Structures of the Polymer Electrolyte Complexes PEO_6:$LiXF_6$ (X = P, Sb), Determined from Neutron Powder Diffraction Data

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The crystal structures of the polymer electrolyte complexes PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$ have been obtained from powder diffraction data collected from deuterated molecules on the OSIRIS neutron powder diffractometer at ISIS, Rutherford Appleton Laboratory. The structures are similar to that recently reported for the PEO_6:$LiAsF_6$ complex and consist of rows of Li^+ ions encapsulated within columns formed by pairs of nonhelical PEO chains. The Li^+ ion is coordinated by five ether oxygens. The anions reside between the columns and are not coordinated to the Li^+ ions. Despite broad similarities, the structures do exhibit differences, and these differences are discussed.

Introduction

Polymer electrolytes consist of salts, e.g., $LiCF_3SO_3$, dissolved in solid high-molecular-weight polymers, such as PEO $(CH_2CH_2O)_n$. The thermodynamic driving force for dissolution of the salt arises from coordination of the cations by the ether oxygens of the polymeric ligands. Many salt:polymer combinations are possible.[1,2] Such polymer electrolytes represent a fascinating class of compounds, but very little is known about their structural chemistry. Technologically, polymer electrolytes are capable of sustaining ionic conductivity in the solid membrane, and as a result, they are of great interest as a replacement for liquid electrolytes for lithium batteries, permitting the design of all-solid-state devices. The levels of ionic conductivity that can be obtained in such polymer electrolytes at room temperature, are too low for most applications unless they are extensively plasticized by low-molecular-weight additives. There is a great deal of interest in developing more highly conducting polymer electrolytes free from such low-molecular-weight additives. According to conventional wisdom, ion transport in polymer electrolytes arises in the amorphous phases above their glass transition temperatures and is facilitated by motion of the polymer chains. This can be summarized as the dynamic view of ion transport in these systems. In contrast, we emphasize the structural view. We have discussed the importance of aligning or organizing the polymer chains in order to enhance the levels of ionic conductivity.[3,4] The advantages of this approach have been demonstrated independently by other groups, such as Wright and co-workers[5] and Golodnitsky and Peled.[6] The former group has prepared ordered polymer electrolytes with conductivities at 40 °C that are $^1/_2$ order of magnitude higher than can be obtained from the PEO:$LiN(SO_2CF_3)_2$ system. The latter group demonstrated an enhancement in the ionic conductivity in PEO:LiI on stretching the polymer film. Such stretching has been shown to align (order) the chains, resulting in an increase in conductivity exceeding $^1/_2$ order of magnitude in the direction of stretch. Ultimate organization will occur in the crystalline state. It is also known that ionic conductivity in the amorphous state is generally higher in polymer/salt systems that form a crystalline 6:1 complex, making investigation of the structures adopted by 6:1 complexes of particular interest. We recently, and for the first time, obtained the structure of a crystalline complex with six ether oxygens per cation, PEO_6:$LiAsF_6$.[7] The crystal structure consists of rows of Li^+ ions contained within tunnels formed by pairs of interlocking PEO chains. The structure differs markedly from those previously determined for 3:1, 4:1, or 1:1 structures such, as PEO_3:$LiCF_3SO_3$,[8] PEO_4:KSCN,[9] or PEO:$NaCF_3SO_3$.[10] In this paper, we seek to explore whether the unusual structure of PEO_6:$LiAsF_6$ is unique or whether other related anions would permit retention of the same structure at 6:1. This is of particular importance given the relationship of the 6:1 complexes

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Table 1. Selected Bond Distances (Å), Angles (°), and Torsional Angles (°) in PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$

