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The mixed-salt effect in a polymer-based ionic conductor

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Abstract. The effect of the mixing of lithium triflate and sodium iodide at high and equal concentrations in a polymer-based (poly(ethylene oxide)) ionic conductor are investigated. A variety of characterisation techniques, namely conductivity, x-ray diffraction, DSC and NMR, are employed. The salient observations involve enhanced conductivities, reduced microviscosity, greatly enhanced mobility of those lithium ions observed by NMR and a recurring absence of NMR observability of a substantial fraction of the cations. The data are interpreted as indicating that the effects of mixing of the salts are to enhance greatly the volume of available amorphous phase.

Another feature of the interpretation is the inhomogeneous distribution of the various cations and anions around the different phases present in the materials.

1. Introduction

In an earlier paper (Tunstall *et al* 1988, hereafter referred to as I), we presented nuclear magnetic resonance data, taken between 100 and 400 K, on a range of high molecular weight poly-(ethylene oxide) (PEO) samples doped with substantial concentrations of lithium trifluoromethane sulphonate (lithium triflate). Such a doped polymer is a fast ionic conductor, with the lithium and triflate ions as the charge carriers.

Analysis of the properties of the material is complicated by the coexistence of an amorphous, crystalline complex and pure PEO components at the same temperature, with the relative proportions changing as the temperature is varied. The experiments in I established nuclear resonance as a powerful technique in aiding the understanding of the internal structure and dynamics of the samples on a microscopic scale. It is clear that improved ionic conductivity arises if more of the sample is made amorphous, and, consequently, less crystalline.

Recently, Moryoussef *et al* (1985) performed experiments on the conductivity of PEO/alkaline earth salt complexes; these revealed the interesting result that, for example, complexes fabricated using a mix of CaBr_2 and CaI_2 had a greater conductivity than complexes fabricated with either the bromide or the iodide alone. It was suggested that this was due to a plastifying effect of the presence of mixed salts favouring the formation of an amorphous phase at the expense of the crystalline phase.

In this paper we present data on PEO complexes with sodium iodide (NaI) and with lithium triflate, including both single-salt and mixed-salt doping, for the two ratios of EO:salt of 8:1 and 4:1. The data were acquired by both macroscopic techniques for evaluating phase proportions (differential scanning calorimetry (DSC) and x-ray diffraction analysis) and a microscopic technique (NMR), as well as by measurements of overall conductivity results. The aim of the paper is both to extend and test the suggestions in I on other systems, and to evaluate the potential of the observation of Moryoussef *et al* (1985) as a technique for improving ionic conductivities in polymer electrolytes.

A preliminary report of part of this work has already appeared (MacCallum *et al* 1988).

2. Experimental procedure

2.1. Samples

PEO with molecular weight 4×10^6 and NaI (reagent grade) were supplied by Aldrich Ltd. LiCF_3SO_3 , 'lithium triflate', was supplied by 3M Ltd. The PEO was stored under vacuum over P_2O_5 for at least two weeks before use whereas both salts were vacuum dried at elevated temperature (150 °C for 48 h), cooled, and then used immediately. The required compounds were formed by the solvent-free ball-mill method (Gray *et al* 1986) where polymer and salt are ground together by stainless steel balls at 77 K then annealed at elevated temperature.

2.2. Conductivity

Films for conductivity measurement were hot-pressed in an argon dry-box and their conductivity determined by the AC impedance technique over the frequency range 1– 10^6 Hz to determine the bulk conductivity independently of electrode processes. Details of the pressing method, experimental cell and procedure have been published elsewhere (Gray *et al* 1986).

2.3. X-ray diffraction

The spectra were taken on a Philips PW-1010 powder diffractometer, using Cu $K\alpha$ radiation.

2.4. DSC

Thermograms were obtained using a Perkin Elmer DSC-1B apparatus, taken at a rate of 8 K min^{-1} (although no noticeable changes in the data appeared when this rate was varied over the range 1–16 K min^{-1}).

