Effect of crosslinking on the a.c. conductivity of poly(3,6,9,12-tetraoxatridec-1-ene)/lithium perchlorate mixtures

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Samples of poly(3,6,9,12-tetraoxatridec-1-ene) were crosslinked to varying degrees and doped with lithium perchlorate. The glass transition temperature, T_g, was increased by about 20 K at 11% crosslinking, but the levels of conductivity remained the same as those for the uncrosslinked material up to about 5% crosslinking. The temperature dependence of the a.c. conductivity was predominantly non-Arrhenius and the data were analysed using the Vogel–Tammann–Fulcher equation and the Adam–Gibbs configurational entropy model. Both approaches appear valid at low crosslink densities but may not be applicable at higher levels of crosslinking. Activation energies associated with the segmental motion in the polymer were around 55 kJ mol^{-1} on average.

(Keywords: ion conduction; polymer–salt mixtures; comb–branch networks; ethylene oxide macromers)

INTRODUCTION

The use of comb-shaped polymers with short side chains composed of ethylene oxide oligomers as media for the dissolution of inorganic salts has been reported by a number of workers[1–6]. These form homogeneous polymer–salt solutions which exhibit moderately good levels of conductivity and have been studied as polymer electrolytes for use in high energy density batteries. A polymer formed from the ethylene oxide macromer 3,6,9,12-tetraoxatridec-1-ene has been prepared recently[7] which exhibited reasonably high levels of a.c. conductivity of approximately 5×10^{-5} S cm^{-1} at room temperature, but because it has a low glass transition temperature (T_g), the polymer–salt mixtures are viscous fluids at ambient temperatures. The polymer can be readily crosslinked to form non tacky, elastomeric, films which can be handled conveniently and are amenable to the formation of homogeneous polymer–salt solutions. However, it has been reported that in certain systems, when crosslinks are introduced, there can be a significant loss in conductivity due to restrictions imposed on chain motion by the crosslink sites. This effect is examined here for samples of poly(3,6,9,12-tetraoxadec-1-ene) which have been crosslinked to varying degrees.

EXPERIMENTAL

Monomer preparation

The monomer 3,6,9,12-tetraoxatridec-1-ene was prepared by the method suggested by Mathias *et al.*[8]. The monomethyl ether of triethylene glycol (0.6 mol) was dried under nitrogen and converted to the potassium salt by adding small pieces of potassium metal (0.076 mol) to the liquid. The flow of nitrogen was reduced and replaced gradually by acetylene which was bubbled through the liquid at a temperature of 448–458 K. This was continued for 2.5 h and then the flow of acetylene was gradually replaced by nitrogen while cooling the reaction mixture to room temperature. The crude vinyl ether was extracted with carbon tetrachloride and washed thoroughly with water to remove unreacted alcohol. The final product (I) was obtained by fractional distillation (332 K, 1.33 Pa) and characterized

$$CH_2{=}CH{-}O{-}(CH_2CH_2O)_3{-}CH_3 \qquad (I)$$

using n.m.r. and i.r. spectroscopy, and also microanalysis (theoretical, C=56.82%, H=9.54%, O=33.64%; found, C=56.80%, H=9.59%, O=33.61%). The divinyl ether (II) was obtained in a similar manner using triethylene glycol as the starting material.

$$CH_2{=}CHO(CH_2CH_2O)_3{-}CH{=}CH_2 \qquad (II)$$

Fractional distillation for product II was accomplished at 343 K and 1.33 Pa. Micro analysis: theoretical, C=59.39%, H=8.97%, O=31.64%; found, C=59.31%, H=9.00%, O=31.69%.

Polymerization

Monomer I can be readily polymerized using a BF$_3$-etherate initiator under anhydrous conditions[7,8]. Crosslinked samples were prepared by mixing appropriate amounts of monomers I and II in a septum sealed flask which was first flame dried under vacuum. The mixture was degassed using at least three freeze–thaw cycles and then cooled to 233 K. A freshly prepared solution of BF$_3$-etherate in 1,2-dichloroethane was injected into the mixture which was then allowed to warm up to about 280 K over a period of 1 h. At this temperature a highly exothermic reaction takes place and the mixture becomes very viscous.