	PEO_6:$LiPF_6$	PEO_6:$LiSbF_6$		PEO_6:$LiPF_6$	PEO_6:$LiSbF_6$
Li−O1	2.17(3)	2.16(4)	C1−C2−O1	115(6)	108(6)
Li−O4	2.17(3)	2.14(4)	O1−C3−C4	105(6)	102(5)
Li−O2	2.17(3)	2.16(4)	C3−C4−O2	99(6)	107(6)
Li−O5	2.17(3)	2.19(4)	O2−C5−C6	122(6)	125(6)
Li−O3	2.18(3)	2.19(4)	C5−C6−O3	94(6)	113(7)
			O3−C7−C8	108(5)	117(7)
P(Sb)-F1	1.55(2)	1.82(1)	C7−C8−O4	100(5)	96(5)
P(Sb)-F2	1.55(2)	1.83(1)	O4−C9−C10	85(5)	98(5)
P(Sb)-F3	1.56(2)	1.83(1)	C9−C10−O5	115(5)	115(7)
P(Sb)-F4	1.56(2)	1.82(1)	O5−C11−C12	122(6)	155(11)
P(Sb)-F5	1.55(2)	1.81(1)	C11−C12−O6	102(6)	113(7)
P(Sb)-F6	1.55(2)	1.82(1)	O6−C1−C2	113(5)	137(7)
C1−C2	1.56(2)	1.55(1)	C2−O1−C3	109(5)	113(7)
C3−C4	1.55(2)	1.55(1)	C4−O2−C5	123(5)	126(7)
C5−C6	1.55(2)	1.55(1)	C6−O3−C7	128(6)	110(6)
C7−C8	1.56(2)	1.55(1)	C8−O4−C9	110(5)	109(6)
C9−C10	1.56(2)	1.54(1)	C10−O5−C11	119(5)	122(7)
C11−C12	1.56(2)	1.54(1)	C12−O6−C1	117(6)	119(7)
C2−O1	1.43(2)	1.42(1)	O6−C1−C2−O1	2.82 *c*	−52.40 $\bar{g}$
O1−C3	1.42(2)	1.42(1)	C1−C2−O1−C3	161.01 *t*	−65.63 $\bar{g}$
C4−O2	1.43(2)	1.42(1)	C2−O1−C3−C4	−107.32 $\bar{g}$	−171.90 *t*
O2−C5	1.43(2)	1.42(1)	O1−C3−C4−O2	−109.87 $\bar{g}$	−21.56 *c*
C6−O3	1.43(2)	1.42(1)	C3−C4−O2−C5	175.27 *t*	−152.82 *t*
O3−C7	1.43(2)	1.43(1)	C4−O2−C5−C6	−158.74 *t*	−165.46 *t*
C8−O4	1.43(2)	1.42(1)	O2−C5−C6−O3	−58.49 $\bar{g}$	28.97 *c*
O4−C9	1.43(2)	1.42(1)	C5−C6−O3−C7	19.31 *c*	39.32 *c*
C10−O5	1.43(2)	1.42(1)	C6−O3−C7−C8	169.64 *t*	157.55 *t*
O5−C11	1.43(2)	1.42(1)	O3−C7−C8−O4	89.51 *g*	45.39 *g*
C12−O6	1.43(2)	1.42(1)	C7−C8−O4−C9	−176.87 *t*	152.68 *t*
O6−C1	1.42(2)	1.42(1)	C8−O4−C9−C10	157.02 *t*	−178.41 *t*
			O4−C9−C10−O5	−80.30 $\bar{g}$	−42.77 *c*
			C9−C10−O5−C11	−130.20 $\bar{g}$	−124.04 $\bar{g}$
			C10−O5−C11−C12	129.98 *g*	114.71 *g*
			O5−C11−C12−O6	−91.21 $\bar{g}$	−49.33 $\bar{g}$
			C11−C12−O6−C1	3.22 *c*	−62.08 $\bar{g}$
			C12−O6−C1−C2	145.58 *t*	−151.27 *t*

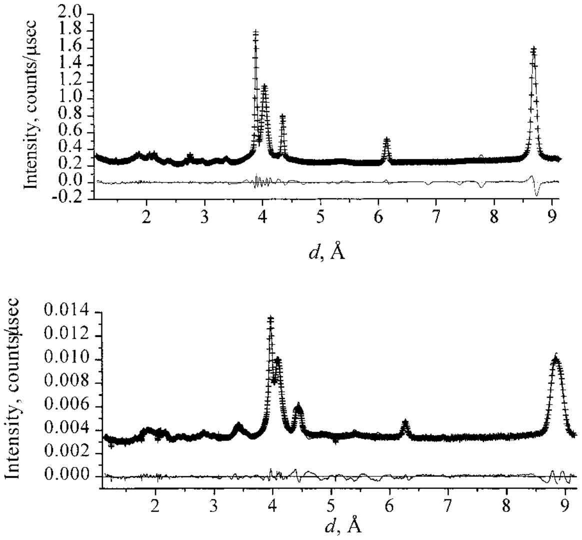

Figure 1. Observed (crosses), calculated (solid line), and difference neutron powder diffraction patterns for $(PEO)_6$:$LiPF_6$ (top) and $(PEO)_6$:$LiSbF_6$ (bottom).

to ionic conductivity mentioned above. Two systems have been studied, for which the sizes of the XF_6 anions are, respectively, smaller and larger than that of AsF_6, specifically, PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$.

