $(T-T_g)$ of 50 K -○-; 80 K -◇-; and 110 K -□-

is based on the configurational entropy theory of Adam and Gibbs[23] and predicts that the maximum will be located at smaller salt concentrations the greater the value of Q. It was suggested that the observed maximum in conductivity was then simply competition between the build up of charge carriers in the system and the consequential increase in T_g which impedes ion mobility as the polymer matrix becomes more rigid.

This proposition would not explain the conductivity maximum observed at a fixed temperature above T_g where the chain flexibility should be constant. A more likely explanation is that as the number of ions increases, oppositely charged ion clouds will begin to form and start to retard ion transport. Thus the build up of charge carriers is eventually offset by the retarding effect of ion clouds and at high salt concentrations, $[Li^+]/[O] > 0.125$, the conductivity will decrease as the latter effect begins to dominate. If, as reported earlier[21], the % ionization of the salt tends to decrease with increasing concentration this could also be a factor contributing to the observed conductivity behaviour.

The movement of the conductivity maximum in the isothermal curves shown in *Figure 3(a)*, to higher salt concentrations with increase in temperature can be rationalized by recognizing that at higher temperatures the increase in polymer chain motion will assist ion transport and partially compensate for the retarding effect of the ion clouds.

Other salt systems. Representative log σ against $1/T$ data for PDPPGI solutions at a fixed [salt]/[O] ratio of 0.125 are shown in *Figure 4* for $NaClO_4$, $ZnCl_2$ and LiCl systems. The levels of conductivity in each system are in the order $NaClO_4 > ZnCl_2 > LiCl$ which is in the same order as the ΔT_g increases. As suggested earlier, it appears that the greater the increase in T_g the better the conductivity and this supports the supposition that the increase in T_g reflects the effective interaction of the salt ions with the polyether chains. The relative magnitude of ΔT_g is then indicative of the number of available charge carriers in the polymer.

Most of the published data point to the fact that the highest conductivities in polyether systems are achieved when the chains are most mobile. Thus a low T_g is advantageous if reasonable ambient or above ambient temperature conductivities are to be obtained. One might then conclude that if there is little elevation of T_g when a salt is added to a polymer forming a homogeneous amorphous mixture, as with the LiCl/PDPPGI system, then superior levels of conductivity should be displayed. The opposite is observed here and it is evident that one has to contend with two opposing effects. If the polymer can solvate the ions efficiently then there is a good supply of free ions to act as charge carriers but this also raises the T_g because the complexed ions crosslink and stiffen the polymer chains. When the ionization of the salt in the polymer is low, the T_g of the mixture is also low but there are only a few ions to act as charge carriers and so the conductivity is correspondingly low.

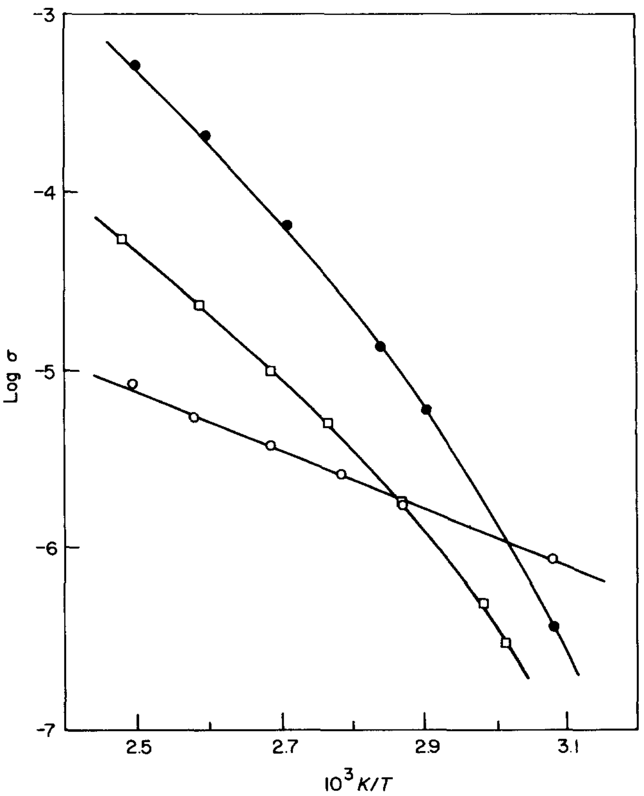

Figure 4 Log conductivity as a function of reciprocal temperature for PDPPGI/$NaClO_4$ —●—; PDPPGI/$ZnCl_2$ —□— and PDPPGI/LiCl —○— at a fixed salt to polymer ratio of 0.125