The reaction mixture was left for 24 h at room temperature before the crosslinked sample was swollen by

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the addition of chloroform then washed repeatedly with acetone and methanol to remove any unreacted monomer or sol fraction from the network. The crosslink density is difficult to measure precisely and so apparent crosslinking is quoted which reflects the amount of monomer II used in the feed mixture.

The materials obtained were transparent non sticky elastomers and easily handled. Films could also be prepared by carrying out the polymerization in a thin layer of reaction mixture spread on a petri dish under nitrogen. The product was easily peeled off the glass plate and formed a flexible elastomeric sheet.

Polymer–salt mixtures

Homogeneous amorphous solutions of the networks and $LiClO_4$ were prepared by allowing the polymer to swell in a methanol solution of the salt. The mixtures were stirred and the methanol was allowed to evaporate over a period of 48 h. The material was then dried in a vacuum oven at 330 K for 72 h and the dry polymer–salt mixture was weighed to confirm the amount of salt incorporated into the network. The concentration of the salt in the polymer was varied by adjusting the weight of salt in the methanol to that of the polymer. The different compositions are expressed as the cation concentration per ethylene oxide unit in the polymer. The ether oxygen adjacent to the main chain was not included in this calculation to allow comparison with other systems previously studied in this laboratory[3,6,7].

Network swelling

The polymer networks exhibited extensive swelling when exposed to water, methanol, ethanol, chloroform and hexane. This is not an exhaustive list of swelling solvents, merely a representative selection. A weighed sample of polymer was immersed in the swelling liquid for 48 h at 292 K. It was then removed, placed in a weighed container and excess surface solvent removed by blowing dry nitrogen over the sample for about 30 s. The weight of liquid absorbed/g polymer was then estimated.

Glass transition temperatures

A differential scanning calorimeter (Perkin–Elmer DSC2) was used to measure the glass transition temperature (T_g) of the uncrosslinked polymer, the polymer networks and the polymer network–salt mixtures. The value of T_g was taken as the onset of the baseline shift which occurs during the transition from the glass to the rubber-like state at a heating rate of $20\,K\,min^{-1}$. The value of T_g for the uncrosslinked polymer was found to be 206 K. Other values are given in *Table 1*.

Table 1 Variation in glass transition temperature with the apparent per cent crosslinking

Apparent per cent crosslinking	T_g (K)	Apparent per cent crosslinking	T_g (K)
0	206	7.0	215
0.2	206	9.0	219
2.0	210	11.0	226
3.0	211	40.0	241
5.0	211	100.0	331

Table 2 Swelling characteristics of the polymer as a function of apparent per cent crosslinking and for a 5% crosslinked sample in several solvents

Liquid	Weight absorbed liquid/g 5% crosslinked polymer	Apparent per cent crosslinking	Weight MeOH absorbed/g polymer
Hexane	0.25	0.2	6.95
Methanol	2.57	1.2	4.53
Ethanol	4.66	2.0	3.36
Water	6.47	5.0	2.57
Chloroform	14.67	11.0	1.99

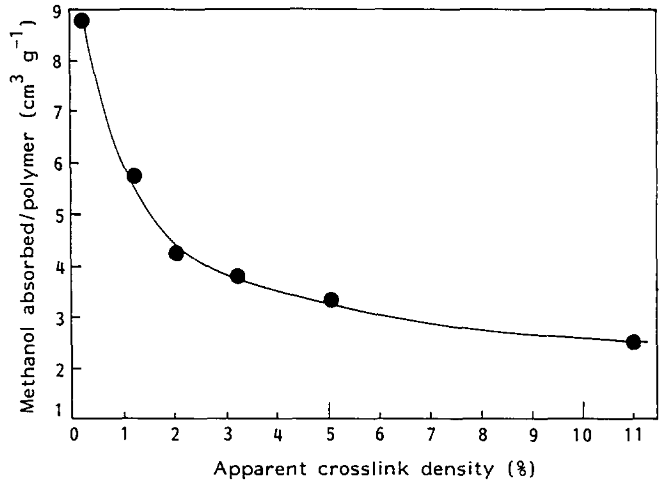

Figure 1 Volume of methanol absorbed by 1 g of polymer measured at different levels of apparent per cent crosslinking

A.c. conductivity

Measurements were made as described elsewhere[6], using an a.c. conductivity meter (1.59 kHz) and under anhydrous conditions in a glove box. The sample was allowed to equilibrate for 1 h at each temperature before a measurement was made following each incremental rise. The range covered was ambient to ~410 K.

