Morphology and ionic conductivity of some lithium ion complexes with poly(ethylene oxide)

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Deposition of $LiBF_4$–PEO crystalline complexes from methanol gives a material (phase II) melting at ~340K while deposition from acetone–chloroform mixtures gives a material with a melting point of ~433K (phase I). Both materials have the same 1:4 stoichiometry (Li^+:ethylene oxide) and each gives the same wide-angle X-ray scattering pattern though phase II has the broader reflections. The observations are interpreted in terms of a double helical model with long sequences of the same helical sense for phase I, but with less long range order and frequent reversals of helical sense for phase II. The presence of both phases in $LiCF_3SO_3$ complexes is attributed to the contribution of the anion towards complex stability in methanol. The conductivities of the semicrystalline materials are compared with those of amorphous PEO gels complexed with $LiBF_4$. The highest ambient temperature conductivities are obtained from complexed gels.

Keywords Poly(ethylene oxide); lithium; complex; morphology; conductivity; structure

INTRODUCTION

In a previous paper[1] the structure and morphology of some crystalline and amorphous sodium ion–poly(ethylene oxide) (PEO) complexes were correlated with their ionic conductivities. Complexes of PEO with certain sodium and lithium salts have received some attention because of possible applications as solid electrolytes in which conduction is considered to arise from essentially cationic migration[2,4].

The sodium ion complexes are deposited from methanolic solutions, with 1:4 (Na^+:ethylene oxide) stoichiometry in two crystalline forms which give rise to two distinct endotherms on differential thermal analysis (d.t.a.) traces. The principal lamellar phase (phase I) melts at temperatures which depend on the PEO chain length and the macroconformation of the complexed molecular unit but is the same for both iodide and thiocyanate anions. For annealed, high molecular weight PEO samples, phase I melts at 467K.

The lower temperature endotherm at 325–340K is observed in linear and some network PEO complexes. Notwithstanding the approximate coincidence of this endotherm with the melting range of pure PEO, the absence of X-ray reflections characteristic of pure PEO indicates that the 325–340K endotherm arises from the disordering of a second complexed phase (phase II).

The presence of phase II in a network complex and in semicrystalline materials having interlamellar chains[1] suggests that phase II arises from complexation with chains having less conformational freedom than is required for formation of phase I.

Here, we report some preparations of $LiBF_4$–PEO and $LiCF_3SO_3$–PEO complexes prepared from both methanolic and acetone–chloroform solutions. We also report on their ionic conductivities.

EXPERIMENTAL

Poly(ethylene oxide), lithium fluoroborate, lithium trifluoromethylsulphonate and the solvents were all standard laboratory chemicals used as supplied.

Crystalline complexes were prepared using PEO 5×10^6 and PEO 4000. Samples prepared from methanolic solutions were dissolved in stoichiometric proportions by heating and the solvent was removed from homogeneous solutions using a vacuum pump while heating was maintained. Complexes from acetone–chloroform were prepared by dissolving the polymer in chloroform and adding a solution of the salt in acetone. The complex gradually precipitated from this solvent mixture and after leaving overnight, the solvents were decanted off and the residual solvents were removed under vacuum.

The PEO 600 and PEO 400 maleate gels were prepared as described elsewhere[1]. Gels were saturated with salts by immersing them in solutions in acetone–chloroform in the presence of undissolved salt for approximately 2 weeks. Unsaturated samples were prepared using smaller quantities of salt for shorter soaking periods. Solvents were removed by heating to ~373K under vacuum and maintaining the vacuum for extended periods of several days. After cutting to shape (~1 cm thick) for conductivity measurements the samples were again stored under vacuum over silica gel before inserting in the conductivity cells where measurements were carried out in the presence of phosphorus pentoxide.