2.5. NMR

Pulsed NMR measurements were performed at 50 MHz using a purpose-built apparatus with an Oxford Instruments 8T superconducting magnet. Samples were annealed in vacuo at 120 °C for 48 hours. The vacuum-sealed sample tubes were located within a 10 mm diameter transmitter/receiver coil giving a B_1 field of 15 G (calculated from the

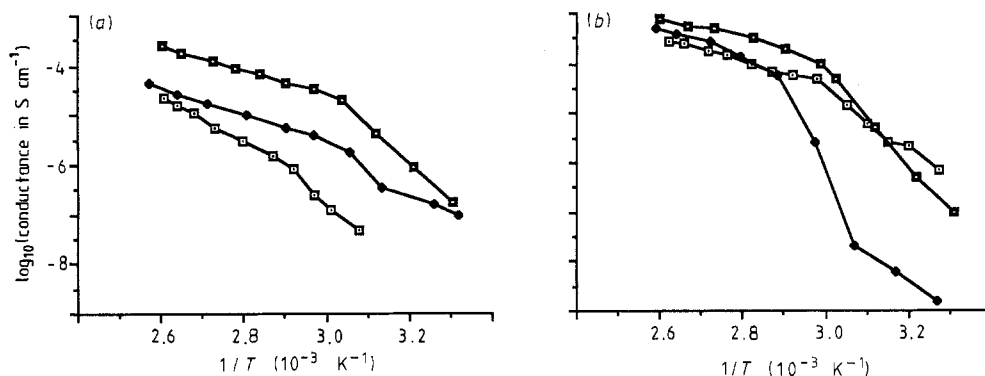


Figure 1. The logarithm of conductance against reciprocal temperature $10^3 T^{-1}$: (a) for the 4:1 EO:salt single- and mixed-salt polymer: ■, mixed salt; ◆, NaI; □, LiCF_3SO_3 . (b) The same as in (a) for the 8:1 EO:salt polymer.

^1H $\frac{1}{2}\pi$ requirement). The fraction of a given nuclear species (^1H , ^7Li , ^{19}F) belonging to either the crystalline or amorphous phases was determined on a heating cycle by the free induction decay (FID)/spin-echo technique pioneered by Berthier *et al* (1983), where short- T_2 FIDs were associated with crystalline polymer or immobile salt species, and longer- T_2 FIDs with amorphous polymer or mobile salt species.

The information on the fractions of nuclei observed by the NMR technique was obtained using the system, developed in I, of careful monitoring of the relative amplitudes of the lithium and sodium nuclear signals and the fluorine and proton signals, taken together with the assumption that all the fluorines remain observable all the time. ^{19}F and ^1H are of course spin- $\frac{1}{2}$ nuclei, so the possibility of any nucleus being unobservable is greatly reduced.

3. Results

Arrhenius plots of the conductance versus T^{-1} are presented for the two sets of samples in figures 1(a) and 1(b). Typically, a large activation energy (E_a) behaviour at low temperature is followed by small- E_a behaviour at high temperature. A feature of both sets of curves is the improved conductivity of the mixed-salt system over both the single-salt materials, with the high salt concentration set, 1(a), showing the most marked improvement on mixing of salts. Even the data in figure 1(b) represent a factor of 2 improvement at high temperature on mixing the salts. It is worth noting also that the high temperature value of the conductance of the single-salt systems in figure 1(b) is similar to that of the mixed-salt system in figure 1(a), as though one of the salts in the mixed salt of 1(a) was playing no role in the conductivity. This is clearly not the case however as can immediately be seen by looking at the low temperature ($10^3/T > 3.1$) comparison between these sets of curves. In this higher temperature regime, then the single-salt 8:1 curves differ dramatically from each other and from the 4:1 mixed-salt conductivity, both in magnitude and in the rate of change with temperature. Other data to be presented below reinforce this point. Here the mixed salt of 1(a) has a conductivity lying in between the single-salt conductivities of figure 1(b). The x-ray data, figure 2, displayed in histogram format, provide some evidence that the crystalline element in the mixed salt has strong similarities with the crystalline element in the 4:1 lithium triflate

