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2001 J. Phys.: Condens. Matter 13 8245

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Using crystallography to understand polymer electrolytes

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Received 7 February 2001

Published 23 August 2001

Online at stacks.iop.org/JPhysCM/13/8245

Abstract

Crystallography provides a unique insight into the structural properties of polymer electrolytes. Knowledge of the crystal structures helps in the understanding of the structural chemistry of such electrolytes and facilitates the design of electrolytes with a higher conductivity for applications in new devices such as all-solid-state batteries. In the present paper we present a detailed survey of the structural properties of all the crystalline phases of poly(ethylene oxide)-based polymer electrolytes along with various approaches to structure elucidation from powder diffraction data. The inter-relationship between the crystal structure and conductivity of the polymer electrolytes is also discussed.

1. Introduction

Polymer electrolytes are complexes composed of salts e.g. NaI, NaCF₃SO₃, LiN(SO₃CF₃)₂ or LiPF₆ dissolved in high-molecular-weight polymers such as poly(ethylene oxide) (PEO) (CH₂CH₂O)_n (Bruce 1995, Gray 1997). These materials have the potential to operate as electrolytes in all-solid-state batteries. Conductivities approaching 10⁻⁴ S cm⁻¹ at room temperature may be obtained in these compounds, but higher levels are required for battery applications (Bruce 1996). In order to develop a short-term solution to the problem of conductivity, low-molecular-weight plasticizers are added to form gel electrolytes. Such materials yield sufficiently high conductivity for applications but suffer from many of the problems associated with liquid electrolytes. The need for a true high-molecular-weight solid polymer electrolyte with a conductivity exceeding 10⁻⁴ S cm⁻¹ at room temperature remains paramount. In order to achieve this a better understanding of the conduction mechanism is required. Our understanding of polymer electrolyte structure lags significantly behind the effort to improve ionic conductivity, yet such an understanding is likely to play a significant role in enabling the realization of higher ionic conductivity.

It is generally assumed that conductivity occurs only in amorphous polymer:salt systems. Some polymer:salt combinations form only amorphous phases regardless of composition. In contrast, the polymer:salt combinations which form crystalline compounds do so at certain limited and discrete compositions, usually corresponding to a high salt content (low ether oxygen to cation ratio), e.g. 1:1, 4:1, 6:1 or 8:1. It has been shown by Frech *et al* (1997) that the main structural features of polymer electrolytes are largely retained on passing from the crystalline to the amorphous state. However, unambiguous *ab initio* determination of an amorphous polymer electrolyte structure has not proved possible in most cases. Establishing structures of crystalline polymer electrolytes provides a unique insight into the structural chemistry and a route, in combination with spectroscopic studies, to the structure of the amorphous phases. It may also hold the key to the design of materials with higher ionic conductivity.

Single-crystal diffraction is the best choice for structure determination. However, sufficiently high-quality single crystals of polymer electrolytes are impossible to grow or separate from bulk polycrystalline samples. This leaves powder diffraction as the only available tool for direct structure elucidation. *Ab initio* structure determination from powder data is a considerable challenge when compared to the single-crystal method. In the case of powders a 3D diffraction pattern obtainable from a single crystal is compressed into one dimension, which inevitably leads to the loss of information due to the overlap of reflections. A variety of methods have been developed to deal with the overlap problem (Rietveld 1969, Pawley 1981, Le Bail *et al* 1988) and to solve crystal structures from powder diffraction data (Andreev *et al* 1996, Shankland *et al* 1997, Kariuki *et al* 1997, Altomare *et al* 1998, David *et al* 1998, Pagola *et al* 1999).

In this paper we present an overview of the structural studies of polymer electrolytes which also reflects the substantial progress which has been made in the development of methods for *ab initio* structure determination from powder diffraction data.