At present the best results are obtained when the initial polymer T_g is as low as possible and the salt used is dissolved effectively in the polymer matrix.

Apparent activation energies. With the possible exception of some of the data for the PDPPGI/LiCl mixtures, the log σ against reciprocal temperature plots are curved and are not described by the Arrhenius equation. The results are more accurately represented by the empirical Vogel–Tamman–Fulcher (VTF) equation

$$\sigma = AT^{-1/2}\exp\{-B/(T-T_0)\} \qquad (3)$$

where A is a constant, B is a constant, but has been regarded as being related to an apparent activation energy and T_0 can be taken as the temperature at which the configurational entropy in the system approaches zero[24]. Although T_0 is not accessible experimentally it is normally assumed to have a value of ~50 K below T_g. Alternatively one can use an experimental T_g as an approximation for T_0.

The data were treated in three ways with $\log(\sigma T^{1/2})$ plotted against different reciprocal temperature functions. In method (i) it was plotted against $(T-T_g^0)^{-1}$ where T_g^0 is the glass transition temperature of the undoped polymer, which for the PDPPGI sample used here has a value of 220 K. For method (ii) the plot involves $(T-T_g)^{-1}$, where T_g is now taken as that of the actual salt/polymer complex under study. In method (iii) a non linear least squares analysis of the data was made thereby allowing the unknown parameters A, B and T_0 to assume the values suited to the best fit. The data when plotted using methods (i) and (ii) are linear and typically are as shown in *Figures 5* and *6* for $LiClO_4$ and $ZnCl_2$ respectively. The relevant parameters are gathered in *Table 1* where the slope B is converted to an activation energy B'. This conversion may not be particularly meaningful, however, and it is more instructive to consider how B may be interpreted. This can depend on the model adopted for the system and it has been demonstrated[25] that the VTF equation can be derived from the configurational entropy approach developed by Gibbs *et al.*[23,24] in which B is expressed as

$$B = \frac{T_0 S_c^* \Delta\mu}{k_B \Delta C_p T} \qquad (4)$$

where S_c^* is the minimum configurational entropy required for a cooperative rearrangement of a polymer chain segment involved in ion transport in the matrix, and $\Delta\mu$ is the height of the potential energy barrier per monomer unit hindering this type of segmental rearrangement. The heat capacity change is that measured during the change from the glass to the liquid at a temperature T, and k_B is the Boltzmann constant. Adam and Gibbs[23] have also suggested that it is reasonable to assume that $S_c^* = k_B \ln 2$, hence $\Delta\mu$ can be estimated from a knowledge of ΔC_p and T_0; the latter has been estimated using the VTF equation and ΔC_p can be measured directly[20].

The values of ΔC_p calculated at the glass transition from the d.s.c. measurements were found to lie in the range 25–40 J K^{-1} mol^{-1} (polymer) for the PDPPGI-salt mixtures after correction for salt content. It was also found that for the salt free PDPPGI ΔC_p was 29.0 J K^{-1} mol^{-1} which compared favourably with ΔC_p for the pure poly(propylene glycol) sample of 29.7 J K^{-1} mol^{-1}. This suggests that the PDPPGI behaves very much as though it was pure poly(propylene glycol) which may not be surprising considering the PPG in the side chain comprises ~95% of the molecule. The results also suggested that there was a small but steady increase in ΔC_p as the salt concentration increased. The relevant data