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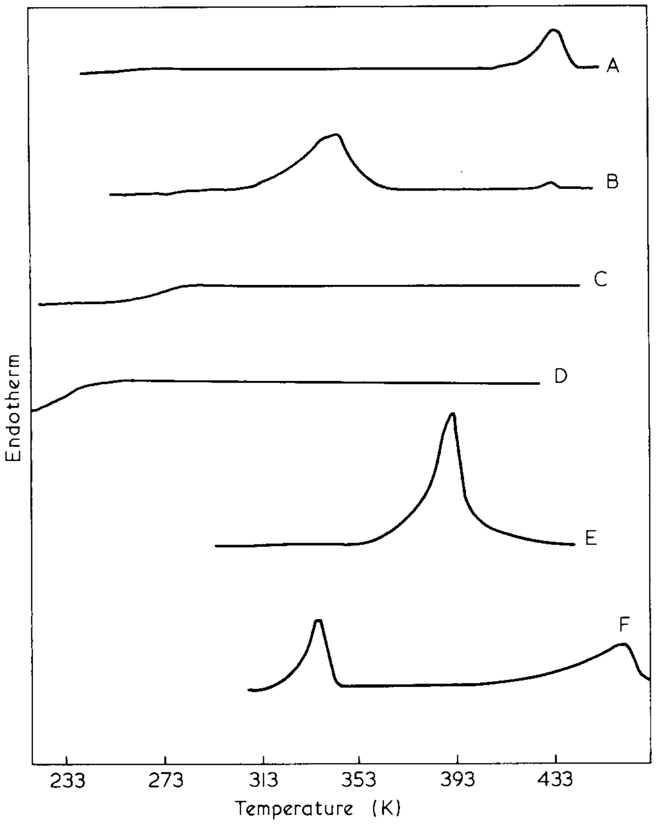

Figure 1 D.t.a. tracings of lithium ion–PEO complexes: A, $LiBF_4$–PEO 5 x 10^6 deposited from acetone–chloroform ($LiBF_4$–PEO 4000 deposited from methanol melts at ~413K); B, $LiBF_4$–PEO 5 x 10^6 deposited from methanol; C, PEO 400–maleate gel–$LiBF_4$ (saturated); D, PEO 400–maleate gel uncomplexed; E, $LiBF_4$; F, $LiCF_3SO_3$–PEO 5 x 10^6 deposited from methanol

Salt content was determined by flame photometry on aqueous solutions prepared by leaching of salt from small fragments of surface-cleaned gel. The PEO 400 saturated gel was found to have stoichiometries of 1 mole sodium ions per 6–7 moles ethylene oxide units. The unsaturated PEO 400 gel, however, apparently contained only ~10% of this proportion of cation, but the shorter soaking times may have led to some variability in salt concentrations.

Differential thermal analysis (d.t.a.) was carried out using a Stanton Redcroft model 671 and wide-angle X-ray diffraction analysis was carried out using a Philips X-ray diffractometer.

Conductivity measurements were performed as described elsewhere[1] at frequencies of 100 Hz and 1000 Hz. The lower frequency values are reported for the semicrystalline samples where some interfacial polarization was in evidence. However, at the two frequencies the results were the same for amorphous gels, suggesting that the latter were dielectrically homogeneous. Duplicate preparation of samples gave reproducible conductivity plots.

DISCUSSION

Sample morphologies

D.t.a. traces of linear PEO complexes with $LiBF_4$ and $LiCF_3SO_3$ (1:4 salt:ethylene oxide stoichiometry) are shown in *Figure 1*. The $LiBF_4$–PEO 5×10^6 complex deposited from methanol is largely composed of phase II whereas that from acetone–chloroform is mainly the higher melting phase I. However, the $LiBF_4$–PEO 4000 complex deposited from methanol occurs entirely in the high melting form. The $LcCF_3SO_3$–PEO 5×10^6 trace has approximately equal proportions of each endotherm and resembles that for the sodium ion complexes[1] with respect to the temperatures of the endotherms, although the latter normally have a rather smaller proportion of the lower endotherm. Thus the melting temperature of the higher melting phase (463–467K for high molecular weight PEO) is apparently independent of the nature of either the anion or cation for NaI and NaSCN complexes[1] and for $LiCF_3SO_3$–PEO. $LiBF_4$–PEO complexes prepared so far have a high melting endotherm at a slightly lower temperature (433K) than the other three complexes. This may have a morphological explanation (since samples of high molecular weight PEO–$LiCF_3SO_3$ complexes with melting temperatures over the range 443–463K have been prepared) or it may relate to the lower melting temperature of the pure salt (388K).

However, we assume for the present that the 433K endotherm in $LiBF_4$–PEO 5 x 10^6 represents the melting of a crystalline phase which is essentially isomorphous with phase I of the $LiCF_3SO_3$ and Na^+ complexes and is henceforth also referred to as phase I. The lower endotherm apparently occurs over approximately the same range in all four complexes.

Wide-angle X-ray diffractometer traces of the phase I and phase II materials, pure PEO and pure $LiBF_4$ are shown in *Figure 2*. Notwithstanding their different melting temperatures phase I and phase II materials appear to have X-ray reflections at the same 2θ values.

