Structure of an amorphous polymer electrolyte, poly(ethylene oxide)$_3$: LiCF$_3$SO$_3$

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The amorphous phase formed on melting the crystalline polymer electrolyte PEO$_3$:LiCF$_3$SO$_3$ has a short-range structure in which all of the lithium ions are located within the poly(ethylene oxide) helix.

Polymer electrolytes are compounds formed by the dissolution of salts in polar high molar mass macromolecules which form strong interactions with cations. They form the basis of a new electrochemical technology which includes thin film all-solid-state lithium batteries. Electrolytes based on poly(ethylene oxide), PEO, may form crystalline or amorphous phases. A major advance has recently been made in establishing the structures of crystalline polymer electrolytes, but it is the amorphous materials which exhibit high ionic conductivity and it is therefore their structures which are of particular interest. By combining high-resolution IR spectroscopic studies of both crystalline and amorphous phases with the results of an X-ray diffraction analysis of the crystalline phase, we have established the structure of an amorphous polymer electrolyte consisting of a lithium salt, LiCF$_3$SO$_3$, dissolved in the high molecular mass PEO, such that there are three host oxygen atoms for each Li$^+$ ion present.

The structure of crystalline PEO$_3$:LiCF$_3$SO$_3$ consists of a parallel array of separate PEO chains each associated with its own set of ions, in which each chain adopts a helical conformation.[1] A single lithium ion is located within each turn of the helix which is coordinated directly by three ether oxygens. The coordination environment around the Li$^+$ ion is completed by two further oxygens, one from each of two CF$_3$SO$_3^-$ anions thus forming a five-coordinate arrangement in an approximate trigonal-bipyramidal geometry. The CF$_3$SO$_3^-$ anions bridge neighbouring lithium ions by donating one of their oxygens to each of two lithiums, while the remaining oxygen of each CF$_3$SO$_3^-$ group is uncoordinated. The CF$_3$ groups sit outside the dimensions of the helix. The crystal structure does not change from −173 °C until the melting point at 179 °C.

In the molten phase there is no long-range order, as is evident from the absence of Bragg peaks.[2] It is clear from a study of vibrational spectra, however, that similar short-range order to that in the crystalline phase persists. Fig. 1 shows the symmetric stretching mode ν_s(SO$_3$) as a function of temperature. This mode is known to be affected by both changes in the ionic environment of CF$_3$SO$_3^-$ (*i.e.* by any alteration in neighbouring cation numbers or positions) and by variation in the way 'solvent' is coordinated to neighbouring cations.[3]

Distinct bands which appear in the IR spectra of low molar mass liquid PEO oligomer–LiCF$_3$SO$_3$ solutions in this region have been previously assigned as 'free' ions (1032 cm^{-1}), simple ion pairs (1041 cm^{-1}) and a more highly associated ionic species described as an ionic aggregate (1050 cm^{-1}), following the Raman spectra-based assignments of ref. 3. In the room-temperature IR spectrum of high molecular mass PEO$_3$:LiCF$_3$SO$_3$ there is only a single band at 1046 cm^{-1}. It is seen that apart from the expected increase in bandwidth as the temperature is raised, the frequency shift of the band on melting is < 1 cm^{-1}.

IR spectra of PEO$_3$:LiCF$_3$SO$_3$ are shown in Fig. 2 for the CF$_3$ symmetric deformation mode, δ_s(CF$_3$), over the temperature range 25–190 °C. This mode is particularly sensitive to variation in the ion association due to a shifting of the electron density between the CF$_3$ and the SO$_3$ ends of the anion as a result of association with a cation.[4] In this spectral region IR bands of oligomer–LiCF$_3$SO$_3$ solutions are assigned as 'free' ions (752 cm^{-1}), simple ion pairs (757 cm^{-1}), and an aggregate species (763 cm^{-1}). We will focus our attention on the δ_s(CF$_3$) region because of the more distinct frequency separation of the various triflate ion species in the PEO$_3$:LiCF$_3$SO$_3$ compounds.