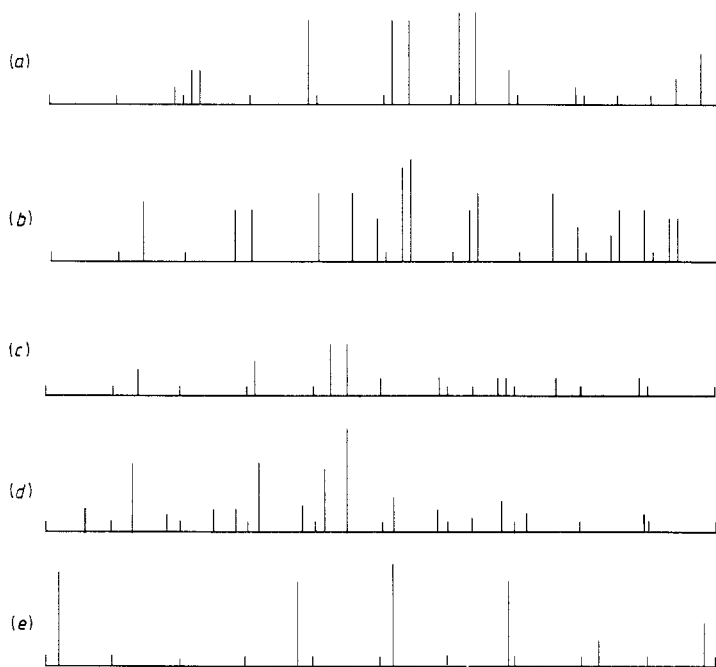


Figure 2. X-ray histograms for several of the samples studied by other techniques in this paper, and one histogram for 4:1 PEO with sodium triflate. The latter spectrum was taken to see if the mixed-salt spectrum showed any evidence of a sodium triflate complex. (a) pure PEO; (b) 4:1 P(EO):NaI; (c) P(EO):mixed; (d) 4:1 P(EO):Li triflate; (e) P(EO):Na triflate.

polymer. There are no signs of any pure PEO (which does appear in single-component 8:1 samples) and no signs of any unmixed pure salts, which have failed to dissolve in the PEO matrix. The 4:1 single-component samples in figure 2 exhibit histograms very similar to previously published x-ray data, with evidence for the presence of pure PEO in the NaI system (Robitaille and Fauteux 1986, Fauteux *et al* 1987).

The DSC thermograms for the two concentrations of the single-salt and mixed-salt systems, figure 3(a) and 3(b), show very clearly the macroscopic thermal properties of the new phase generated by the mixing process. In figure 3(a) the 4:1 mixed-salt sample features a slightly larger peak around 330 K than for the single-salt systems. The point noted earlier, however, of the existence of pure PEO lines in the x-ray spectra of the 4:1 NaI sample, to be expected since the stoichiometric complex in PEO:NaI has the molar ratio EO:NaI of 3:1 (Fauteux *et al* 1987), is not corroborated in the DSC thermogram by the appearance of a larger 330 K endotherm than for the 4:1 triflate sample. The mixed system then shows a very broad endotherm over the range 360–450 K. This process appears to finish before either of the single-salt systems begin their high temperature endothermic rise. The latter point, and the broadness of the mixed-salt endotherm, would suggest that the crystalline phases existing in the mixed-salt material are less stable and melt over a wide range of temperatures.

The mixed-salt effect is also shown up in figure 3(b), for the more dilute salt samples; in these samples the contrast between the results for the mixed- and for the single-salt systems is less dramatic, as was the case for the conductivity plots of figures 1(a) and 1(b).

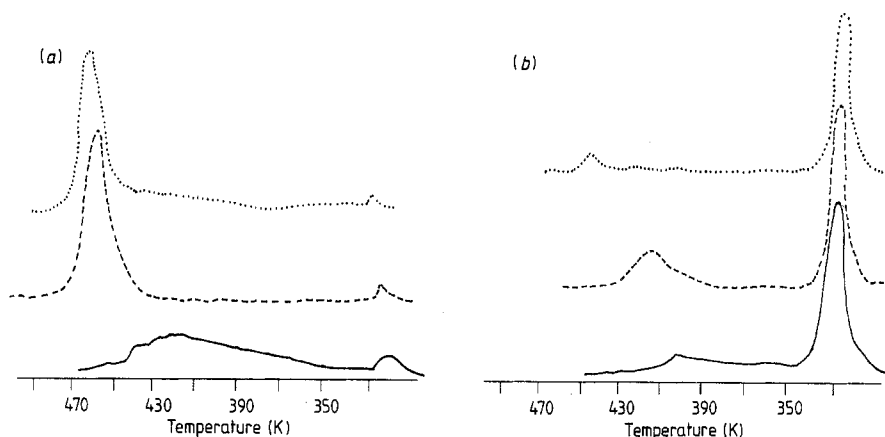


Figure 3. DSC thermograms: (a) for 4:1 polymers. —, mixed-salt polymer; ---, lithium triflate polymer; ···, sodium iodide polymer. (b) As in (a) for 8:1 samples.