2. Early solutions of polymer electrolyte structures

Hibma (1983) reported the crystal structure of a polymer electrolyte, PEO₄:KSCN, which was determined using fibre diffraction data from a low-quality single crystal. The unit cell was monoclinic, space group *C2/c*, with eight separate PEO chains each containing four ethylene oxide units. The proposed structural model was confined to two dimensions (a projection of the structure onto the *ac*-plane, with the chain axis being parallel to the *b*-axis) due to the limited number of experimental peaks, 34, compared to 48 unknown coordinates of non-hydrogen atoms needed for a 3D model. A ringlike shape of the PEO chain in the projection suggested that the chain was likely to be helical. The K⁺ cations were positioned outside the helix with no apparent coordination to ether oxygens. A rather poor agreement between calculated and experimental diffraction data, Bragg *R*-factor (*R_B*) of 11%, placed in some doubt the validity of the reported structures. Subsequent independent structure solution of the same and several other 4:1 complexes described in the next section revealed a different structural model which agrees better with the experimental data.

Chatani *et al* (Chatani and Okamura 1987, Chatani *et al* 1990) determined the structures of PEO₃:NaI, PEO₃:NaSCN and PEO:NaSCN. The structures were solved using fibre diffraction data. All three structures are monoclinic and described either in *P21/a* or *P21/c* space groups. In the case of PEO₃:NaI the iodide anion was placed using the Patterson method (Buerger 1959). Subsequently, the position of Na⁺ was found by a trial-and-error procedure. The position and the conformation of the PEO chain was established on the basis of unit cell dimensions and the available free space after placement of the salt atoms. The chain adopts a

twofold helical structure with $(t_2gt_2gt_2\bar{g})_2$ conformation. The symbols t and g stand for *trans* and *gauche* values of the torsion angles in the chains. Each sodium cation is coordinated by three ether oxygens from a single PEO chain and by two iodide anions. Despite a relatively poor agreement with the experimental data ($R_B = 14\%$), the correctness of the established structural model has been verified many times by using it as a starting point for solving several other structures with the same polymer:salt ratio beginning with $\text{PEO}_3:\text{NaSCN}$. As reported by the authors, the structure of $\text{PEO}:\text{NaSCN}$ was found by a trial-and-error method based on the previously reported structure of $\text{PEO}:\text{HgCl}_2$ (Yokoyama *et al* 1969). The final structural model in which each sodium cation is coordinated by two ether oxygens from a single chain, two sulphurs and two nitrogens from four different SCN^- anions agrees better with the experimental data ($R_B = 10\%$) and confirms the zig-zag conformation of the PEO chain established earlier.

3. Structure solutions using data from a high-resolution powder diffractometer and the Rietveld method

The development of new powerful, high-intensity and high-resolution, laboratory diffractometers together with the arrival of the Rietveld method and the adaptation of direct methods of structure solution from single-crystal to powder data, marked a new era in the structure determination of polymer electrolytes. These advances ensured more reliable solutions of more complex structures.

Lightfoot *et al* (1992) reported the structure of $\text{PEO}_3:\text{NaClO}_4$. This structure was determined using powder diffraction data from a Stoe STADI/P high-resolution system with a linear position-sensitive detector. The constrained Rietveld method, as implemented within the GSAS program package (Larson and Von Dreele 1987), was employed to elucidate the structure starting from $\text{PEO}_3:\text{NaI}$ as the model structure and replacing I by Cl. The missing oxygen atoms of the ClO_4^- anion were located from successive difference Fourier maps. The final structure provided an excellent agreement with the experimental diffraction profile with the weighted profile R -factor (R_{wp}) equal to 6.9%. As in the $\text{PEO}_3:\text{NaI}$, the chain in $\text{PEO}_3:\text{NaClO}_4$ is helical with all C–C bonds being *gauche* and all C–O bonds *trans*. The sodium cation is five coordinate involving three oxygens from the chain and two oxygens from two different perchlorate anions.