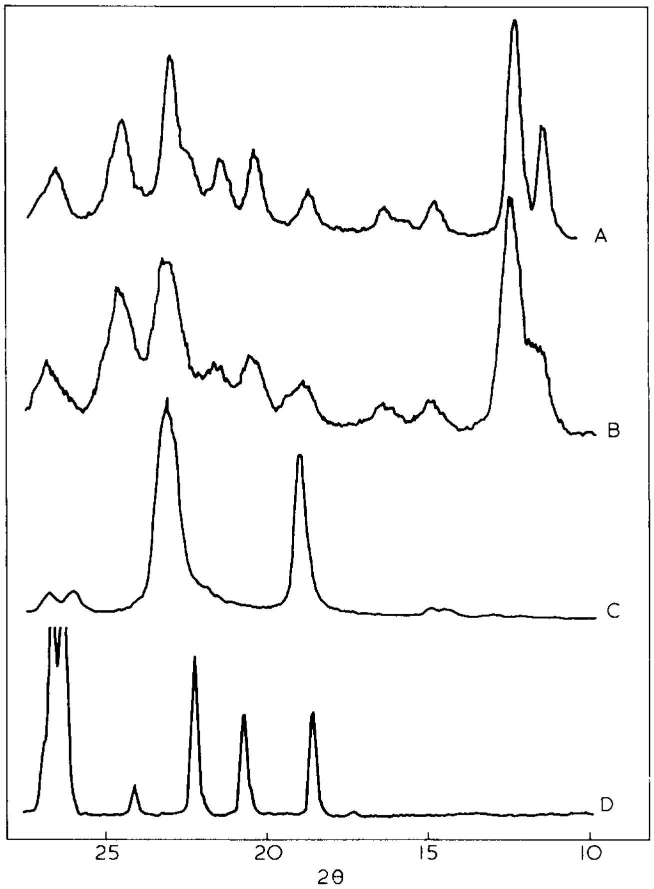

Figure 2 Wide-angle X-ray diffractometer tracings of $LiBF_4$–PEO complexes: A, $LiBF_4$–PEO 5 x 10^6 deposited from acetone–chloroform; B, $LiBF_4$–PEO 5 x 10^6 deposited from methanol; C, pure PEO; D, pure $LiBF_4$

Following investigations on several preparations we have been unable to identify unambiguously any X-ray reflections which are not common to both complexes although the intensity of the lowest-angle reflection of pair of reflections at $2\theta \sim as^\circ$ is variable in phase II samples. However, the reflections of the phase II material are broader suggesting order of a shorter range than in phase I. The small proportion of lower temperature endotherm in *Figure 1A* indicates that the reflection at $2\theta \sim 23^\circ$ in *Figures 2A* and *2B* should not be identified with the major reflection for pure PEO. Furthermore, the absence of reflections for the pure salt in *Figures 2A* and *2B* testifies to the essential completion of complex formation in the materials deposited from both methanol and acetone–chloroform. X-ray reflections characteristic of pure PEO are similarly absent from the $LcCF_3SO_3$–PEO complex.

Thus, phases I and II appear to have essentially the same crystal structure but distinctly different melting temperatures. These observations may be reconciled in terms of the double helical model already proposed[3] for sodium and lithium ion–PEO complexes. Long sequences of the cation–double helix molecular unit would have to form in solution—prior to deposition on the crystal face—from chain molecules in comparative isolation. The sequences would be free from excessive entanglement so obviating the necessity for reversals of helical sense. Such sequences may perhaps form by intramolecular twisting initiated at a loop. With rise in temperature in the solid state untwisting of the molecular strands in long sequences within the crystal lattice would be difficult even following the breakdown of chain–cation interactions and the migration of ions throughout the system. Untwisting should be effectively prevented if the sequence were long enough to re-enter the same or an adjacent lamella or if strands were to separate and re-enter lamellae with different partners. Thus, melting of phase I would only occur when sufficient free volume is available for the double helices to disorder as discrete molecular units, essentially irrespective of their complexing ions. In the case of NaSCN–PEO at least, there is evidence[1] that the inflexible molecular unit is quite stable in the melt.