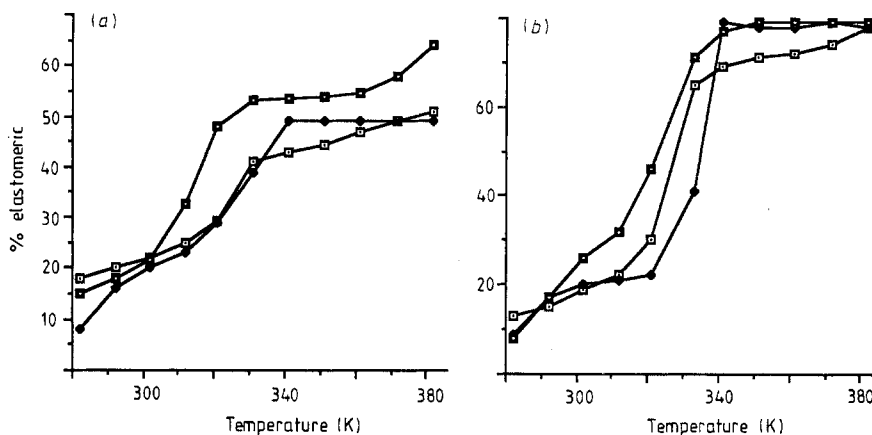


Figure 4. The ratio of the proton long- T_2 component to the total proton intensity, expressed as percentage elastomer: (a) for the 4:1 samples: ■, mixed salt; ◆, NaI; □, LiCF_3SO_3 . (b) As in (a) for the 8:1 samples.

In figures 4(a) and 4(b), the percentage elastomer as a fraction of the total sample is detailed, based on the proton nuclear spin resonance amplitudes of the long- T_2 component of the free induction decay. (See I for the background to this technique.)

We have argued, in I, that this resonance amplitude technique is not an unambiguous determinant of the elastomeric fraction, since there can be substantial long- T_2 NMR signals originating from the crystalline complex. In I we were led to this conclusion by the strong temperature dependence of the fraction below the melting temperature of the pure PEO part, a feature which reappears in the samples studied here. (Note that, in this NMR work one of our single-salt lithium triflate electrolyte samples does not quite have the correct molar concentration of PEO to salt, being 9:1 rather than 8:1.)

In figures 5(a) and 5(b) similar elastomeric fraction data, based on the lithium and fluorine nuclear resonances is presented (no partition of ^{23}Na NMR signal amplitudes into short- and long- T_2 components was possible).

Figure 6 shows the T_2 behaviour of the lithium resonance in the single-salt triflate

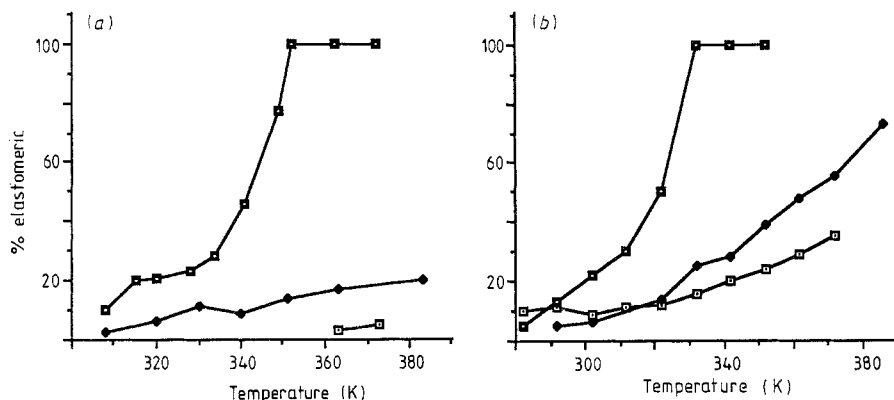


Figure 5. The ratio of the long- T_2 ${}^7\text{Li}$ (${}^{19}\text{F}$) resonance intensity to the total ${}^7\text{Li}$ (${}^{19}\text{F}$) intensity: (a) for the mixed-salt polymer at 4:1 salt concentration. \blacksquare , ${}^7\text{Li}$; \blacklozenge , ${}^{19}\text{F}$. Some fluorine data for the 4:1 single-salt sample \square ${}^{19}\text{F}$ are included for comparison. (b) As in (a) for 8:1 samples.

