Ionic Conductivity in the Crystalline Polymer Electrolytes PEO₆:LiXF₆, X = P, As, Sb

Zlatka Stoeva, Isabelle Martin-Litas, Edward Staunton, Yuri G. Andreev, and Peter G. Bruce*

Contribution from the School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews KY16 9ST, UK

Received November 13, 2002; E-mail: p.g.bruce@st-and.ac.uk

Abstract: Ionically conducting polymers (salts dissolved in a polymer matrix) are of great interest because they uniquely exhibit ionic conductivity in a soft but solid membrane. As such, they are critical to the development of devices such as all-solid-state lithium batteries. The established view of ionic conductivity in polymer electrolytes is that this occurs in amorphous materials above their glass transition temperature and that crystalline polymer electrolytes are insulators. In contrast, we show that three crystalline polymer electrolytes, poly(ethylene oxide)₆:LiXF₆, X = P, As, Sb, not only conduct but do so better than the analogous amorphous phases! It is also shown that the conductivities of all three 6:1 complexes are similar, consistent with the dimension of the bottlenecks to conduction derived from their crystal structures. An increase in ionic conductivity with reduction of molecular weight of the crystalline polymer electrolyte (from 2000 to 1000) is reported and shown to relate to the increase in crystallite size on reducing molecular weight.

Introduction

Polymer electrolytes were first discovered by Wright in 1973.[1] They consist of salts, e.g. LiI, dissolved in solid polymers, e.g. poly(ethylene oxide) $[(CH_2CH_2O)_n]$. Many salts, including those containing di- and trivalent cations, have been combined with a variety of polymers in order to form polymer electrolytes.[2−4] The polymer must contain a Lewis base (usually an ether oxygen), which serves to coordinate the cations, thus promoting dissolution of the salt. Polymer electrolytes are unique materials in that they support ionic conductivity in a flexible yet solid membrane. The considerable potential of these materials as solid ionic conductors was first recognized by Armand in 1978. Since that time there has been intense interest in the synthesis and characterization of this class of materials as well as considerable focus on their potential use as solid electrolytes in electrochemical devices such as rechargeable lithium batteries, electrochromic displays, and smart windows.[5] Polymer electrolytes also represent a fascinating class of coordination compounds in the solid state.[6] They may be related to more conventional coordination compounds such as the oxo-crown ethers. Despite some 30 years of intensive interest, it is only in recent times that substantial progress concerning the structure of these materials has become possible through advances in the methods of crystal structure determination from powders.[7−10]

Driven by their potential application in devices, there has been much interest in the mechanism of ion conduction in solid polymer electrolytes.[11,12] These materials may be prepared as crystalline or amorphous solids. Studies in the late 1970s to early 1980s demonstrated that ionic conduction was confined to the amorphous polymer electrolytes above their glass transition temperature, T_g, with the chain dynamics playing a critical role in the conductivity mechanism.[13−15] This realization established the direction of research since that time. Many new polymer electrolytes have been synthesized in an effort to minimize the crystallinity and to achieve even lower T_g values, thus enhancing chain dynamics and hence increasing the level of ionic conductivity. Recently it has been shown by various authors that the addition of ceramic nanopowders to the bulk polymer can enhance the conductivity.[16,3] Importantly, such fillers can also increase the cation transference number. These strategies succeeded in raising the level of conductivity by several orders of magnitude to $10^{-5}-10^{-4}$ S cm^{-1} at 25 °C. However, it has proved difficult to increase further the level of ionic conductivity by synthesising new amorphous polymer

(1) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589.
(2) *Solid-state electrochemistry*; Bruce, P. G., Ed.; Cambridge University Press: Cambridge, 1995.
(3) Gray, F. M. *Polymer Electrolytes*; RSC materials monographs; The Royal Society of Chemistry: Cambridge, 1997.
(4) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993.
(5) Gray, F. M. *Solid Polymer Electrolytes*; VCH Publishers Inc.: New York, Weinheim, Cambridge, 1991.
(6) Bruce, P. G. *Philos. Trans. R. Soc. London* **1996**, *A 354*, 415.
(7) Lightfoot, P.; Mehta, M. A.; Bruce, P. G. *Science* **1993**, *262*, 883.
(8) Andreev, Y. G.; Lightfoot P.; Bruce, P. G. *J. Chem. Soc., Chem. Commun.* **1996**, 2169.
(9) Andreev, Y. G.; MacGlashan, G. S.; Bruce, P. G. *Phys. Rev. B* **1997**, *55*, 12011.
(10) MacGlashan, G. S.; Andreev, Y. G.; Bruce, P. G. *Nature* **1999**, *398*, 792.
(11) Ratner, M. A. In *Polymer Electrolytes Reviews−1*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987; p 173.
(12) Druger, S. D.; Ratner, M. A.; Nitzan, A. *Solid State Ionics* **1983**, *9/10*, 1115.
(13) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91−95.
(14) Gorecki, W.; Donoso, P.; Berthier, C.; Mali, M.; Roos, J.; Brinkmann, D.; Armand, M. B. *Solid State Ionics* **1988**, *28−30*, 1018.
(15) Wintersgill, M. C.; Fontanella, J. J.; Pak, Y. S.; Greenbaum, S. G.; Almudaris, A.; Chadwick, A. V. *Polymer* **1989**, *30*, 1123.
(16) Croce, F.; Appetechi, G. B.; Persi, L.; Scrosati, B. *Nature* **1998**, *394*, 456.

electrolytes. Such a level of conductivity is too low for many applications. It is possible to breakthrough this barrier in ionic conductivity by adding low molecular weight solvents forming, in effect, gels in which a liquid is trapped in a polymer matrix. However, such materials suffer from many of the disadvantages of liquid electrolytes, such as leakage, volatility, and poor mechanical property.[17] Angell has described an elegant approach based on using a molten salt (with short local renewal times for the ion dynamics) and adding sufficient polymer to obtain a rubbery solid. These polymer-in-salt materials can yield high levels of ionic conductivity with salts such as chlorate and perchlorate, but it is has proved difficult to obtain comparable performance with other salts, and the explosive nature of chlorate/perchlorate salts precludes potential application.[18] There was much need for new directions in the search for ionically conducting polymers.