A year later the same group of authors (Lightfoot *et al* 1993) determined the first polymer electrolyte structure containing the Li^+ cation and a more complex, triflate, anion, $\text{PEO}_3:\text{LiCF}_3\text{SO}_3$. Based on the similarity of the unit cell sizes and the same space group, the starting position of the polymer chain and the cation were obtained, with some adaption, from the structure of $\text{PEO}_3:\text{NaSCN}$. Subsequent refinement of the partial structural model using the Rietveld method and difference Fourier synthesis allowed the authors to determine the position of the CF_3SO_3^- anion. The final structural model (figure 1) produced an excellent fit to the experimental pattern ($R_{wp} = 4\%$). As in other 3:1 complexes mentioned above the conformation of the helical chain in $\text{PEO}_3:\text{LiCF}_3\text{SO}_3$ is $(t_2gt_2gt_2\bar{g})_2$. The Li^+ ions are located within the chain forming a zig-zag pattern along the axis of the helix. Each lithium cation is coordinated by five oxygens, three ether oxygens from a single chain and two from the two adjacent anions. Every CF_3SO_3^- in its turn bridges two Li^+ ions forming chains parallel to the PEO chain.

Further progress in structural studies of polymer electrolytes was achieved by solving several 4:1 structures of the type $\text{PEO}_4:\text{MSCN}$ where $\text{M} = \text{NH}_4, \text{K}, \text{Rb}$ (Lightfoot *et al* 1994, Thomson *et al* 1996). The structure of $\text{PEO}_4:\text{NH}_4\text{SCN}$ was determined *ab initio*. First, the S

atom of the thiocyanate was located using direct methods. This was followed by alternating use of the Rietveld method and the difference Fourier technique applied to the whole powder diffraction profile to determine the remainder of the structure. The final refinement performed using slack constraints produced an excellent match to the experimental pattern ($R_{wp} = 5\%$). The isomorphous structures of the complexes with K^+ and Rb^+ cations were determined by Rietveld refinement using the refined $PEO_4:NH_4SCN$ complex as an initial structural model. In all the above 4:1 complexes the PEO chain adopts a helical arrangement which encloses the cation (figure 2) and there are four separate chains in the unit cell each containing eight ethylene oxide units. However, the chain conformation $t_2gt_2gt_2\bar{g}t_2\bar{g}$ is different from that in previously determined 3:1 complexes. The helix becomes 'fatter' in order to accommodate the larger cations. Such a conformation provides five ether oxygens to coordinate each cation. Two of the five oxygens coordinate two cations simultaneously. In addition, the cation is coordinated by two nitrogens from the two neighbouring thiocyanate anions. The nitrogen of each thiocyanate bridges two neighbouring cations along the chain. As in all 3:1 complexes, there are no interchain links in the 4:1 structures. Each PEO chain is associated with a dedicated set of cations and anions. The successful structure solution of the 4:1 complexes proved that the previously suggested structural model of $PEO_4:KSCN$ (Hibma 1983) with the K^+ positioned outside the PEO chain was in error.

Despite the obvious advances in the field of structure solution of polymer electrolytes due to the availability of new high-resolution powder diffractometers and developments of new methodology, there remained many failures in determining structures of several existing PEO/salt complexes. Thus, for example, all attempts to solve the structures of $PEO:NaCF_3SO_3$ and $PEO_3:LiN(CF_3SO_2)_2$ by applying direct methods or the Rietveld method proved unsuccessful. This generated a need for a new and powerful method of *ab initio* structure determination from powder diffraction data.

4. The simulated annealing era

4.1. The method

The requirements for a new method of structure determination from powders were the following. The method should be able to succeed in the absence of any prior knowledge of the molecular/atomic arrangement within the unit cell. In view of the limited amount of information available from powder diffraction compared to single crystals any new method must narrow the amount of crystallographic space which has to be searched. To do this the new approach must make use of the known covalent (inter-atomic) connectivity within the constituent molecular fragments (e.g. PEO chain or a complex anion) while treating them as highly flexible moieties so that no assumptions concerning the position, orientation or conformation of the moieties are made *a priori*.