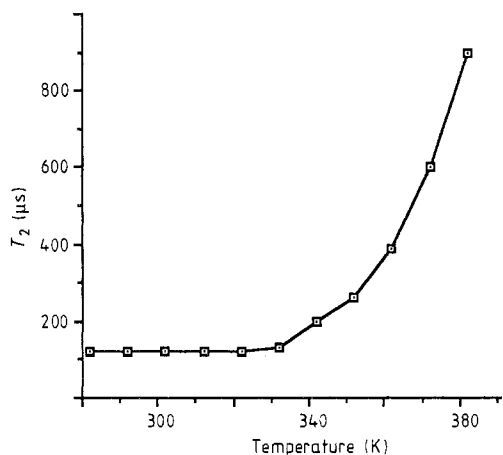


Figure 6. The length of the free induction decay for the ${}^7\text{Li}$ resonance in a single-salt, lithium triflate, 9:1 sample, plotted against temperature. A plot of the same data for a 4:1 lithium triflate sample produces a straight horizontal line at $120\ \mu\text{s}$.

systems; no two-component behaviour was observed, just a steady lengthening of T_2 as the temperature increased in the dilute system. The ${}^7\text{Li}$ behaviour in the mixed salts in figures 5(a) and 5(b) is then in very dramatic contrast to the single-salt results.

In tables 1 and 2 below we present data, based on a comparison of the contribution to the NMR total signal intensity of different nuclei in the same sample and temperature range, giving evidence that some of the ${}^7\text{Li}$ and ${}^{23}\text{Na}$ nuclei are not observed by the NMR technique. We first encountered this problem in I, where the non-observed fraction was shown to be both temperature and sample dependent. Figure 7 replots the data from figure 4 of I for convenience. The data presented here on mixed salts are less complete than in I, in the sense that full temperature scans have not been taken.

Finally we note that spin-echo ${}^1\text{H}$ data revealed that generally the mixed-salt systems produced shorter T_2 s; e.g. a $90^\circ\text{-}\tau\text{-}180^\circ$ pulse sequence at 80°C on $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$ produced a T_2 of about 10 ms, whereas the $\text{P}(\text{EO})_4$ -mixed salt gave a T_2 of about 2 ms. Such a measurement of T_2 can provide an indication of micro-viscosity (Bloembergen *et al* 1948).

4. Discussion

We discuss the results in the context of the following areas:

- (i) the heterogeneity and phase behaviour of the samples;

Table 1. Contribution of ${}^7\text{Li}$ to the NMR total signal intensity for the two ratios of single- and mixed-salt systems.

$\text{P(EO)}_4\text{LiCF}_3\text{SO}_3$	$\text{P(EO)}_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$	$\text{P(EO)}_8\text{LiCF}_3\text{SO}_3$	$\text{P(EO)}_8(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$
45% temperature independent (see figure 4 of I)	45% temperature independent	45%, rising to 100% at ~ 350 K (see figure 4 of I)	50%, rising to 70% by 385 K

Table 2. Contribution of ${}^{23}\text{Na}$ to the NMR total signal intensity for the two ratios of single- and mixed-salt systems. A striking feature is the temperature independence of the fraction in the $(\text{PEO})_4$ -mixed-salt system, column 2 of table 1, when these observed lithium nuclei are exhibiting a transition from short- to long- T_2 behaviour, figure 5(b). Similarly, figure 5(a) shows that the lithium observed in the $(\text{PEO})_8$ -mixed-salt system is fully of long- T_2 type by 330 K, a temperature at which the crystalline complex is in large part unmelted.