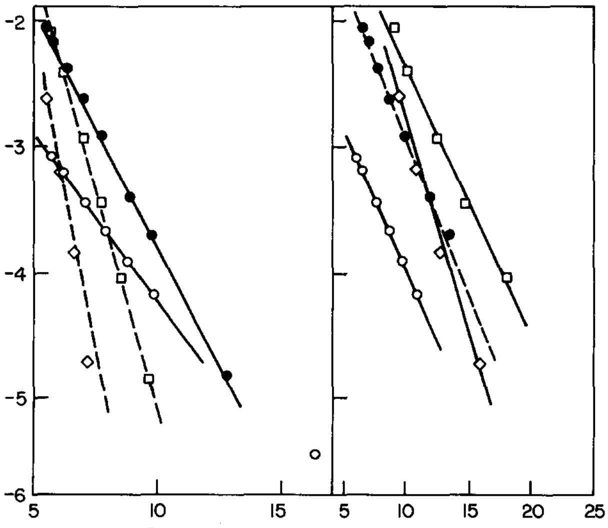

Figure 5 VTF plots for PDPPGI/$LiClO_4$ using methods (i) and (ii) as described in the text. 0.0125 -○-; 0.05 -●-; 0.125 -◇-; 0.25 -□-

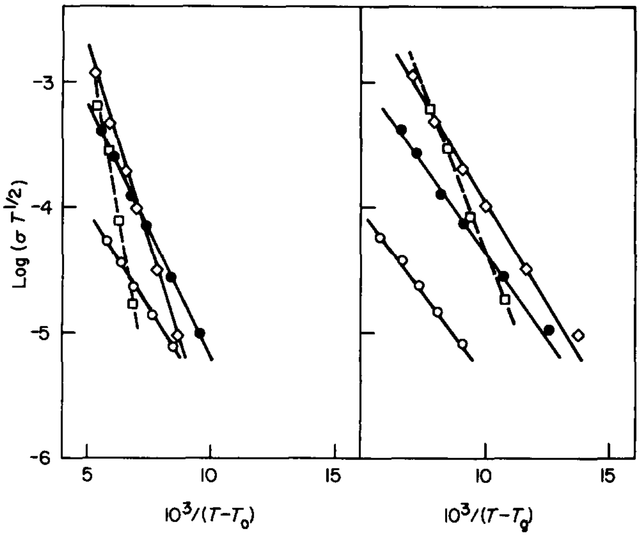

Figure 6 VTF plots for PDPPGI/$ZnCl_2$ using methods (i) and (ii) as described in the text. 0.0125 -○-; 0.05 -●-; 0.125 -◇-; 0.25 -□-

Table 1 Apparent activation energies derived from the slope of the VTF plots for poly(di poly(propylene glycol)itaconate)-salt mixtures

Salt	[Salt]/[O]	Method (i)[a] B' (kJ mol^{-1})	Method (ii)[b] B' (kJ mol^{-1})
$LiClO_4$	0.0125	5.13	4.49
	0.050	7.75	4.97
	0.125	13.59	4.06
	0.250	18.65	6.22
$NaClO_4$	0.05	7.30	3.83
	0.125	15.10	3.98
$ZnCl_2$	0.0125	6.17	5.55
	0.050	7.86	5.16
	0.125	12.12	6.42
	0.250	19.80	10.36

[a] Method (i) uses $T_0 = T_g^0$ of the undoped polymer
[b] Method (ii) uses $T_0 = T_g$ for each polymer/salt mixture

Table 2 Heat capacity changes and activation energies for poly(di-poly(propylene glycol)itaconate)–salt mixtures calculated using method (iii) and equation (4)

Salt	$\frac{[\text{Salt}]}{[\text{O}]}$	B (K)	T_0 (K)	(T_g-T_0) (K)	ΔC_p ($\text{J K}^{-1}\,\text{mol}^{-1}$)	$\Delta\mu$ (kJ mol^{-1})
$LiClO_4$	0.0125	953.8	187.3	41.2	27.0	47.8
	0.050	1204.0	201.5	47.0	29.7	63.4
	0.125	1301.5	234.5	48.0	35.2	79.9
	0.250	1801.2	250.3	44.7	38.6	119.0
$NaClO_4$	0.05	1082.5	213.4	40.6	32.8	61.1
	0.125	1728.4	223.2	67.3	38.1	123.3
$ZnCl_2$	0.125	1546.0	214.7	47.3	32.3	87.7