Crystallographic studies of the crystalline complexes provide unprecedented detail concerning structure. We showed previously for 3:1 complexes that the structures are preserved on going from the crystalline to the amorphous phase of the same composition, with only a loss of register between the chains.[11] Therefore the crystallographic studies reported here provide a solid foundation for understanding the structure in the amorphous phase with consequences for conduction in the amorphous state.

Experimental Section

The complexes were prepared by the solvent-casting method using deuterated PEO [Polymer Source Inc., MW = 28 400 (for PEO_6:$LiPF_6$) and MW = 2000 (PEO_6:$LiSbF_6$)]. The same crystalline complexes were obtained for a range of PEO molecular weights up to at least 1 million. However, particularly for the $LiSbF_6$ system, the degree of crystallinity was higher at low molecular weight. The deuterated PEOs were dried under vacuum at 45 °C for 48 h before being combined with lithium hexafluorophosphate powder (Merck KGaA, Selectipur, 99.9%) or lithium hexafluoroantimonate (Strem Chemicals, 97%). The $LiSbF_6$ was dried by heating under vacuum at 50 °C for 3 days, and $LiPF_6$ was used as-received. Although deuterated, we shall still refer to the polymer as PEO. All manipulations were performed in an argon-filled glovebox. Stoichiometric amounts of the polymer and the salt were dissolved separately in anhydrous acetonitrile (Aldrich, 99.8%), and the solutions were mixed and stirred overnight. The resulting solutions were then cast onto Teflon plates, and the solvent was allowed to evaporate slowly at room tem-

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perature. The deposited films were dried under vacuum at 45 °C for 24 h to remove any residual solvent and to improve the crystallinity. The films were free-standing. Forming the complexes in different ways, particularly by hot pressing the salt and polymer in the absence of a solvent, influenced the degree of crystallinity but not the crystal structure. For the neutron diffraction experiment the films were placed into an airtight cylindrical vanadium sample holder.

Neutron diffraction patterns (Figure 1) were collected in the range of *d* spacings from 1 to 10 Å on the OSIRIS[12] powder diffractometer at the ISIS pulsed spallation source, Rutherford Appleton Laboratory. The similarity of the PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$ patterns to that of PEO_6:$LiAsF_6$ suggested that the complexes were isostructural. This allowed us to undertake structure elucidation using the Rietveld method[13] and to employ a starting structural model based on that of the arsenic analogue.[7] Soft constraints on the bond angles and bond lengths similar to those used in the refinement stage of the structure determination of PEO_6:$LiAsF_6$ were employed. The refinements involved 1734 data points, 50 atoms in the asymmetric unit, 162 variables, and 135 soft constraints. For both PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$ the powder data could be indexed on monoclinic cells and with systematic absences that unambiguously determined the space group as $P2_1/a$. Refinement was carried out using the GSAS program package.[14] These steps produced final refinement structures, Figure 2, that yielded good fits to the experimental patterns (see Figure 1) with $R_{wp} = 0.042$ and $R_{wp} = 0.035$ for the PF_6 and SbF_6 complexes, respectively. Selected interatomic distances and angles are listed in Table 1.