$\text{P(EO)}_4\text{NaI}$	$\text{P(EO)}_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$	$\text{P(EO)}_8\text{NaI}$	$\text{P(EO)}_8(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$
65% temperature independent	55% temperature dependent	75%, rising to 100% at ~ 370 K	55% temperature independent

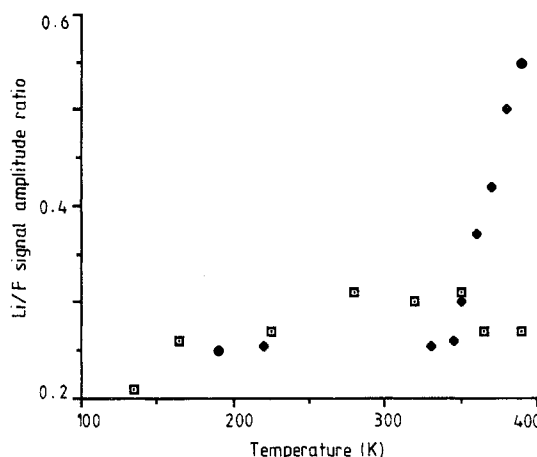


Figure 7. The relative increase of ^7Li NMR intensity in a single-salt, lithium triflate system as a function of temperature, replotted from figure 4 of I.

(ii) the dynamics of all the species, both ions and polymer host.

Clearly we need to know more about area (ii) after having established what information we can about the area (i), i.e. it will be important to try to understand the dynamics of the relevant ions in each of the different phases of the samples.

We list below the salient features of our results that bear on the areas (i) and (ii).

(i) In mixed salts, we observe substantially improved conductivities for the same total ionic content over almost the whole concentration and temperature range. (Figures 1(a) and 1(b).)

(ii) Room temperature x-ray data, figure 2, indicate that the crystalline complex is of the lithium triflate type.

(iii) DSC measurements indicate that the crystalline complex starts to melt at much lower temperatures. (Figures 3(a) and 3(b).)

(iv) The proton NMR results indicate that, at any given temperature, far more of the polymer backbone motion in the sample as a whole is fast enough to average out dipolar interactions between the nuclei. (Figures 4(a) and 4(b).)

(v) A larger fraction of the fluorine nuclei seem to have either the high diffusivity indicated by long- T_2 behaviour, or, if they are static, to have highly mobile magnetic environments. (Figures 5(a) and 5(b).)

(vi) The ^7Li NMR data indicate a very mobile magnetic environment for these nuclei, contrasting sharply with single-salt systems. (Figures 5(a), 5(b) and 6.)

(vii) NMR inter-nuclear comparison indicates that large numbers of ^7Li and ^{23}Na are not observed, although this result is similar to the single-salt result. (Tables 1 and 2 and figure 7.)

Looking at the x-ray, DSC and proton NMR scans together, they all exhibit evidence for the existence of pure PEO at room temperature in the dilute systems, figures 2, 3(a) and 4(a), where this evidence is presented in the last two techniques by the size of the step at the melting temperature of pure PEO (~ 330 K). In the more concentrated samples (i.e. at the 4:1 molar ratio), the proton NMR indicates some freeing of motional constraints at this temperature, and as already indicated the PEO:NaI system shows pure PEO x-ray lines below this temperature, but the DSC scans for all three samples exhibit only very small endothermic events around 330 K. The mixed-salt proton NMR shows the

disappearance of the motional constraints occurring at a noticeably lower temperature than for the pure-salt systems. The proportion of the sample involved is approximately the same in the pure-salt samples, but a rather higher proportion of the sample sees the development of proton motion in the range 310–340 K, and this proportion increased sharply in the mixed-salt system above 360 K.

We argued in I that the observation of a temperature variation in the elastomeric (amorphous) fraction below 330 K in the PEO:triflate system provided evidence for proton motion in the crystalline complex fraction, either associated with the outer regions of the spherulite, where the distinction between crystalline and amorphous phases becomes blurred, or associated with the modes of vibration of the polymer chains in a fraction of the conformers into which the crystalline complex splits. Our mixed-salt proton NMR results for the elastomeric fraction exhibit a more pronounced variation over a wider range than did the pure-salt results. One is tempted to explain such variation, therefore, in the same way; either the spherulite edges are even more blurred, and extensive, or the range of conformers is increased in the mixed-salt systems. To fit in with either of these theories, the observed x-ray lines must be coming either from the inner well-defined core of the spherulite, or the x-ray pattern must be identical for the full range of conformers, since the lines in the patterns are quite well defined. The DSC results provide a clue: the very wide range of temperature over which the crystalline complex dissolution is observed indicates to us the presence of a range of quasi-crystalline environments more consistent with the blurred spherulite model than with a broad band of conformers.