As in the case of ν_s(SO$_3$) there is only a single band in Fig. 2, at 760 cm^{-1}, which is assigned to the aggregate species. The lowering of this frequency from the value of 763 cm^{-1} which is observed in liquid oligomer–LiCF$_3$SO$_3$ solutions is possibly due to packing effects in the crystalline state, *e.g.* from a decrease in the rotational or reorientational motion of the CF$_3$ groups. Knowledge of the crystal structure permits an unambiguous assignment of the ν_s(SO$_3$) mode and the δ_s(CF$_3$) mode shown in Figs. 1 and 2, respectively. These vibrational states arise from a CF$_3$SO$_3^-$ ion, two oxygen atoms of which bridge in a monodentate arrangement two Li$^+$ ions that lie adjacent to

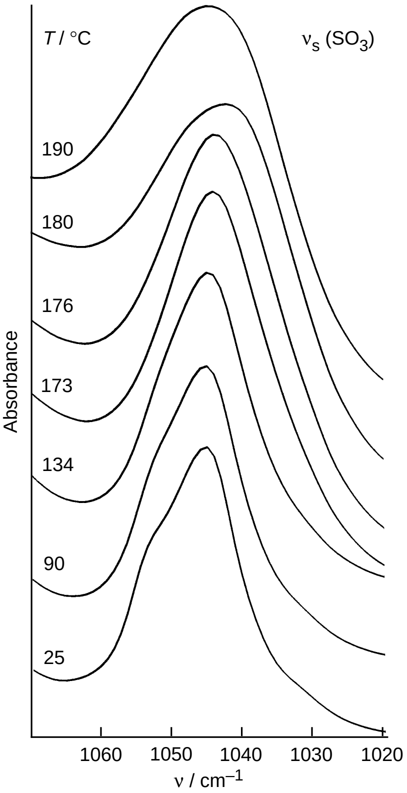

Fig. 1 Symmetric stretching mode, ν_s(SO$_3$), as a function of temperature for poly(ethylene oxide)$_3$: LiCF$_3$SO$_3$

each other within the polymer helix. Each anion is essentially a $[Li_2CF_3SO_3]^+$ species in terms of the vibrational modes of the $CF_3SO_3^-$ ion. This assignment is consistent with a study of $LiCF_3SO_3$ in acetone and poly(propylene oxide)[5] in which the highest frequency component in the $\nu_s(SO_3)$ spectral region was assigned to the isolated triple ion $[Li_2CF_3SO_3]^+$.

The frequency of the $\delta_s(CF_3)$ band does not change as the temperature is increased up to the onset of melting although thermal broadening of the band is apparent. Above the melting point there is a broad feature centred at 763 cm^{-1}, which is the frequency expected for a $[Li_2CF_3SO_3]^+$ species. The question arises: what is the nature of the $[Li_2CF_3SO_3]^+$ species? They cannot be individual, isolated $[Li_2CF_3SO_3]^+$ triple ions as have been previously observed in the oligomer–$LiCF_3SO_3$ solutions with somewhat lower salt concentrations,[6] since the presence of such moieties would necessarily require the presence of 'free' $CF_3SO_3^-$ ions on charge balance considerations. These would in turn give rise to a band at 752–753 cm^{-1}, and no absorption can be observed in this region. In principle, the charge balance might also be satisfied by a $[Li(CF_3SO_3)_2]^-$ species, which would be observed spectroscopically at *ca.* 757 cm^{-1}. There is indeed a shoulder at 180 °C (but not, apparently, at higher temperatures) which might correspond to such a species, but its intensity is very weak in comparison with the $[Li_2CF_3SO_3]^+$ band and hence is considered to be of minor importance.

Vibrational bands in the 800–1000 cm^{-1} region are due to a mixture of CH_2 rocking and C–O stretching and are very sensitive to the local conformation of the polyether backbone.[7] We observe no major shift in the frequency of these modes between the spectrum of the highest temperature crystalline phase and the amorphous phase, suggesting that the basic lithium–polyether backbone interaction does not alter when the crystals melt.