The formation of long helical sequences of the same helical sense in solution should be favoured by preferential cation–polyether interactions. The cations would act as templates for the progressive formation of the double helix as each helical cage is formed. However, preferential cation–solvent interactions should be expected to inhibit this process so that in the extreme case, interaction of the cation with the polymer chain may only become effective with most or all of the solvent removed. At this stage, the PEO chains may be so highly concentrated that entanglements prevent the formation of long sequences of double helix. Only short sequences, interrupted by reversals of sense or changes in partner for a given molecular strand, may be possible. In this material, thermal disintegration of the molecular unit should occur more readily than in phase I, so that melting may involve untwisting of helical strands initiated at reversals of helical sense.

Two further observations are in accord with this general picture:

(i) melt-recrystallized samples of high molecular weight PEO–$LiBF_4$ complexes give the same melting endotherms as their solution deposited precursors; this indicates that chain entanglement in the melt prohibits interconversion of the two forms;

(ii) the PEO 4000–$LiBF_4$ complex deposited from methanol melts in the higher melting region (see *Figure 1A*).

If the solvent control of the macroconformation derives from the degree of entanglement encountered by high molecular weight chains then complexes with PEO molecular weights below the critical entanglement region (~ 300 chain atoms for PEO according to Berry and Fox[5]) should exhibit no solvent dependence on their solid-state stabilities, always crystallizing in their most stable form.

However, the occurrence of large proportions of high melting phase I in high molecular weight PEO–$LiCF_3SO_3$ deposited from methanol suggests that in this case the anion may play a rôle in stabilizing the complex in solution.

Thus, the distinct difference in melting temperatures of the phase I and phase II materials may be accounted for by their distinctly different melting processes—the former melt by disordering of integrated molecular units, the latter by disintegration of the molecular units. Further work is required for a detailed understanding of the structure and morphology of phase II but the greater lithium ion solvation by methanol giving rise to the greater proportion of phase II material in high molecular weight PEO complexes is in accord with these general considerations.

Conductivity measurements

Plots of $\log_{10}\sigma$ vs. $1/T$ for $LiBF_4$–PEO and $LiCF_3SO_3$–PEO are shown in *Figure 3*. σ is the conductivity in $(\text{ohm cm})^{-1}$ and T is the absolute temperature. The general levels of conductivity in the various samples increase with the state of disorder of the PEO chains.

Although the $LiBF_4$–PEO phase II material displays a distinct rise in conductivity at its melting temperature, neither the $LiBF_4$–PEO phase I material nor the $LiCF_3SO_3$–PEO sample with approximately equal proportions of each phase reveal any tendency for a transition to a lower activation energy process with enhanced conductivity at temperatures approximately coincident with phase II melting (330–340K). In this respect, these materials differ from the stoichiometric or slightly salt deficient linear PEO–sodium ion complexes in which the low activation energy process is apparently a consequence of both phase II melting and ion migration between vacancies in phase I. Thus, in NaI–PEO stoichiometric semicrystalline complexes the level of conductivity at temperatures above ~ 340K is comparable with that in amorphous gels. Suppression of vacancies in 'excess salt' samples gives rise to lower levels of conductivity with increasing slope of $\log_{10}\sigma$ vs. $1/T$ with increase in T presumably denoting a process dependent on the availability of interstitial or intermolecular free volume.

Armand and coworkers[2] have measured conductivities of a range of salt deficient (4.5 or 5:1 stoichiometry) lithium ion complexes deposited from acetonitrile. Salt deficiencies would give rise to greater proportions of non-crystalline complexed component (particularly above the melting point of any pure PEO crystals) and lithium ion solvation by acetonitrile should ensure high proportions