The ^{19}F NMR results, figures 5(a) and 5(b), provide evidence that in the mixed-salt systems a very much higher fraction of the triflate ions are in mobile magnetic environments compared with the pure-salt samples; the linear monotonic rise in this fraction as a function of temperature in both the dilute and concentrated samples fits well with the progressive dissolution of the spherulite model, and with the spreading of the DSC endothermic structure over a broad range of temperatures.

The ^7Li NMR results provide the greatest contrast between mixed- and pure-salt systems, figures 5(a) and 5(b). We should bear in mind here the additional information of figure 6, which makes clear that the single-salt triflate system, at a salt concentration of 9:1, does eventually acquire long- T_2 character at high temperature, but not in a way that allows one to separately partition the material between the phases. The Li signal from the 4:1 single-salt sample resolutely remains short- T_2 -type up to quite high temperatures.

If we assume that the x-ray data, figure 2, indicate that the inner crystalline complex, at least at 300 K, is wholly of lithium triflate type, then the complex occupies half of the 4:1 mixed sample and we may further suppose that the other half is elastomeric in character, with predominantly sodium iodide salt dissolved. This leaves all the lithium locked up in the complex, and makes difficult any explanation of the clearly elastomeric environment in which all the observable lithium moves above 330 K, figure 5.

It is more likely, then, that the complex at 300 K has a crystal structure of lithium triflate type, but nonetheless containing substantial quantities of sodium iodide. This scenario liberates lithium triflate to the elastomeric fraction of the sample, which is then identified as the observable fraction. There were difficulties with this explanation also, however, since we have recrystallisation measurements indicating (MacCallum *et al* 1988) that all of the triflate does go into the crystalline complex.

Refining our argument further, we suppose that there is, at temperatures around room temperature, total crystallisation of the triflate, of which a small inner proportion

goes into PEO with lithium ions to form a highly crystalline core complex giving x-ray lines characteristic of lithium triflate complex. In line with our arguments above concerning the proton NMR data, we now suppose that there is an outer region of the crystalline complex, still with triflate ions but shared with sodium and lithium ions. This outer complex must be more disordered than a sodium triflate complex, since the x-ray spectra do not show any evidence for any such complex. As well as the complex we must have a substantial elastomeric fraction containing about half of the lithium ions, some sodium ions and the bulk of the iodine ions. Such a structure would appear to have the potential to explain the results if the unobservable lithium nuclei are distributed partly in the complex core but mainly in the outer section of the complex.

An approximate distribution of the salt would be as given in table 3 (where the amount of material in each phase is expressed as a percentage of the total amount of each material in the sample).

The restriction on the size of the inner core of the complex is imposed by the fact that above 330 K no short- T_2 NMR signal is observed on the ^7Li resonance. If the 10% of Li postulated for this phase is split into 5% observable and 5% unobservable, in single-salt polymer, then a 5% signal is just on or below our detectability limits (when one attempts to view it on top of a much larger long- T_2 signal). The next, outer spherulite section has to take the rest of the triflate and the lithium in this section has to account for all the rest of the unobservable lithium. Clearly the disordered nature of this structure helps in 'wiping-out' both lithium and sodium intensity. This is the part of the sample whose melting is the dominant effect in the DSC scans.

The location of the missing nuclei remains problematic, in both mixed-salt and single-salt samples. Certainly the nuclei are missing in all the samples at low temperature, below 330 K. It seems highly probable also, from the trends in the experimental results, that at high enough temperature when the samples are in the full elastomeric state, then the nuclei are all observed. It is clear again that the nuclei are missing in the mixed-salt samples even when the lithium- T_2 for the observed nuclei is long (in the triflate 9:1 sample, figure 7, the reappearance of the missing nuclei seems to be correlated with the melting of the crystalline complex). Any explanation of the missing nuclei, based on the hypothesis of a very long T_1 , leading to unobservability of the resonance, seems highly unlikely, given the large temperature range over which the phenomenon persists. The most reasonable hypothesis appears to be therefore that the missing nuclei occupy particular sites in the crystalline complex or have particular neighbouring sites occupied. In the mixed-salt system the definition of the complex in this case must include the 'blurred' edges of the spherulites (see above). Indeed we have argued previously that the 'wipe-out' is even more comprehensive in the disordered spherulite regions. The fact that the percentage of missing nuclei at low temperature in a particular salt system

Table 3. Phase proportions of 8:1:1 mixed-salt polymer at 320 K.