Table 3 Activation energies for PDPPGI–salt mixtures estimated from data plotted according to the Arrhenius relation but measured over restricted temperature ranges

Salt	$\frac{[\text{Salt}]}{[\text{O}]}$	Temperature range (K)	Activation energy (kJ mol^{-1})
$LiClO_4$	0.05	320–360	60
		360–400	39
	0.125	320–360	122
		360–400	62
	0.250	360–400	128
$NaClO_4$	0.05	320–360	64
		360–400	39
	0.125	320–360	121
		360–400	84
$ZnCl_2$	0.05	320–360	47
		360–400	60
	0.125	320–360	74
		360–400	96
LiCl	0.05	320–400	38.0
	0.125	320–400	31.0

are collected in *Table 2*, except for the LiCl/PDPPGI system which was not amenable to this treatment.

The conductivity data for the LiCl solutions correspond more closely to the Arrhenius relation and activation energies were estimated according to that equation. As a comparison, activation energies were estimated from the Arrhenius plots for each system by approximating a linear portion over a given temperature range on the curved plots. These values are listed in *Table 3*.

DISCUSSION

The apparent activation energies listed in *Table 1*, which were calculated from the VTF equation using methods (i) and (ii) are of a similar magnitude to those reported by other workers[19,26] and are usually less than 20 kJ mol^{-1}. However, in the light of the analysis using method (iii) the physical significance of these data is questionable.

Method (iii) is a much more satisfactory approach and when combined with equation (4) produces some interesting data. The values of T_0 can be obtained without making any assumptions and it is gratifying to see that these lead to values of $(T_g - T_0)$ very close to the expected difference of 50 K, which lends credence to the further analysis of the data using the Adam–Gibbs approach. These values are also in reasonable agreement with Fontanella *et al.*[16] who reported $(T_g - T_0)$ in the range 34–46 K for crosslinked polypropylene oxide mixed with $LiClO_4$ at a $[Li^+]/[O]$ ratio of 0.125.

The corresponding $\Delta\mu$, estimated for several of the systems studied here have much higher values than the corresponding B' derived by methods (i) and (ii) and are similar in magnitude to the approximate activation energies listed in *Table 3*, derived using the Arrhenius equation. In general there appears to be an increase in $\Delta\mu$ with increasing salt concentration but the data are insufficient to make particular comments on this trend.

Papke *et al.*[25] have estimated that if ion transport involves a dissociative process requiring rupture of cation–ether bonds then the activation energy for a Na^+–ether oxygen bond disruption would be about 59 kJ mol^{-1}. If four bonds were required to be broken then the activation energy for that process would exceed 200 kJ mol^{-1}. This is calculated for a gas phase reaction and is probably much larger than would be required for an exchange reaction in the condensed state. Cox and his coworkers[27,28] have found that when exchange reactions between free cryptands and metal cryptate complexes are studied in solution the activation energies for the exchange of ion with the solvent are much smaller (~20–30 kJ mol^{-1}). They also found that there was a direct bimolecular cation exchange between two ligands when dissolved in a poor solvating medium and that while the rate constants were low the bimolecular pathway was essential. These authors tended to favour an associative exchange mechanism rather than a dissociative one and considered that cation transport was unlikely to involve much loss of donor–cation interaction with an intermediate species being formed in which the cation is shared between donor atoms on each ligand during transport.

This is an appealing mechanism to apply to the polymeric systems, where movement of a coordinated polymer segment brings the ion close to another set of binding sites on an adjacent chain and undergoes an associative exchange. As molecular motion in these systems would be relatively sluggish compared even with a low viscosity solvent this mechanism seems to be more likely to occur than a dissociative one. Consequently values of $\Delta\mu$ could be expected to be intermediate between those for the gas phase reaction and those in dilute solutions, and so the $\Delta\mu$ calculated are not unreasonable and are probably more realistic than the B' values in *Table 1*. Their comparability with the Arrhenius estimations suggest that the analysis using equation (4) could prove useful as an indicator of the energetics in polymer systems. Thus while the mechanism of ion transport in these systems is still largely speculative, derivation of $\Delta\mu$ values for other systems could prove useful in helping to understand the process and will be examined more closely in future publications.