RESULTS

Swelling

The swelling behaviour of a sample with a nominal 5% crosslinking was examined in a selection of liquids and the effectiveness of each was estimated from the weight absorbed per g of polymer. The results obtained were an average of three measurements and are shown in *Table 2*. Chloroform is clearly the best in the group and the non polar hexane is the least effective. While not the best swelling agent, methanol was selected for doping purposes because it was a good solvent for the salt (avoiding water) and, because it is relatively volatile, it can be removed easily from the polymer–salt mixture during sample preparation. The swelling characteristics of the networks in methanol with apparent per cent crosslinking varying from 0.2% to 11%, are also shown in the second and third columns of *Table 2*. The amount of methanol absorbed decreases with increasing per cent crosslinking and appears to approach an asymptotic limit in this solvent around 11% crosslinking, as can be seen in *Figure 1*.

Glass transition temperature

When a polymeric material is progressively crosslinked the T_g of the network increases because of the restrictions imposed by the crosslinks on the freedom of motion of the polymer backbone. Samples with an apparent per cent crosslinking of up to ~100% were prepared and the values of T_g rose steadily, but not uniformly, by ~125 K as can be seen in *Table 1*. After an initial small increase of 5 K the T_g seemed to remain constant between 1% and 5% crosslinking after which there was a sharper rise up to 11% which slowed down at higher crosslink densities. However, one cannot read too much into these trends as the per cent crosslinking is only an apparent value and may not be particularly accurate.

These results are for salt free polymers but the addition of salt to the network also introduces a second (non covalent) type of crosslink where the cations coordinate with the ether oxygens of the side chains to form both intra- and intermolecular interactions which lead to a more rigid structure. The effect can be seen in the data reported in *Table 3* for samples with varying crosslink densities and different salt concentrations which can be compared with an uncrosslinked sample. Thus an increase in T_g of 74 K was observed at a $[Li^+]/[EO]$ ratio of 0.25 for the uncrosslinked sample which was similar to the 76 K increase obtained for a 5% crosslinked sample at the same salt concentration. This indicates that the effect of the salt on T_g was similar for both, at low crosslink densities. As higher conductivities are associated with a low T_g in the polymer–salt mixture, both of these variables should influence the ion conduction in crosslinked systems.

Effect of crosslinking on conductivity (σ)

A comparison of the temperature dependence of the $\log \sigma$ (conductivity) for an uncrosslinked sample and networks with apparent crosslink densities of 2%, 5% and 11% at a fixed value of $[Li^+]/[EO] = 0.05$, is shown in *Figure 2*. There is virtually no change in conductivity up to 5% crosslinking and only when this increases to 11% is there a noticeable decrease in $\log \sigma$.

The dependence of $\log \sigma$ on salt concentration is also apparent from *Figure 3* for 0%, 2%, 5% and 11% crosslinking. There it can be seen that the majority of the results exhibit a non-linear temperature dependence of $\log \sigma$, with the exception of some of the data for the 11% crosslinking where there is an approach to Arrhenius behaviour, particularly at low salt concentrations. The normal practice is to use the Vogel–Tammann–Fulcher (VTF) equation[9–11]

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

to analyse the non-Arrhenius behaviour. Here A, B and T_0 are constants whose structure will depend on the model applied.