As part of an extensive study of the structural chemistry of polymer electrolytes we investigated the structure of the crystalline complex poly(ethylene oxide)$_6$:LiAsF$_6$ (six ether oxygens per cation).[9] The structure suggested the possibility of ion transport in the static ordered environment of a crystalline polymer electrolyte. This is in contrast to the established view for the last 25 years, which has considered all crystalline polymer electrolytes to be insulators. Here we present results that demonstrate ionic conduction in three crystalline polymer electrolytes, poly(ethylene oxide)$_6$:LiXF$_6$, where X = P, As, Sb. A brief preliminary report describing ionic conductivity in crystalline polymer electrolytes has been presented by us recently.[19] Here the nature of the conduction pathways in the crystalline 6:1 polymer electrolytes is discussed for the first time, as is the influence of the anion type on the size of the bottlenecks to cation migration. The previously unreported effect of crystallite size on the conductivity is also described and discussed.

A different approach to introducing order by for example forming liquid crystalline polymer electrolytes or materials consisting of ordered nonconducting blocks separating sheets containing PEO and salt has been explored and serves to demonstrate the importance of organization in enhancing ionic conductivity in the polymeric state.[20]

Crystalline polymer electrolytes represent an important new direction in which to search for better ionic conductivity in polymers.

Experimental Section

All manipulations of air-sensitive materials were carried out in an argon-filled high-integrity glovebox (MBraun). LiPF$_6$ (Stella SC hemita electrochemical grade for 99.99%) was used as received. LiAsF$_6$ (ABCR, 99.8%) and LiSbF$_6$ (STREM, 98%) were dried at 50 °C for 24 h under dynamic vacuum. Methoxy-end-capped poly(ethylene oxide) (Fluka, 98%) with an average molar mass of 1000, 1500, and 2000 was dried for 4 days at 30 °C, also under dynamic vacuum. Masses of salt and polymer appropriate for the formation of a 6:1 complex were weighed out and dissolved together in dry acetonitrile, and following complete dissolution the acetonitrile was permitted to evaporate slowly. The resulting white powders were dried overnight under dynamic

vacuum at 35 °C. IR spectroscopy (FTIR spectrometer Nicolet 860) confirmed the absence of H$_2$O and CH$_3$CN from the powders. For conductivity measurements the powders were pressed into self-supporting disks at room temperature.

Formation of amorphous PEO$_6$:LiSbF$_6$ was achieved by combining the salt with poly(ethylene oxide) of average molar mass 100 000. The polymer was previously dried at 55 °C for 12 h under dynamic vacuum. The salt and polymer were ground together at liquid nitrogen temperatures and then, on returning to room temperature, the material was pressed into a disk. This was first heated at 100 °C for 4 h under a pressure of 1000 kg/cm^2 and then cooled slowly to room temperature.

Powder X-ray diffraction was carried out using a Stoe STAD/P powder diffractometer with Cu K$_{\alpha 1}$ radiation operating in transmission mode and employing a small angle position sensitive detector (PSD). Data were collected with a step width of 0.02° in 2θ. To avoid contact with air, the polymer electrolyte samples were sealed in Lindemann (glass) capillaries or between Mylar films, depending on whether the samples were in the form of a powder or a film.

Differential scanning calorimetry was carried out using a Netzch DSC 204 Phoenix with heating and cooling rates of 5°/min.

The DMTA (dynamic mechanical thermal analysis) measurements were made using a Rheometric Scientific DMTA with an MK111 analyzer operating in the shear mode. Measurements were recorded at a heating rate of 2°/min and a frequency of 1 Hz.

Conductivity data were obtained using ac impedance measurements carried out with a Solatron 1255 frequency response analyzer and an 1187 electrochemical interface, both under the control of a PC. A polarizing potential of 25 mV was employed, and data were collected over the frequency range 10^{-1}–10^5 Hz. The polymer electrolyte disks were sandwiched between two stainless steel plates in a two-electrode cell, which was itself located within an argon-filled stainless steel chamber. The chamber was placed in a thermostatic bath in order to control the temperature of the cells.

Results and Discussion

In the amorphous phase of a polymer electrolyte above its glass transition temperature, T_g, the polymer chains are constantly undergoing local segmental motion. A consequence of these local dynamics is that free volume is constantly being created and destroyed. Ions are located in suitable coordination sites within the polymer which, for a cation such as Li$^+$ in poly-(ethylene oxide), would involve coordination by the ether oxygens. For ion transport to occur, free volume, or more specifically a suitable coordination site, must be created by the chain dynamics adjacent to the existing site. When this occurs, the ion may migrate to the new site, where it will reside until the chain dynamics dictate the availability of another adjacent site. It is clear that the local chain dynamics plays a critical role in controlling the rate of ion transport. Given this mechanism, to achieve levels of conductivity comparable to conventional liquid electrolytes, it would be necessary to achieve local solvent reorganization times, and hence local viscosity, corresponding to that observed in conventional low molecular weight solvents. This is something that is difficult to achieve in a polymer environment. The relatively slow local solvent reorganization (segmental motion) in polymers, even with low T_g, limits the level of conductivity that can be achieved. Indeed, despite strenuous efforts, the maximum conductivity (10^{-4} S cm^{-1} at 25 °C) in such amorphous polymer electrolytes has remained too low for many applications. If, however, the sites to which an ion migrates were already present and aligned in the structure, rather than relying on chain dynamics to generate