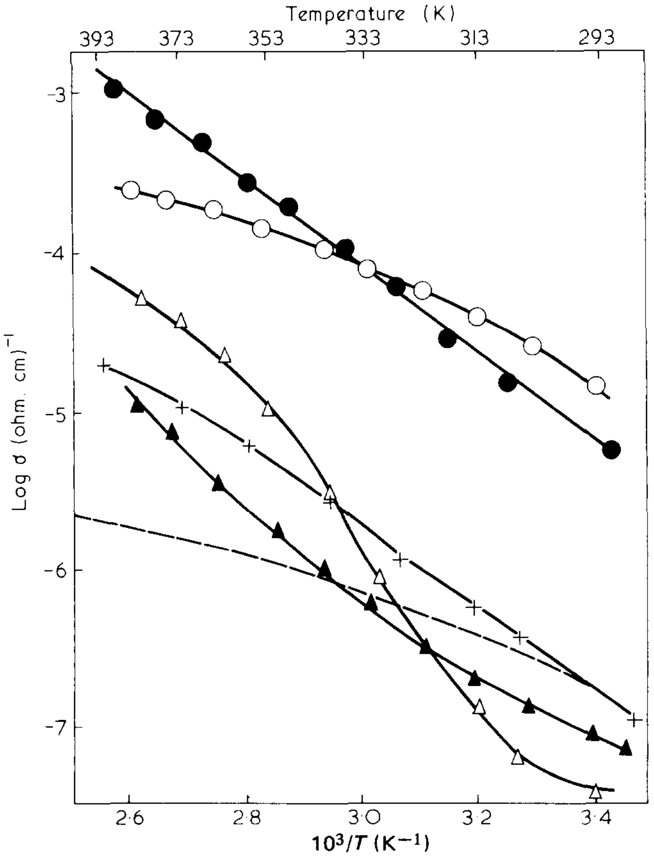

Figure 3 Conductivity of lithium ion–PEO complexes (100 Hz): ●, PEO 400 maleate gel–$LiBF_4$ (saturated); ○, PEO 400 maleate gel–$LiBF_4$ (unsaturated); △, PEO 5 x 10^6–$LiBF_4$ deposited from methanol (phase II); ▲, PEO 5 x 10^6–$LiBF_4$ deposited from acetone–chloroform (phase I); — — —, PEO 600 maleate pure gel; +, PEO 5 x 10^6–$LiCF_3SO_3$ deposited from methanol (both phases I and II present – see *Figure 1F*)

of phase II in the crystalline component. The conductivities of most of the lithium ion complexes including $LiCF_3SO_3$–PEO (1:4.5 stoichiometry) is reported to be 10^5 (ohm cm)$^{-1}$ at ~350K which is in close agreement with the value given by the present work. Moreover, the published plot for LiSCN–PEO (1:5 stoichiometry) shows similar levels of conductivity for this complex and no suggestion of a transition to a lower activation energy process over the range 293–393K. This suggests that the failure to observe such a process in, at least, the $LiCF_3SO_3$ crystalline complex of the present work should not be attributed to a low concentration of vacancies. However, Armand and coworkers report a high conductivity of 10^{-5} (ohm cm)$^{-1}$ at ambient temperatures for a salt deficient $LiBF_4$–PEO sample—a value close to those for the $LiBF_4$–PEO 400 maleate gels shown in *Figure 3*. For the reasons discussed above, this sample might be expected to have both a higher amorphous content than stoichiometric samples and low concentrations of phase I crystals as in the case of the methanol-deposited sample of the present work.

These observations suggest that lithium ion phase I material does not permit enhanced ionic conductivity at temperatures above phase II melting to the degree observed in sodium ion phase I material. This may be accounted for in terms of a stronger interaction of the smaller cation with the oxygens of the polyether chains in accord with the well-known tendency for lithium ions to bind to electron donating centres with interactions having greater degrees of covalent character than in the case of larger alkali metal ions. In the proposed double helix, the cations are accommodated in cages along the helix axis bounded above and below by 4 oxygen atoms. The larger cations are accommodated in more expanded cages and transfer through the sides of the cages would appear easier than along the helical tubes. However, on the basis of any model, differences in cation–anion pairing must enter into consideration when accounting for differences in conduction.

Nevertheless, in both amorphous complexes there is a marked enhancement of conductivity, the process in the unsaturated gel proceeding at a lower activation energy than that of ~50 kJ mol^{-1} in the saturated gel. A similar enhancement has been observed in gels containing $LiCF_3SO_3$ although there is a slightly lower level of conductivity in this case. In accounting for the differences in conduction behaviour between gels and semicrystalline materials consideration should be given to comparisons between respective expected activation energies for escape from complexed sites and for transport between sites. Constraints applied to the chains of the amorphous network should reduce the opportunity for optimum coordination of cations by oxygens particularly with respect to the coordination within a double helical crystalline arrangement. Furthermore, given weaker site interactions a low activation energy for conduction in the unsaturated gel may reflect the small size of the lithium ion in relation to the hole sizes within the amorphous network. As appears to be the case for the diffusion of smaller inert gases in elastomers[6], the formation of conducting pathways may not require complete displacements of chain segments. The behaviour of the saturated gel complex reflects a lower complex site vacancy concentration at ambient temperatures and the temperature dependence of the total free volume in the system.

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