Table 3 The effect of added salt on the glass transition temperature of uncrosslinked and crosslinked samples

Per cent crosslink	$\frac{[Li^+]}{[EO]}$ T_g 0	0.0125	0.025	0.05	0.125	0.25
0	206	216	224	238	260	280
0.2	206	216	220	239	259	282
3.25	210	220	223	236	263	285
5.0	211	223	226	238	264	287
11.0	226	236	239	264	274	–

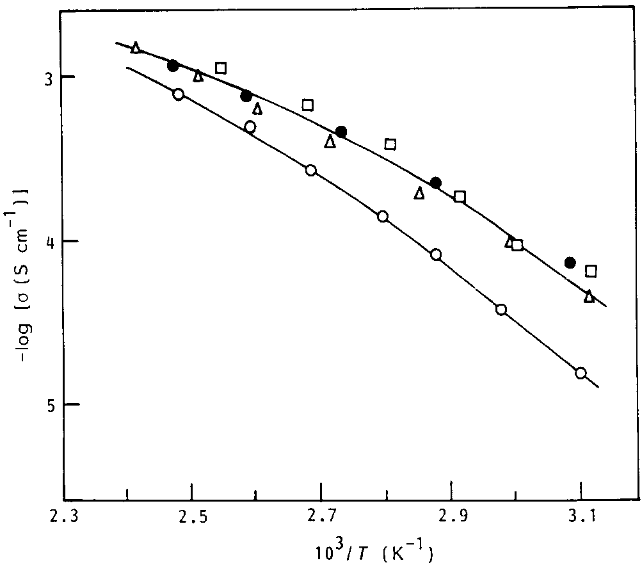

Figure 2 Temperature dependence of the log σ for networks at a fixed salt concentration of $[Li^+]/[EO] = 0.05$. Apparent per cent crosslinking: (●), 0%; (△), 2%; (□), 5%; (○), 11%

It has been observed previously[6,7] that the Adam–Gibbs configurational entropy model[12] has proved reasonably successful in the interpretation of the conductivity behaviour of similar systems. In this analysis, T_0 is the temperature at which the configurational entropy is vanishingly small and is predicted to be 50 K lower than T_g. The constant B can be cast in the form

$$B = T_0 S_c^* \Delta\mu / kT\Delta C_p \qquad (2)$$

where k is the Boltzmann constant, ΔC_p is the heat capacity change on moving from the glass to the rubber-like state, $\Delta\mu$ is the activation energy barrier which must be overcome by a minimum chain segment undergoing a spatial rearrangement, and S_c^* is the configurational entropy associated with such a segmental motion, which can be approximated by $k \ln 2$. Values of A, B and T_0 were estimated from each data set by using a non linear least squares minimization procedure. If the average value of $\Delta C_p = 29.45\ \mathrm{J K^{-1} mol^{-1}}$, calculated for the uncrosslinked polymer–salt complex[7], is assumed for the crosslinked samples then $\Delta\mu$ values can also be obtained. The results are listed in *Table 4* for four levels of crosslinking. The model seems to apply reasonably well for samples of up to 5% crosslinking for which values of $(T_g - T_0)$ range between 39 and 61 K, with an average of 50.6 K in good agreement with the predictions. At 11% crosslinking, however, values are much higher and the $\log \sigma - 1/T$ plots tend towards linearity. This suggests that this approach is no longer applicable to these highly crosslinked networks.

It should be emphasized that the method of arriving at values of A, B and T_0 for these systems makes no prior assumptions concerning a model, but the actual values obtained from the minimization procedures used may not always be the best and will depend on the accuracy of the data set used. Thus the A, B and T_0 values quoted must be regarded as averages and any observed trend or lack of trend cannot be regarded as necessarily being meaningful. The interpretation here is based on the apparent similarity of the calculated $(T_g - T_0)$ values to the Gibbs–DiMarzio prediction[13], which is taken to be