	Inner crystal	Disordered spherulite	Elastomer
	5% PEO	45% PEO	50% PEO
	10% Li	45% Li	45% Li
	10% Tri	45% Na	55% Na
		90% Tri	100% I
Ratio			
PEO:total salt	4:1	4:1	4:1

is rather independent of the concentration of the salt would seem to preclude any ion-pair explanation, where, for example, a Li^+ ion is not observed because the nearest-neighbour site is occupied by a CF_3SO_3^- ion (thus creating the necessary quadrupole interaction).

Finally, the observed shortening of the spin-echo T_2 in the mixed-salt material indicates that the backbone polymer motion is restricted and/or slower. Yet the individual conducting ions are, as evidenced by the NMR data, moving more quickly where they have been measured. This would appear to indicate that ionic hopping in the mixed-salt polymer is not highly correlated with the torsional motion of the polymer.

4. Conclusion

We compare mixed-salt and single-salt polymer electrolytes, using a wide range of techniques. We have found that the mixed-salt systems are associated with higher conductivities, much broader DSC scans and, most remarkably, considerably more motional freedom for the lithium cations at low temperatures. We conclude that the mixing of salts in the poly(ethylene oxide) matrix leads to an extra phase, probably associated with the outer regions of the spherulites, thus forming the crystalline complex. If the conductivity in the mixed-salt electrolyte continues to be dominated by the elastomeric proportion of the sample, then the evidence from this study is that the enhanced conductivity of the mixed-salt electrolyte is probably due to a large increase in the elastomeric proportion of the sample. In the elastomeric proportion the Li^+ ion can move very easily and its mobility must be increased substantially.

We find evidence for an inhomogeneous distribution of anions and cations within the crystalline complex, with triflate ions aggregating near the centre of the spherulites. The loss of cation signal at low temperatures already present in single-salt systems appears in much the same way in mixed-salt material, and we again find the behaviour difficult to explain.

We believe that the topological disorder conferred by the mixing of salts introduces a modulation of the stereo-regularity and hence the ion-ion and ion-solvent interactions necessary to the formation of the crystalline adduct. This leads to a more disordered, and thermally more labile, crystalline phase than for the typical single-salt system. If the crystalline domains are spherulitic in nature, with inherently more disorder in the extremities (Rabek 1980) then the mixed-salt effect generates a lowering of the thresholds for polymer chain motion across the temperature range. This in turn leads to a more extensive amorphous phase, giving a larger conductivity than for single-salt systems.

References

- Berthier C, Gorecki W and Minier M 1983 *Solid State Ion.* **11** 91
Bloembergen N, Purcell E M and Pound R V 1948 *Phys. Rev.* **73** 679
Fauteux D, Lupien M D and Robitaille C D 1978 *J. Electrochem. Soc.* **134** 2761
Gray F M, MacCallum J R and Vincent C A 1986 *Solid State Ion.* **18-19** 282
MacCallum J R, Tomlin A S, Tunstall D P and Vincent C A 1988 *Brit. Poly. J.* **20** 203
Moryoussef A, Bonat M, Fouletier M and Hicter P 1985 *Proc. 6th RISO Int. Symp. Metallurgy and Materials Science (Roskilde)* ed. F W Poulsen, N Hessel Andersen, K Clausen, S Skaarup, O Toft Sorensen (Roskilde: RISO National Laboratory) p 335
Rabek J F 1980 *Experimental Methods in Polymer Chemistry* (London: Wiley-Interscience)
Robitaille C D and Fauteux D 1986 *J. Electrochem. Soc.* **133** 315
Tunstall D P, Tomlin A S, MacCallum J R and Vincent C A 1988 *J. Phys. C: Solid State Phys.* **21** 1039