In order to meet these requirements, the general procedure of the new structure solution method for polymer electrolyte structures is split into four basic stages. First, the cation, the anion and the corresponding fragment of the polymer chain are placed randomly in the asymmetric unit. Second, a series of trial structural models is created in direct crystallographic space by random movements of all moieties within the limits of the asymmetric unit and by randomly changing bond lengths, bond angles and torsion angles of the anion and the chain. Third, for each trial structural model a powder diffraction pattern is calculated and compared with the experimental data by calculating the value of the figure-of-merit function (χ^2). Fourth, a global optimization technique is applied to find the deepest minimum of χ^2 corresponding to

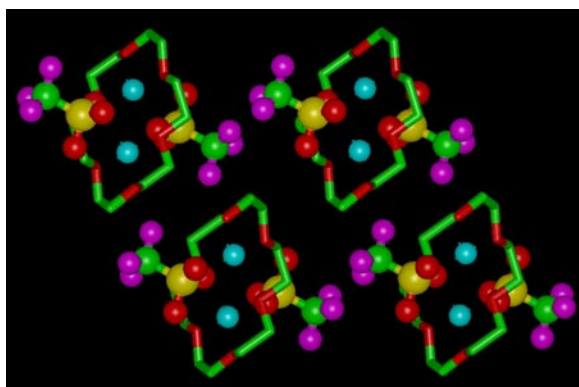


Figure 1. View of the $\text{PEO}_3:\text{LiCF}_3\text{SO}_3$ structure along the fibre axis. Thick green lines represent carbon in the PEO chain and thick red lines represent oxygen. Blue spheres, lithium; green, carbon; magenta, fluorine; yellow, sulphur; red, oxygen. Hydrogen atoms are not shown.

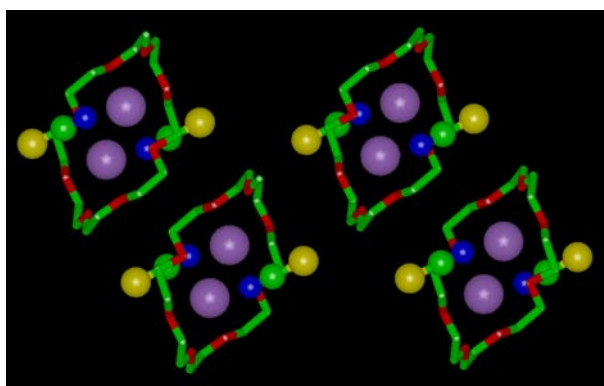


Figure 2. View of the $\text{PEO}_4:\text{KSCN}$ structure along the fibre axis. Thick green lines represent carbon in the PEO chain and thick red lines represent oxygen. Violet spheres, potassium; green, carbon; yellow, sulphur. Hydrogen atoms are not shown.

the true structure. To implement the above stages a versatile crystallographic description of fully flexible molecules (coordinates of individual atoms) in terms of stereochemical descriptors (bond lengths, bond angles and torsion angles) has been developed and a Monte-Carlo-based method of simulated annealing (SA) minimization of the figure-of-merit function χ^2 employing a full-profile fit to the experimental powder pattern has been implemented (Andreev *et al* 1996, 1997a). The new method may be derived from the Rietveld method of structure refinement by making the changes described in table 1. Further details of the structure solution method including the SA minimization can be found in Andreev and Bruce (1998).

4.2. The structures

All the structures discussed in this section were solved using diffraction data from a Stoe STADI/P laboratory powder diffractometer. Neutron diffraction data collected on the OSIRIS diffractometer at ISIS, Rutherford Appleton Laboratory, were used to verify the position of lithium.