REFERENCES

1 Fenton, D. E., Parker, J. M. and Wright, P. V. *Polymer* 1973, **14**, 589
2 Wright, P. V. *Br. Polym. J.* 1975, **7**, 319
3 Xia, D. W., Soltz, D. and Smid, J. *Solid State Ionics* 1984, **14**, 221
4 Fish, D., Xia, D. W. and Smid, J. *Makromol. Chem. Rapid Commun.* 1985, **6**, 761
5 Gorecki, W., Andreani, R., Berthier, C., Armand, M. B., Mali, M., Roos, J. and Brinkman, D. *Solid State Ionics* 1986, **18/19**, 295
6 Ferloni, P., Chiodelli, G., Magistris, A. and Sanesi, M. *Solid State Ionics* 1986, **18/19**, 265
7 Armand, M. B. *Solid State Ionics* 1983, **9/10**, 745
8 Watanabe, M., Nagaoka, K., Kanba, M. and Shinohara, I. *Polym. J.*, 1982, **14**, 877
9 Watanabe, M., Ikeda, J. and Shinohara, I. *Polym. J.* 1983, **15**, 65
10 Watanabe, M., Ikeda, J. and Shinohara, I. *Polym. J.* 1983, **15**, 175
11 Watanabe, M., Sanui, K., Ogata, N., Inoue, F., Kobayashi, T. and Ohtaki, Z. *Polym. J.* 1984, **16**, 711
12 Watanabe, M., Sanui, K., Ogata, N., Inoue, F., Kobayashi, T. and Ohtaki, Z. *Polym. J.* 1985, **17**, 549
13 Watanabe, M., Oohashi, S., Sanui, K., Ogata, N., Kobayashi, T. and Ohtaki, Z. *Macromolecules* 1985, **18**, 1945
14 Gandini, A., Le Nest, J. F., Leveque, M. and Cheradame, H. 'Integration of Fundamental Polymer Science and Technology', Ed. L. A. Kleintjens and P. Lemstra, Elsevier Appl. Sci. Publishers, 1985, p. 250 and references therein
15 Teeters, D. and Fresch, R. *Solid State Ionics* 1986, **18/19**, 271
16 Fontanella, J. J., Wintersgill, M. C., Calame, J. P., Smith, M. K. and Andeen, C. G. *Solid State Ionics* 1986, **18/19**, 253
17 Bannister, D. J., Davies, G. R., Ward, I. M. and McIntyre, J. E. *Polymer* 1984, **25**, 1600
18 Blonsky, P. M., Shriver, D. F., Austin, P. and Allcock, H. R. *Solid State Ionics*, 1986, **18/19**, 258
19 Cowie, J. M. G. and Martin, A. C. S. *Polymer* 1985, **26** (*Commun.*), 298
20 Cowie, J. M. G., Ferguson, R. and McEwen, I. J. *Polymer* 1982, **23**, 605
21 Cowie, J. M. G., Martin, A. C. S. and Ferguson, R. *Polymer* 1987, **28**, (*Commun.*) in press
22 Angell, C. A. and Bressel, R. D. *J. Phys. Chem.* 1972, **76**, 3244
23 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
24 Gibbs, J. H. and Di Marzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
25 Papke, B. L., Ratner, M. A. and Shriver, D. F. *J. Electrochem. Soc.* 1982, **129**, 1694
26 MacCallum, J. R., Smith, M. J. and Vincent, C. A. *Solid State Ionics* 1984, **11**, 307
27 Cox, B. G., private communication
28 Cox, B. G. and van Truong, N. *J. Chem. Soc. Trans. Farad. I* 1984, **80**, 3285