(17) *Advances in Lithium-Ion Batteries*; van Schalkwijk, W. A., Scrosati, B., Eds.; Kluwer Academic/Plenum Publishers: New York, 2002.
(18) Angell, C. A.; Liu, C.; Sanchez, E. *Nature* **1993**, *362*, 137.
(19) Gadjourova, Z.; Andreev, Y. G.; Tunstall, D. P.; Bruce, P. G. *Nature* **2001**, *412*, 520.
(20) Wright, P. V.; Zheng, Y.; Bhatt, D.; Richardson, T.; Ungar, G. *Polymer Int.* **1998**, *47*, 34.
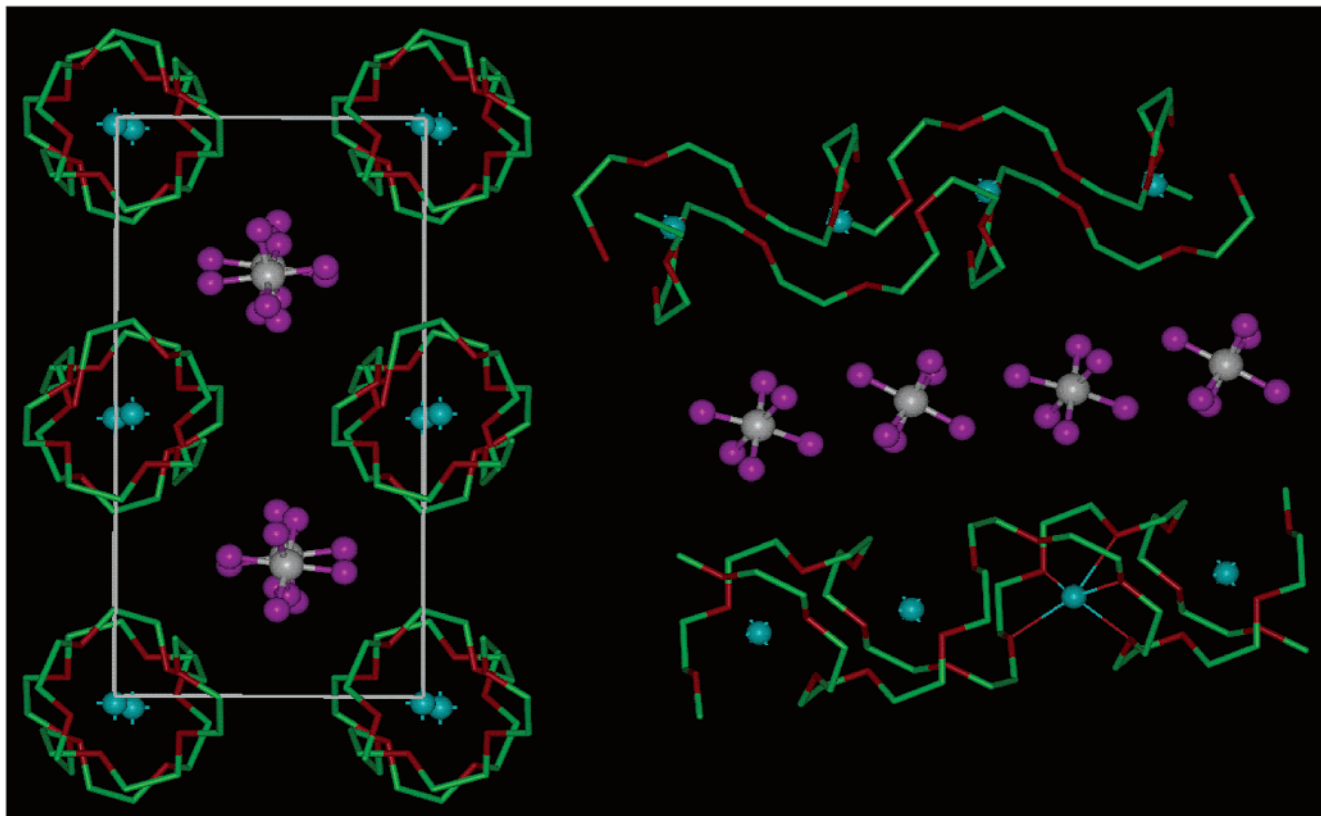
Figure 1. The structures of PEO$_6$:LiAsF$_6$. (Left) View of the structure along *a* showing rows of Li$^+$ ions perpendicular to the page. (Right) View of the structure showing the relative position of the chains and their conformation (hydrogens not shown). Thin lines indicate coordination around the Li$^+$ cation. Blue spheres, lithium; white spheres, arsenic; magenta, fluorine; green, carbon; red, oxygen.

such sites, then ion hopping could take place as soon as sufficient energy were available for the ion to hop. There is no requirement to wait for reorganization of the environment. Such thinking encourages the search for ionic conduction in crystalline polymer electrolytes, despite the earlier studies that suggested ionic conductivity was confined to the amorphous phases above T_g.

A major barrier to studying crystalline polymer electrolytes was the paucity of knowledge concerning their structural chemistry. This has led us over the past few years to develop an understanding of the crystal structures of polymer electrolytes. Crystallography is a powerful tool that can provide much detailed information concerning structural chemistry. However, established methods of single crystal or powder diffraction were unable to reveal the crystal structures of polymer electrolytes. By developing a new method by which complex crystal structures may be solved ab initio from powder diffraction data and that is particularly well suited to the challenge of polymer electrolyte structures, we have been able to establish a number of such structures. Specifically we have determined, for the first time, the structure of the 6:1 complexes PEO$_6$:LiPF$_6$, PEO$_6$:LiAsF$_6$ and PEO$_6$:LiSbF$_6$.[21] The structures of all three complexes are similar. The structure of the first to be determined, PEO$_6$:LiAsF$_6$, is reproduced in Figure 1.[10] Each PEO chain folds to form a half cylinder with pairs of such chains interlocking to form tunnels within which the Li$^+$ ions reside. The Li$^+$ ions are coordinated by five of the six ether oxygens. The anions lie between the tunnels and do not coordinate the cations. The

structure encouraged us to examine the possibility of ionic conduction, particularly Li$^+$ migration in the 6:1 complexes.