Results and Discussion

The structures of PEO_6:$LiPF_6$ and PEO_6:$LiSbF_6$ are similar to that of PEO_6:$LiAsF_6$. As in the hexafluoroarsenate complex, the Li^+ cations are arranged in rows, with each row located along the axis of an axisymmetric surface formed by two PEO chains (Figure 2). The surface approximates a cylinder in the case of PEO_6:$LiPF_6$, but in the case of PEO_6:$LiSbF_6$, it can be better described as a right parallelepiped. Each chain adopts a conformation $ct\bar{g}\bar{g}tt\bar{g}ctgtt\bar{g}\bar{g}g\bar{g}ct$ in PEO_6:$LiPF_6$ and $\bar{g}\bar{g}tcttcctgttc\bar{g}g\bar{g}\bar{g}t$ in PEO_6:$LiSbF_6$, compared to $ctg\bar{g}tgc\bar{g}tcttgt\bar{g}cgt$ in PEO_6:$LiAsF_6$, which defines either a half-cylinder (PF_6 complex) or a half-right-parallelepiped (SbF_6), with the two halves (PEO chains) in each case interlocking on both sides. The above conformational sequences have been derived assuming that torsion angles in the range 0 ± 45° are cis (*c*), 180 ± 45° are trans (*t*), the remainder are either gauche (*g*) or gauche-minus ($\bar{g}$). The cations are coordinated by both chains, involving three ether oxygens from one and two from the other (see Figure 2), with Li−O distances in the range of 2.14−2.19 Å. In both complexes, the third ether oxygen from the second chain is located over 3 Å away from the Li^+ ion and is not involved in the coordination of the cation. There are two Li−Li distances along the chain axis, and these are 7.4 and 4.4 Å for PEO_6:$LiPF_6$, 6.5 and 5.4 Å for PEO_6:$LiAsF_6$ and 7.1 and 5.0 Å for PEO_6:$LiSbF_6$. The separations of Li^+ ions between neighboring chains are 9.1, 9.2, and 9.3 Å for the three complexes in order of ascending anion size. The PF_6^- and SbF_6^- anions do not coordinate the cations (all Li−F distances are greater than 4.5 Å) but, like the anions in the structure of PEO_6:$LiAsF_6$, are located in the interchain space.

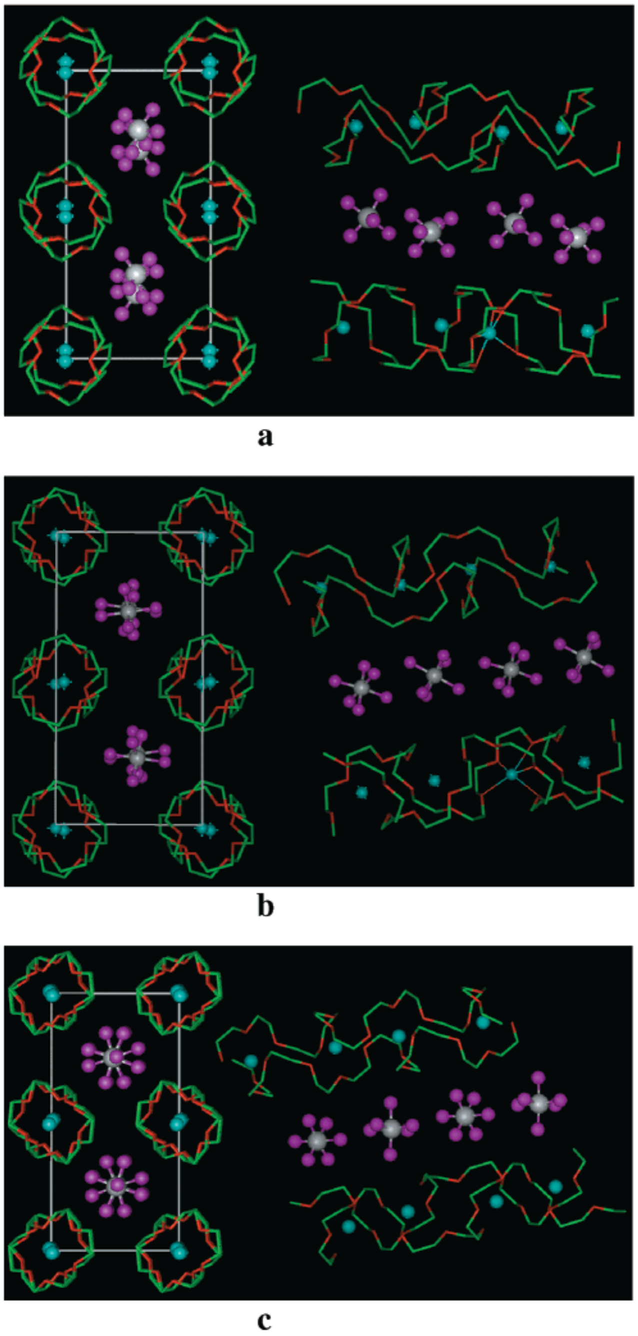

Figure 2. Structures of (a) PEO_6:$LiPF_6$, (b) PEO_6:$LiAsF_6$, and (c) PEO_6:$LiSbF_6$. (Left) View of the structure along *a* showing rows of Li^+ ions perpendicular to the page. (Right) View of the structure showing the relative position of the chains and their conformation (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation; blue spheres, lithium; white spheres, arsenic; magenta spheres, fluorine; green spheres, carbon; red spheres, oxygen.