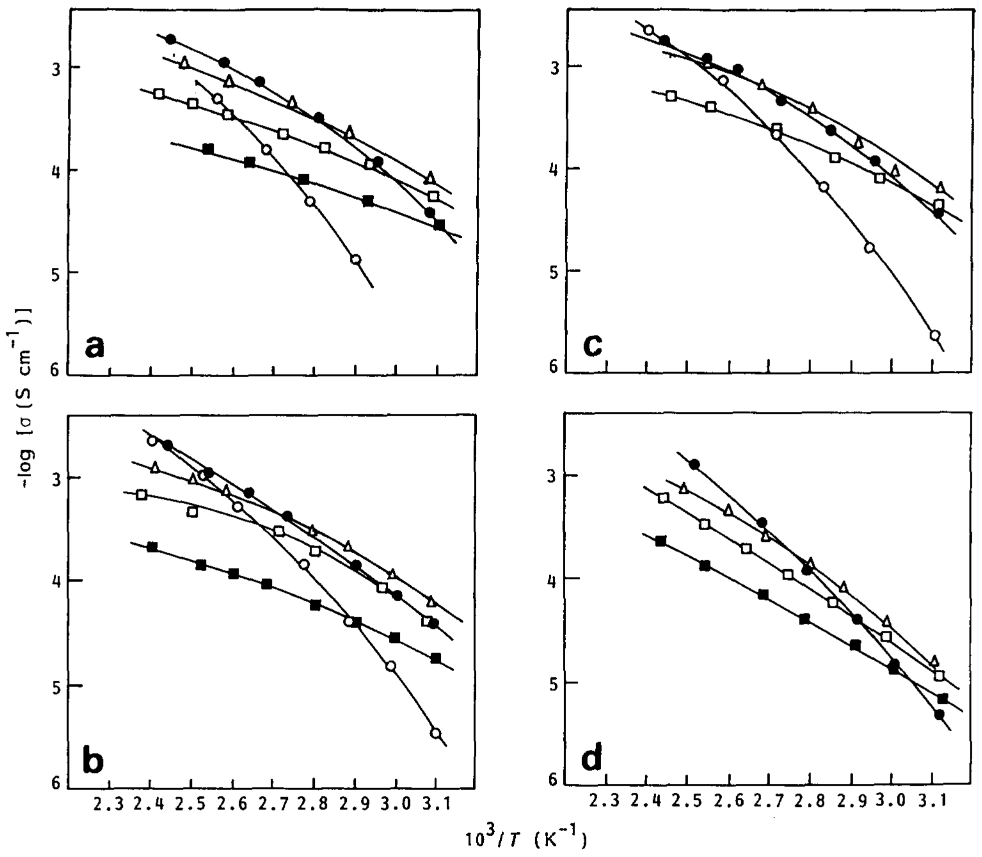

Figure 3 Temperature variation of log σ as a function of salt concentration and crosslinking density. (a) Uncrosslinked; (b) 1.2%; (c) 5%; (d) 11%. $[Li^+]/[EO]$: (■), 0.0125; (□), 0.025; (△), 0.05; (●), 0.125; (○), 0.25

Table 4 VTF analysis of conductivity–temperature data for samples with crosslinking

Per cent crosslinking	$[Li^+]/[EO]$	ln A	B (K)	T_0 (K)	$(T_g - T_0)$ (K)	$\Delta\mu$ kJ mol^{-1}
0.2	0.025	−6.30	953	176	51.0	50.71
	0.050	−5.79	869	197	42.0	44.71
	0.125	−3.74	1088	211	47.5	56.74
	0.250	−3.55	1019	231	50.0	52.86
1.2	0.0125	−7.42	973	171.7	48.3	52.97
	0.050	−5.42	893	199.4	39.1	45.39
	0.125	−4.07	1051	207	53.4	56.10
	0.250	−2.31	1281	225.7	61.3	69.13
5.0	0.025	−6.49	974	171	55.0	54.76
	0.050	−4.22	1210	178	60.0	68.87
	0.125	−5.07	807	222	41.0	40.77
	0.250	−2.01	1318	228	59.0	70.38
11.0	0.0125	−2.41	2998	78	158.0	42.25[a]
	0.025	−1.59	2613	115	114.0	42.50[a]
	0.050	−4.10	1248	196	68.0	71.44
	0.125	−2.14	2772	161	113.0	200.50

[a] Calculated from the Arrhenius relationship

significant. If the model is assumed to be applicable and $(T_g - T_0)$ fixed at a constant 50 K, the recalculation of A and B does not lead to significant changes, so the $\Delta\mu$ values remain the same order of magnitude as those in *Table 4* and no other trends in the data can be seen. In other words, no advantage is gained by prejudging the applicability of this model and the approach used seems to be valid.