Powder X-ray diffraction patterns for the three crystalline complexes prepared with 1000 molecular weight PEO, as described in the Experimental Section, are shown in Figure 2. All three complexes are highly crystalline with relatively sharp diffraction peaks and a high peak-to-background ratio. Disks of the three complexes were subjected to ac impedance measurements, and complex impedance plots for each are shown in Figure 3. Since the disks are formed by pressing a powdered polymer it is important to establish whether there are any grain boundary contributions to the total conductivity. In all three cases only one well formed semicircle is apparent in the impedance plots (Figure 3). The ac response may be described by an equivalent circuit comprised of a parallel combination of a resistance, representing ion transport through the polymer, and a capacitance, representing the dielectric response of the material. Magnitudes of the permittivities were respectively 1 pF cm^{-1} (LiPF$_6$), 3 pF cm^{-1} (LiAsF$_6$), and 1 pF cm^{-1} (LiSbF$_6$), and these are consistent with the bulk electrolyte response, indicating that the associated resistances are those of the bulk (intracrystalline) polymer. Hence the bulk resistance may be obtained from the low-frequency intercept of the semicircle on the Z′ axis.[22] The linear region of the impedance at low frequencies is typical of a rough blocking (no charge transfer) electrode/electrolyte interface. For all three complexes, conductivity measurements were carried out as a function of temperature, and the results are presented in Figure 4. The upper

(21) Gadjourova, Z.; Martin, D.; Andersen, K. H.; Andreev, Y. G.; Bruce, P. G. *Chem. Mater.* **2001**, *13*, 1282.

(22) Bruce, P. G. In *Polymer Electrolytes Reviews − 1*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987; p 237.
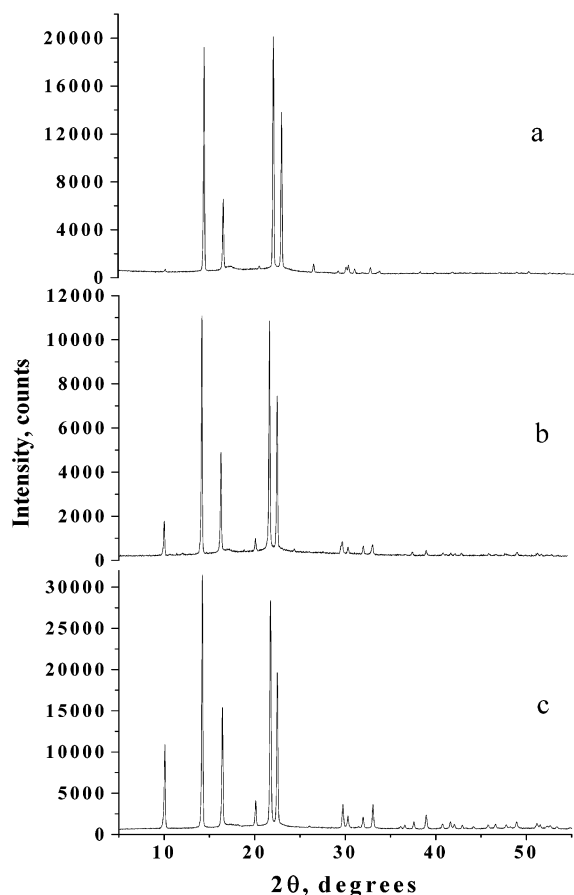
Figure 2. X-ray powder diffraction patterns (Cu K$_{\alpha1}$) of (a) PEO$_6$:LiPF$_6$, (b) PEO$_6$:LiAsF$_6$, and (c) PEO$_6$:LiSbF$_6$.

temperature limit was determined by the stability of the 1000 average molecular weight (M_w) polymer electrolytes and the lower limit by the ability of the equipment to measure resistive samples.

The crystallinity of polymer electrolytes increases on reducing molecular weight; for this reason we have utilized low M_w poly-(ethylene oxides), end-capped with methoxy groups to ensure chemical homogeneity along the entire chain. The limit above which chain entanglement occurs in the case of poly(ethylene oxide) is approximately 3200.[23] The high degree of crystallinity of the 1000 M_w materials has already been mentioned in the context of the X-ray diffraction patterns. Further evidence for the absence of an amorphous phase has been obtained from DSC, DMTA, and NMR spectroscopy. The NMR data were presented previously and will not therefore be repeated here.[19] The Netzch calorimeter used for DSC measurements is an order of magnitude more sensitive than conventional instruments. The results for one of our 6:1 complexes, PEO$_6$:LiSbF$_6$, are shown in Figure 5a. There is no evidence of a glass transition temperature over the entire temperature range from −65 to 100 °C. The exothermic peak at 80 °C is associated with melting of the crystalline complex. This has been confirmed by variable-temperature X-ray powder diffraction, which shows the disappearance of the peaks associated with the 6:1 complex above 80 °C. This conclusion is reinforced by the DMTA results for PEO$_6$:LiSbF$_6$ presented in Figure 5b. The measurements had to be carried out in air. PEO absorbs water from the atmosphere