We therefore conclude that the majority species is $[Li_2CF_3SO_3]^+$ and that in the absence of significant quantity of $CF_3SO_3^-$ or $[Li(CF_3SO_3)_2]^-$, this must be present in the amorphous phase largely as part of an extended ionic chain as in the crystal.

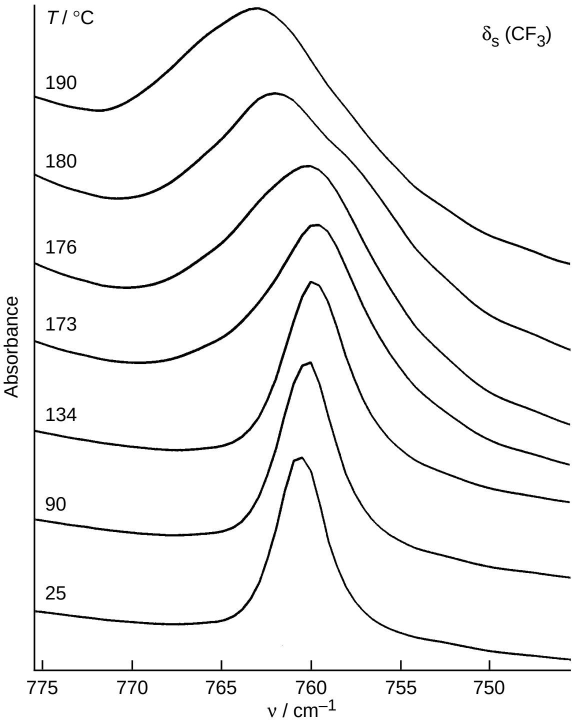

Fig. 2 Symmetric deformation mode, $\delta_s(CF_3)$, as a function of temperature for poly(ethylene oxide)$_3$: $LiCF_3SO_3$

It is evident that the structure of the amorphous phase is very similar to that of the crystalline state, with only a loss of long-range order arising from a loss of register between adjacent PEO chains and some disordering in the helical torsion angles. In particular each chain remains intact with its associated ions: *i.e.* every chain is associated with a dedicated set of cations and anions which do not bond to any of the other chains. In this sense each chain forms an isolated, infinitely long, coordination complex. Interchain interactions are only of the dipole–dipole or van der Waals type and are thus of second-order compared with the intrachain interactions. There is no evidence of cation or anion cross-linking between chains.

It seems unlikely, given the absence of interchain ionic cross-links at the high concentration of 3 : 1, that these would be present to any significant extent in amorphous phases with lower salt content. Beginning at a low salt concentration and then increasing the salt content will load each chain with ions and increase the intrachain cross-link density thus reducing segmental motion, raising T_g and suppressing the ionic conductivity, as has been suggested in a recent study based on a detailed analysis of the polymer dynamics by NMR.[8] The consequences of the assertion that interchain cross-links are of minor significance in amorphous polymer electrolytes at higher oxygen/salt ratios (*i.e.* in phases which may be useful in an electrochemical device) will be considered elsewhere.[9]

It is tempting to speculate that the Li^+ ions may be transported along the chains while remaining within the helix, as suggested by Armand *et al.*[10] nearly twenty years ago. It is known that the polymer chain dynamics are intimately linked to the ionic motion, and it is therefore likely that the Li^+ ions would be 'handed-on' from coil to coil by an appropriate dynamic mode of the polymer, *e.g.* a concertina motion along the axis of the helix. A perfect 3 : 1 structure would have a lithium ion in every coil and conductivity would, as a result, not be possible. However, some defects (Li^+ vacancies) are likely which, although below the level that may be detected by the spectroscopic methods, are sufficient to endow the polymer with some conductivity. At lower salt concentrations (*i.e.* higher PEO : salt ratios) there will, of course, be a substantial proportion of Li^+ ion vacancies in the PEO coils. It is important to note also that for long-range ion transport (*e.g.* d.c. conductivity) it will be necessary to include interchain lithium ion transfer in the overall mechanism, since as we have argued, there is no significant centre-of-gravity motion of the polymer chains for host molecules above the entanglement limit.

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