The activation energies for segmental motion range between 40 and 70 kJ mol^{-1} which are the same order of magnitude as calculated for the uncrosslinked sample[7]. Again, the exception tends to be the 11% crosslinked material but if these data are treated using an Arrhenius equation then at the lower salt concentrations the calculated activation energies obtained of 42 and 48 kJ mol^{-1} are comparable.

Thus the effect of low levels of crosslinking on the ion conduction and chain motion is negligible and these polymer–salt mixtures behave like the uncrosslinked sample.

Isothermal conductivity

If the log σ data are plotted as a function of salt concentration at a series of fixed measuring temperatures, the expected maxima in conductivity are observed, as can be seen in *Figure 4*. These maxima were observed to move to higher salt concentrations with increasing temperature and the trend has been explained by assuming that the initial rise in conductivity is due to the increasing number of charge carriers being introduced into the system. This is ultimately offset by effects such as ion triplet formation, charge cloud effects and restrictions to chain mobility which cause the conductivity to drop, thereby producing the observed maxima. The latter factor can be largely eliminated, however, by replotting the data on a reduced temperature scale where log σ is presented as a function of salt concentration at a fixed temperature above the T_g of each polymer–salt mixture. Two such isothermal plots at $(T_g + 100\ K)$ and $(T_g + 150\ K)$ are shown in *Figure 5* which indicate that the response of the uncrosslinked and crosslinked samples (including the 11%) is essentially identical at comparable chain flexibilities. The maxima

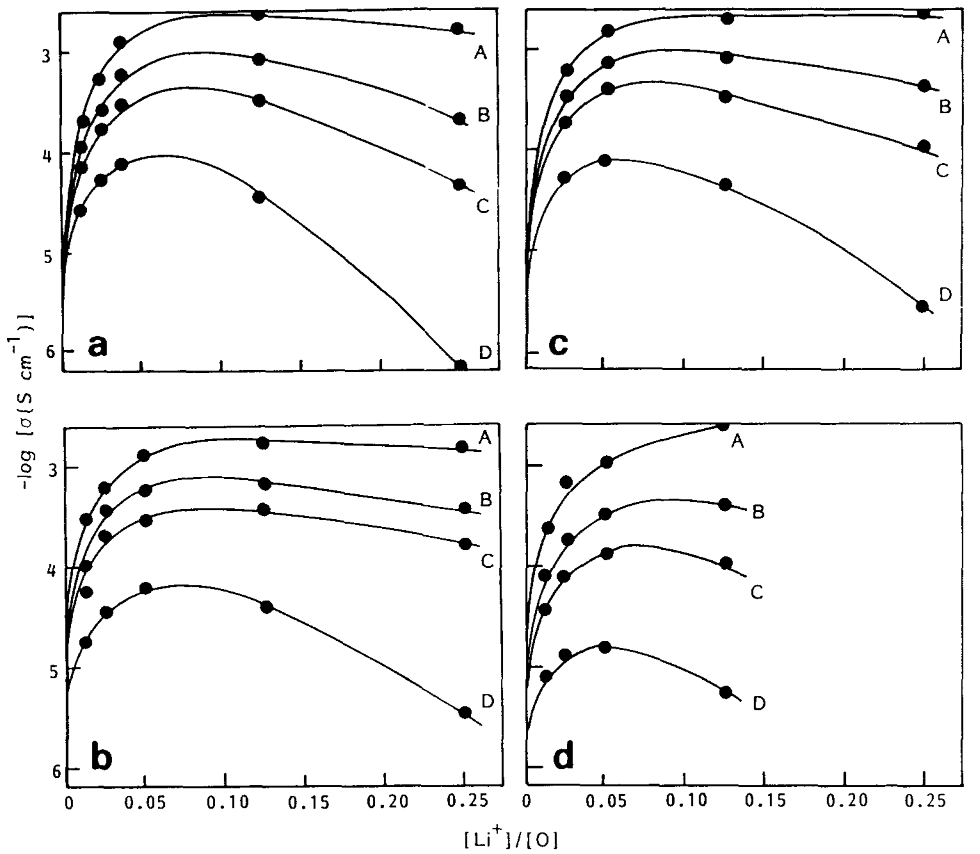

Figure 4 Isothermal variation of log σ with salt concentration for (a) uncrosslinked; (b) 1.2% crosslinked; (c) 5% crosslinked and (d) 11% crosslinked; measured at temperatures of curve A, 328.6 K; curve B, 357.1 K; curve C, 377.3 K and curve D, 416.0 K