(23) Shi, J.; Vincent, C. A. *Solid State Ionics* **1993**, *60*, 11.
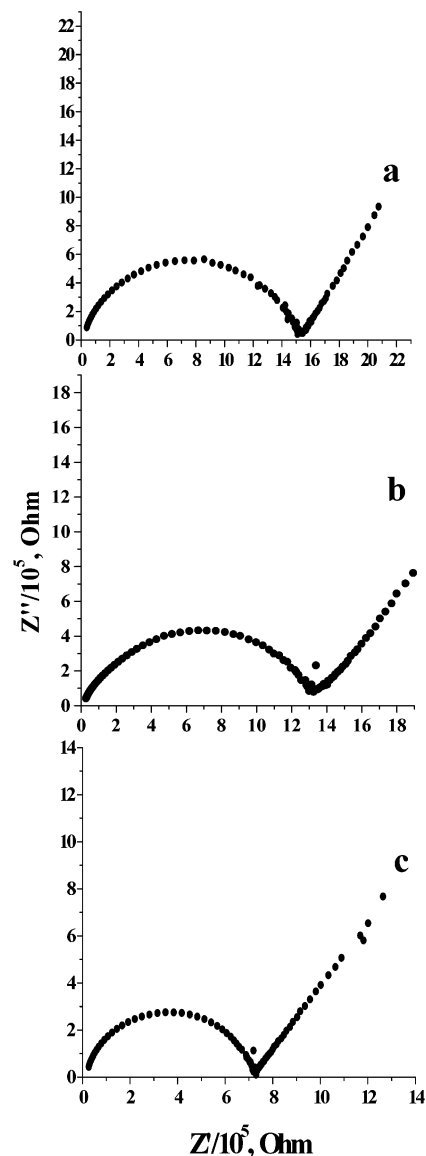
Figure 3. Complex impedance of (a) PEO$_6$:LiPF$_6$, (b) PEO$_6$:LiAsF$_6$, and (c) PEO$_6$:LiSbF$_6$. Thin solid lines represent fitted semicircles.
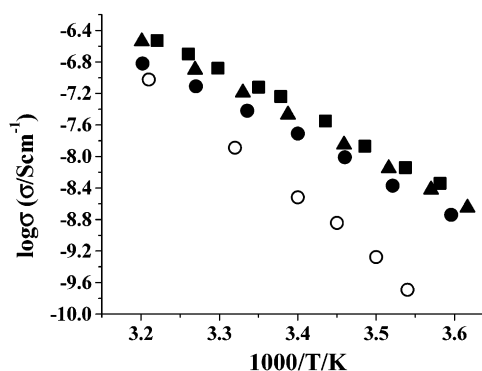
Figure 4. Ionic conductivity σ (S cm^{-1}) of crystalline complexes PEO$_6$:LiPF$_6$, (solid circles), PEO$_6$:LiAsF$_6$ (squares), PEO$_6$:LiSbF$_6$ (triangles), and amorphous PEO$_6$:LiSbF$_6$ (open circles).

above 0 °C, and this is the origin of the large decrease in shear modulus above 10 °C. There is no evidence of a T_g in the range from −80 to +10 °C. Further evidence indicating that the ionic conductivity occurs in a crystalline environment is apparent in
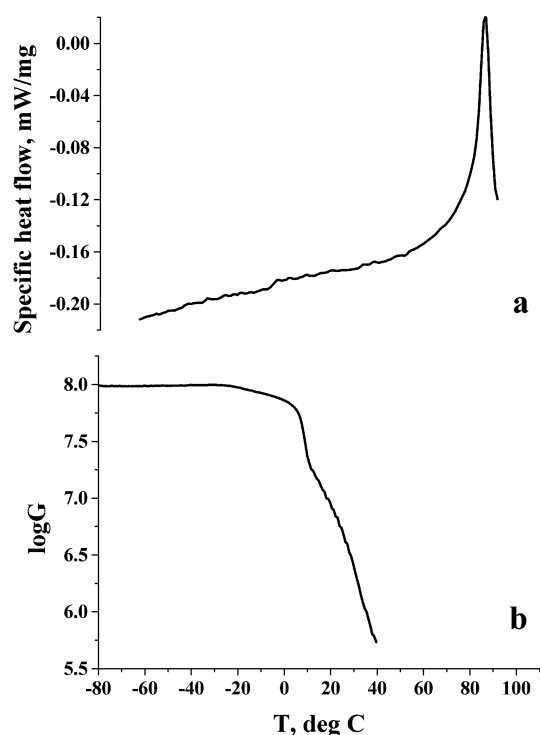
**Figure 5.** (a) DSC and (b) DMTA (G Shear modulus, Pa^{1-}) of PEO$_6$:LiSbF$_6$.

the temperature dependence (Figure 4). Amorphous polymer electrolytes generally exhibit a curved log σ vs 1/T plot, as expected for ion transport facilitated by the segmental motion of the polymer chains. In contrast, all three 6:1 complexes exhibit a linear variation of log σ with 1/T consistent with ion hopping between sites in a static environment. Combining all of the above data, it is evident that the conductivity results presented in Figure 4 correspond to ionic conduction in crystalline polymer electrolytes.

How then do these conductivity results compare with those for the analogous amorphous 6:1 phase? Conductivity data for amorphous PEO$_6$:LiSbF$_6$ are presented in Figure 4 for com-

parison with the corresponding crystalline PEO$_6$:LiSbF$_6$. The glass transition temperature for the amorphous phase is -33 °C;[19] therefore, the data presented in Figure 4 correspond to the amorphous material in the conducting state, i.e., above T_g. The conductivity of the crystalline 6:1 SbF$_6$ complex has a conductivity more than 1 order of magnitude higher than the corresponding amorphous phase at the lower temperatures. This demonstrates not only that ionic conduction occurs in the crystalline state but that it is higher in this state than the corresponding amorphous material. The comparison is not made at the same molecular weight, because of the need to use low and high molecular weights to ensure highly crystalline and highly amorphous phases, respectively. However, we have prepared a 100 000 molecular weight material with good crystallinity and the conductivity is still 1 order of magnitude higher than in the pure amorphous phase with the same molecular weight.

The issue of the proportion of current carried by the cations and anions, i.e., the transference number, has been addressed previously.[19] The experimental NMR studies of the transference number indicate that whereas the anions in amorphous polymer electrolytes are generally more mobile than the cations, the crystal structure appears to impose selectivity for the Li$^+$ ions that alone carry the current.