Although the structures of all three 6:1 complexes determined so far exhibit similar features, there are

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important differences, and it is interesting to compare these differences in more detail. The differences arise from the increasing size of the anion, the volume of which rises by 25% on replacement of PF_6^- by AsF_6^- and by a further 29% on substitution of AsF_6^- by SbF_6^-. The increase in anion size has the effect of pushing apart the columns formed by the pairs of PEO chains, which is reflected in the increase of the b and c lattice parameters, Figure 2. The cell dimensions change from $a = 11.723(4)$, $b = 17.375(4)$, $c = 9.131(2)$ Å, and $\beta = 107.80(2)°$ for PEO_6:$LiPF_6$ to $a = 11.871(4)$, $b = 17.537(3)$, $c = 9.227(3)$ Å, and $\beta = 108.21(1)°$ for PEO_6:$LiAsF_6$ and to $a = 12.01(1)$, $b = 17.787(9)$, $c = 9.296(4)$ Å, and $\beta = 107.91(2)°$ for PEO_6:$LiSbF_6$. However, as these figures show, the increase in cell dimensions is not confined to the b and c axes; a also increases, resulting in an increase in unit cell volume from 1770.27 Å^3 for PEO_6:$LiPF_6$ to 1889.92 Å^3 for PEO_6:$LiSbF_6$. Associated with the increase in a, the PEO columns become stretched along their columnar axis. Despite this stretching, the average Li−O bond length and the coordination number around Li^+ remain the same. It is likely that the conformational changes that occur in the PEO chains (noted above) on replacement of PF_6^- by AsF_6^- and SbF_6^- arise, in part, because of the need to accommodate the dimensional changes of the anion while maintaining the strong cation−ether oxygen coordination so critical to the formation and stability of the complex (see later). There is a further subtlety to the interplay between anion size and the conformation and separation between the PEO columns. The change in the PEO conformation from the cylindrical columns around Li^+ in PEO:$LiPF_6$ to the rectangular cross section of the right parallelepiped in PEO_6:$LiSbF_6$ has the effect of increasing the size of the cavity available for the anion (Figure 2). As a result, the separation of the PEO columns does not increase as much as would be anticipated in the absence of such a conformational change. This is reflected in the fact that the unit cell does not expand in proportion to the increase in the anion size. The degree of disorder in the structures decreases as the anion size increases. The Li^+ and XF_6^- ions together form a zigzag arrangement along the a axis in the PEO_6:$LiPF_6$ complex (Figure 2). This arrangement becomes more linear as the anion size increases. The anions, especially in PEO_6:$LiSbF_6$, are almost eclipsed when viewed along a.

The main terms contributing to the free energy of formation of a polymer electrolyte from its constituent salt and polymer are the lattice energy of the salt and the cation−polymer interactions.[1] The latter must overcome the former if a complex is to form. Consequently, coordination of the Li^+ ions by ether oxygens is of paramount importance to the energetics of the crystal structures described in this paper. In general, Li^+ ions prefer a five- or six-coordinate environment. It is not possible to wrap a single PEO chain around Li^+ such that the chain presents the Li^+ ion with five ether oxygens. Such a situation would impose an undue strain on the PEO chain. If we consider first the more familiar 3:1 crystalline complexes including PEO_3:$LiCF_3SO_3$,[8] PEO_3:$LiN(CF_3SO_2)_2$,[15] and PEO_3:$LiAsF_6$,[16] the Li^+ ion is coordinated by only three ether oxygens, with the remaining two coordination sites being completed by two anions. Any attempt to use two or more PEO chains to coordinate Li^+ by five or six ether oxygens would, because of the 3:1 composition, necessitate extensive sharing of the ether oxygens between Li^+ ions. It is difficult to envisage such a structure forming, hence the 3 + 2 coordination in the 3:1 complexes with the PEO chain adapting a right-handed helical conformation. In contrast, the 6:1 complexes have twice the number of ether oxygens per Li^+ ion, and hence, the use of two chains does not require any sharing of oxygens between Li^+ ions. The fact that all three 6:1 complexes adopt the same basic structure indicates that the structure is preferred and can accommodate changes in the anion size. Finally, bond lengths and angles within the chains and the anions all lie in the range of the previously reported values.

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Supporting Information Available: Table of atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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