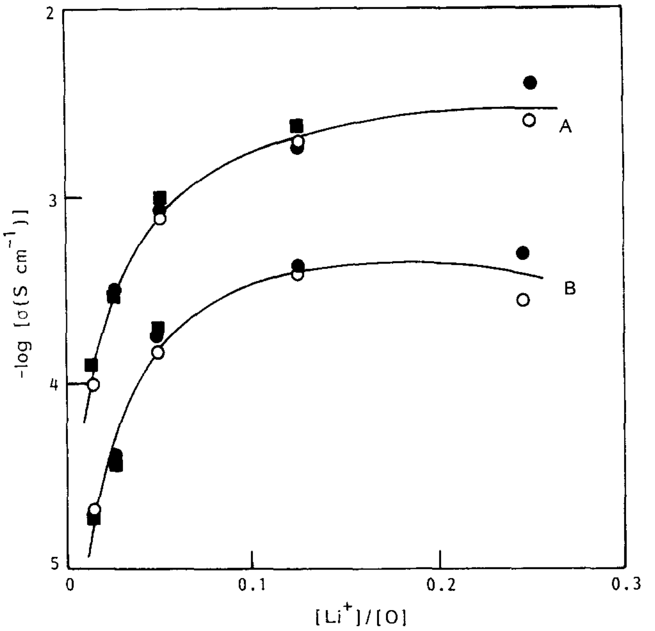

Figure 5 Variation of log σ with salt concentration at curve A ($T_g + 150$ K) and curve B ($T_g + 100$ K) for (○), uncrosslinked; (●), 5% crosslinked and (■), 11% crosslinked samples

are now less well defined and have moved to a higher but essentially constant, salt concentration. These trends have been observed in other systems[6,7].

CONCLUSIONS

The temperature dependence of ionic conductivity in poly(3,6,9,12-tetraoxatridec-1-ene)–salt mixtures remains unaffected by network formation up to an apparent per cent crosslinking of 5%. The crosslinking reaction converts the linear polymer from a viscous fluid at ambient temperatures into a stable, non tacky, rubber-like material, which improves the handling characteristics significantly without loss of performance. The networks swell extensively when exposed to a variety of solvents and this feature can be used to prepare the polymer–salt mixtures by immersing the network in a solution of the required salt. Homogeneous, amorphous solid solutions can be formed by subsequent removal of the solvent. Thin films can also be fabricated by carrying out the crosslinking reaction in a layer of monomer spread on a glass plate. This produced the material in a more convenient sheet form.

REFERENCES

1 Xia, D. W., Soltz, D. and Smid, J. *Solid State Ionics* 1984, **14**, 221
2 Bannister, D. J., Davies, G. R., Ward, I. M. and McIntyre, J. E. *Polymer* 1984, **25**, 1600
3 Cowie, J. M. G. and Martin, A. C. S. *Polym. Commun.* 1985, **26**, 298
4 Blonsky, P. M., Shriver, D. F., Austin, P. and Allcock, H. R. *Solid State Ionics* 1986, **18/19**, 258
5 Fish, D., Khan, I. M. and Smid, J. *Makromol. Chem., Rapid Commun.* 1986, **7**, 115
6 Cowie, J. M. G. and Martin, A. C. S. *Polymer* 1987, **28**, 627
7 Cowie, J. M. G., Martin, A. C. S. and Firth, A-M. *Br. Polym. J.* 1988, **20**, 247
8 Mathias, L. J., Canterbury, J. B. and South, M. *J. Polym. Sci., Polym. Lett. Edn.* 1982, **20**, 473
9 Vogel, H. *Phys. Z.* 1921, **22**, 645
10 Tammann, V. G. and Hesse, W. *Z. Anorg. Allg. Chem.* 1926, **156**, 245
11 Fulcher, G. S. *J. Am. Chem. Soc.* 1925, **8**, 339
12 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
13 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373