Returning to the temperature dependent conductivity of the three 6:1 crystalline complexes presented in Figure 4, all three exhibit similar levels of conductivity as a function of temperature. A value for the activation energy of 1.0 eV was extracted from the gradient of the curves. The crystal structures of the three complexes are broadly similar. A schematic representation of the Li$^+$ diffusion pathway along the polymer tunnels is shown in Figure 6. The Li$^+$ ion resides in a site formed by five ether oxygens, three from one PEO chain and two from the other. In order for a Li$^+$ ion to migrate to another stable five-coordinate site, it has to pass between two ether oxygens, thus entering an intermediate site formed by four ether oxygens defining a rectangle. The Li$^+$ ion then passes through another bottleneck formed by two ether oxygens in order to enter the next five-coordinate site. Such a pathway for ion transport is of course
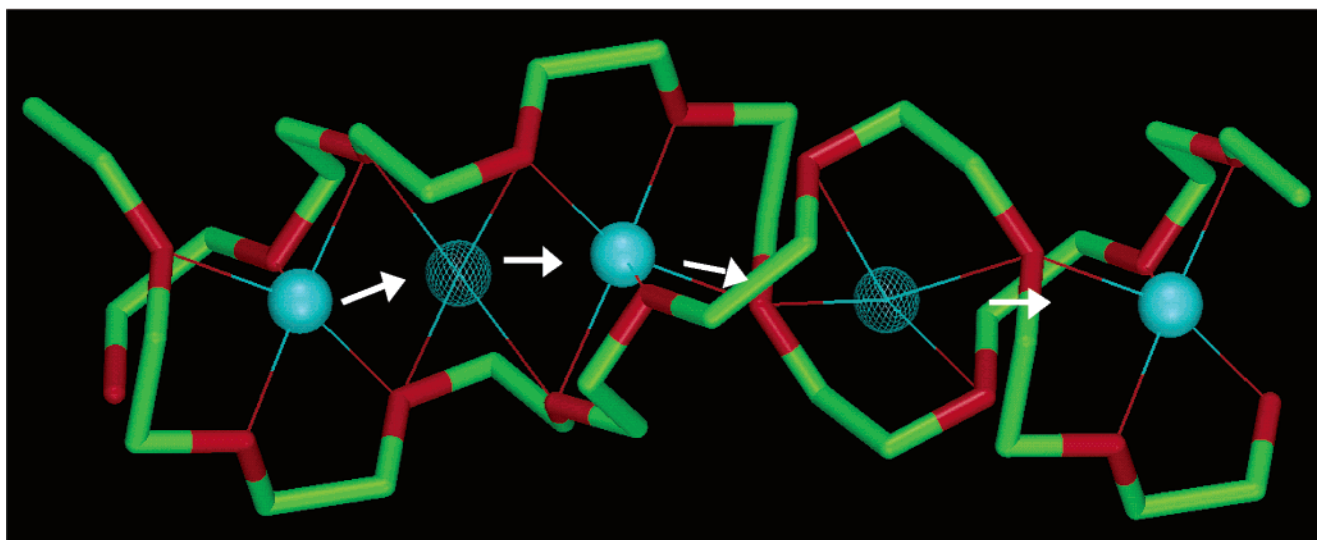
Figure 6. Schematic diffusion pathway of the Li$^+$ cations in PEO$_6$:LiPF$_6$. Thin lines indicate coordination around the Li$^+$ cation; solid blue spheres, lithium in the crystallographic five-coordinate site (note that the fifth thin line is very short in this view); meshed blue spheres, lithium in the intermediate four-coordinate site; green, carbon; red, oxygen. See the text for further details.
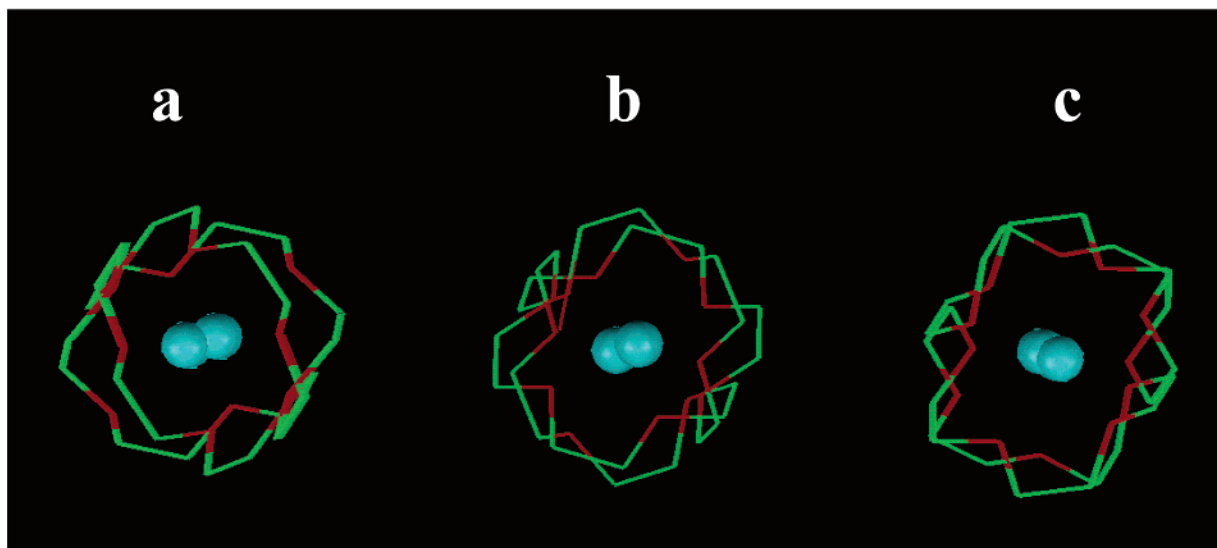
Figure 7. PEO tunnels in (a) PEO$_6$:LiPF$_6$, (b) PEO$_6$:LiAsF$_6$, and (c) PEO$_6$:LiSbF$_6$.

an approximation, since it is based on a static model derived from the crystal structure, whereas in reality there is undoubtedly some flexing of the polymer chains.

In the perfect crystal structure all the five-coordinate Li$^+$ sites would be full. However, no crystalline solid is perfect above 0 K; hence, some defects must be present, resulting in vacant Li$^+$ sites to which the neighboring Li$^+$ ions may migrate.

Although all three 6:1 structures are similar, there are nevertheless differences between them, as is apparent in Figure 7. The three PEO tunnels exhibit different shapes when viewed in cross section. In the case of the LiPF$_6$ material, the tunnels are approximately circular, they become more distorted for the larger AsF$_6^-$ anion, and in the case of the SbF$_6^-$, the tunnel cross sections are rectangular. The differences in these shapes might have suggested differences in the levels of ionic conductivity. However, we have determined the distances, also in cross section, between the ether oxygens on neighboring PEO chains, and these are remarkably similar for all three complexes, 3.0 Å (PEO$_6$:LiPF$_6$), 2.8 Å (PEO$_6$:LiAsF$_6$), and 3.3 Å (PEO$_6$:LiSbF$_6$). These results are consistent with the similar activation energies observed for all three complexes.

Although changing the anion of the salt does not affect the ionic conductivity, significant differences in the level of ionic conductivity have been obtained by varying the molecular weight of the polymer. In Figure 8 we present conductivity data for PEO$_6$:LiSbF$_6$ prepared with molecular weights of 1000, 1500, and 2000, which illustrates the differences that can arise.

A clue to the origin of these differences may be obtained by examining the powder diffraction patterns as a function of molecular weight (Figure 9). For all three complexes, the peak positions and relative intensities are the same, indicating that the crystal structures are invariant with molecular weight. However, on close examination (Figure 10) it is evident that the widths of the peaks do vary, increasing with increasing molecular weight.

The two main factors that determine peak widths in powder diffraction patterns are crystallite size and microstrain. If the former decreases below approximately 3000 Å, the peaks in a powder X-ray diffraction pattern begin to broaden significantly.
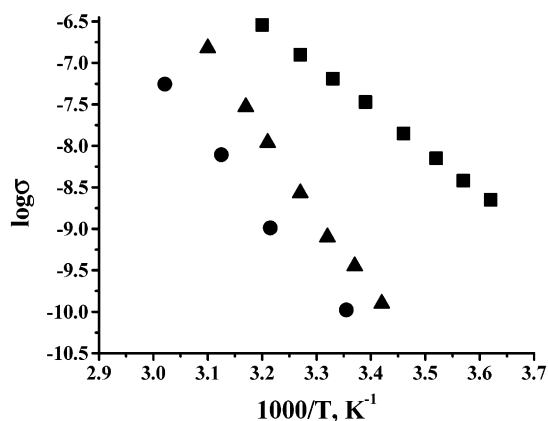

Figure 8. Ionic conductivity σ (S cm^{-1}) of PEO$_6$:LiSbF$_6$, synthesized with M_w of PEO 2000 (circles), 1500 (triangles), and 1000 (squares).

As the strain within the crystal increases, so also do the peak widths in diffraction patterns. Although there is a clear correlation between the variation of conductivity and the peak widths in the powder diffraction data, it is necessary to deconvolute the effects of microstrain from crystallite size to understand, in more detail, the origin of variation in conductivity with the change in molecular weight. The contributions of strain and size to a Bragg diffraction peak appear as Gaussian and Lorentzian components, respectively. We have employed a robust single-peak methodology to decouple these two contributions.[24] The procedure is based on extraction and analysis of Gaussian (β_G) and Lorentzian (β_L) components of the integral breadth of a single Bragg peak corrected for the instrumental broadening. The volume-weighted crystallite size ($\langle D \rangle_V$) and weighted average microstrain ($\tilde{\varepsilon}$) are readily calculated using the values of β_L and β_G, correspondingly.[23] The size/strains analyses of the polymer electrolyte samples were carried out using a strong nonoverlapping 021 reflection. For these experiments, the diffractometer was set up in the high-resolution mode, providing full width at half-maximum of 0.076° in 2θ for the 100 peak from a NIST line shape standard reference material,

(24) Delhez, R.; de Keijser, T. H.; Langford, J. I.; Louër, D.; Mittemeijer, E. J.; Sonneveld, E. J. In *The Rietveld Method*; Young, R. A., Ed.; Oxford University Press: Oxford, 1996; p 132.
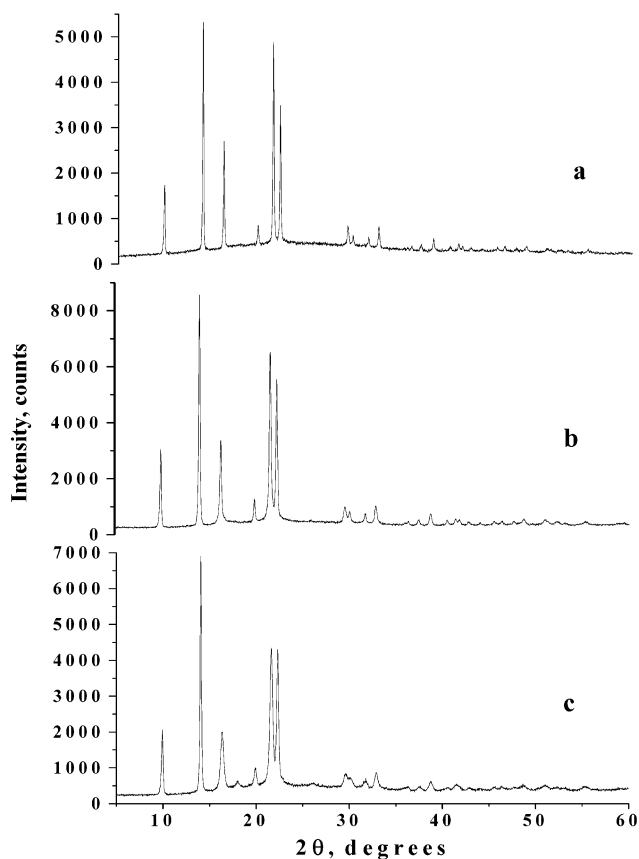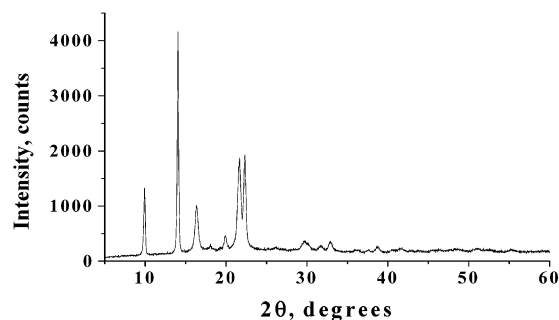
Figure 9. X-ray powder diffraction patterns (Cu K$_{\alpha 1}$) of PEO$_6$:LiSbF$_6$, synthesized with M_w of PEO 1000 (a), 1500 (b), and 2000 (c).
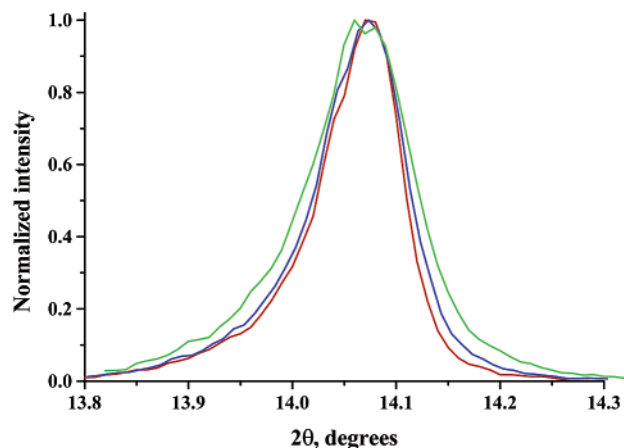

Figure 10. The 201 diffraction peak of PEO$_6$:LiSbF$_6$ synthesized with M_w of PEO 1000 (red), 1500 (blue), and 2000 (green).

LaB$_6$, (SRM 660a). This peak was used to correct the β_G and β_L from the polymer electrolyte samples for the instrumental broadening. To avoid instrumental smoothing, all reflections were measured with a stationary position sensitive detector. An acquisition time of at least 3 h ensured the statistical accuracy of better than 1% in the peak intensity. The results of the size/strain analysis revealed that for all three complexes the crystallite size decreases with the increasing molecular weight of PEO with no significant (less than 0.2%) microstrain present in any of the samples. For the example shown in Figure 10, the crystalline size decreases from 2500 Å ($M_\mathrm{w} = 1000$) through 2300 Å ($M_\mathrm{w} = 1500$) to 2000 Å ($M_\mathrm{w} = 2000$). These results

Figure 11. X-ray powder diffraction patterns (Cu K$_{\alpha 1}$) of PEO$_6$:LiSbF$_6$, prepared by fast evaporation with M_w of PEO 2000.
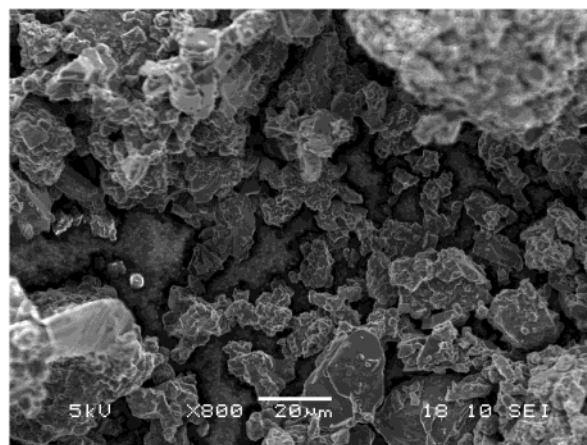
Figure 12. SEM image of PEO$_6$:LiSbF$_6$.

were further reinforced by preparing another PEO$_6$:LiSbF$_6$ ($M_\mathrm{w} = 2000$) sample, but in this case evaporation of the acetonitrile was carried out rapidly. The powder pattern of the resulting material is shown in Figure 11. From this figure it is evident that the peaks are broader than the previously prepared sample using the same polymer and salt but a slower evaporation rate. Analysis of the 201 diffraction peak from the sample prepared by fast evaporation yielded a crystallite size of 1700 Å.

The crystallite size determined from powder diffraction data is in fact the dimension over which the regular crystalline structure is coherent. Disorder beyond this length is sufficient to destroy further coherence. Crystallite size is not therefore necessarily the same as grain size. Indeed, it is often the case that these two dimensions are different, the latter being larger. Scanning electron microscopy carried out on PEO$_6$:LiSbF$_6$ revealed grain sizes for the powders in the range 1−20 μm (Figure 12). The picture then emerges of crystalline domains, disordered with respect to each other, within grains of the polymer electrolyte. The boundaries between the domains are likely to impede ion transport. Furthermore, these materials are 1-dimensional conductors; hence, the inevitable misalignment between adjacent domains further hinders the progress of ions. These factors conspire to make ionic conductivity lower in materials with smaller crystallite size. Note that in pressed powders there appears, from the ac impedance results, little evidence of further resistance to change flow at the grain boundaries (i.e. negligible grain boundary impedances).

Although there is a correlation between the crystallite size and the magnitude of the conductivity, this is not the entire explanation for the variation in conductivity with molecular weight, since it is evident from Figure 8 that the activation

energies differ. We are currently engaged in an in-depth NMR investigation of the conduction process in an attempt to better understand these more subtle issues.

We may conclude that ionic conductivity exists in all three crystalline 6:1 polymer electrolyte complexes, that the conductivity is similar in all three cases, in keeping with the crystal structure of each, and that as the crystallite size increases with decreasing molecular weight higher levels of ionic conductivity are obtained.

The levels of conductivity achieved so far with crystalline polymer electrolytes are still too low for many applications (10^{-4} S cm^{-1}). This work does, however, define a new direction in the search for higher ionic conductivity in the polymeric state. New crystalline polymer electrolytes will undoubtedly be prepared with yet higher conductivities. For example, 2D and 3D systems as opposed to the 1D systems described here. Furthermore, the materials reported here are stoichiometric (6:1) complexes with only a limited number of defects. By analogy with ceramic ionic conductors, introducing more vacancies or interstitials into these materials should substantially increase the ionic conductivity. There is much scope for further advancement of crystalline polymer electrolytes.