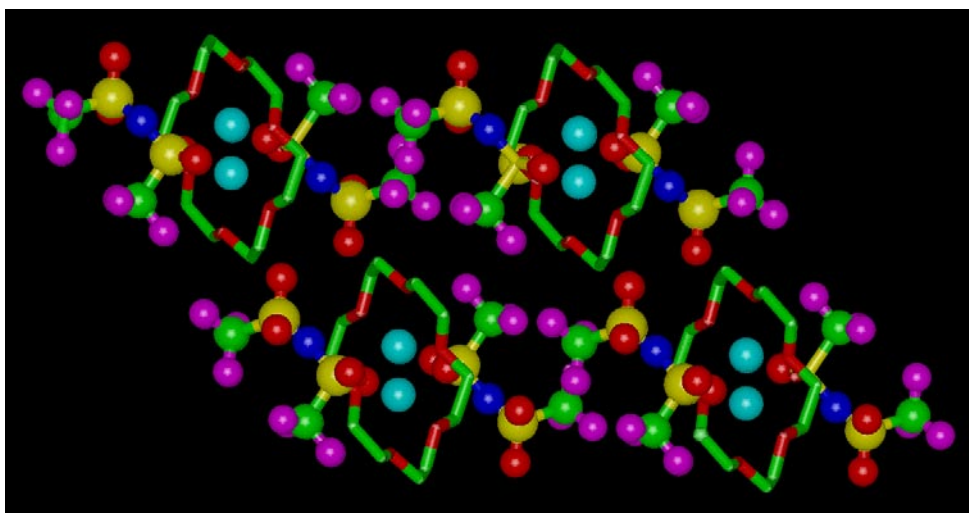


Figure 3. View of the $\text{PEO}_3:\text{LiN}(\text{CF}_3\text{SO}_2)_2$ structure along the fibre axis. Thick green lines represent carbon in the PEO chain and thick red lines represent oxygen. Light blue spheres, lithium; dark blue spheres, nitrogen; green, carbon; magenta, fluorine; yellow, sulphur; red, oxygen. Hydrogen atoms are not shown.

Table 1. Simulated annealing solution versus Rietveld refinement of molecular structures.

Feature	Rietveld refinement	Simulated annealing
Variables, \mathbf{P}	Crystallographic coordinates of atoms	Bond lengths, bond angles, torsion angles
Iterative procedure, $\mathbf{P}^{new} = \mathbf{P}^{old} + \Delta\mathbf{P}$	Non-linear gradient least squares, $\Delta\mathbf{P} = f(\partial\chi^2/\partial P_i)$	Monte Carlo $\Delta\mathbf{P} = \Delta\mathbf{P}_{max} \cdot \mathbf{R}$ R_i —random number [0, 1]
Directional change of χ^2 after each iteration	Downhill only, $\chi_{new}^2 < \chi_{old}^2$	Downhill if $\chi_{new}^2 < \chi_{old}^2$, Uphill if $\chi_{new}^2 > \chi_{old}^2$ and $\exp[-(\chi_{new}^2 - \chi_{old}^2)/\Delta\chi^2] < r$ r —random number [0, 1], $\Delta\chi^2$ —pre-set marginal change in χ^2 , 'temperature'
Constraints	Slack, χ^2 function includes additional penalty terms for violating parameter ranges	Strict, trial model is rejected when parameter range is exceeded

The first polymer electrolyte structure determined using the SA method was that of $\text{PEO}_3:\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Andreev *et al* 1996). 36 parameters including four bond lengths, seven bond angles and nine torsion angles were varied simultaneously to obtain the solution. It was sufficient in this case to treat all like bond lengths (e.g. all six C–F lengths) and bond angles (e.g. all four C–S–O angles) in the imide anion as equal and hence as single variables while keeping all bond lengths and bond angles in the PEO chain fixed at typical (for 3:1 complexes) values. The SA procedure and subsequent refinement by the Rietveld method ($R_{wp} = 5.6\%$) produced the final structure of $(\text{PEO})_3:\text{LiN}(\text{SO}_2\text{CF}_3)_2$ shown in figure 3. Similar to other 3:1 complexes, the conformation of the PEO chains is helical. One cation is

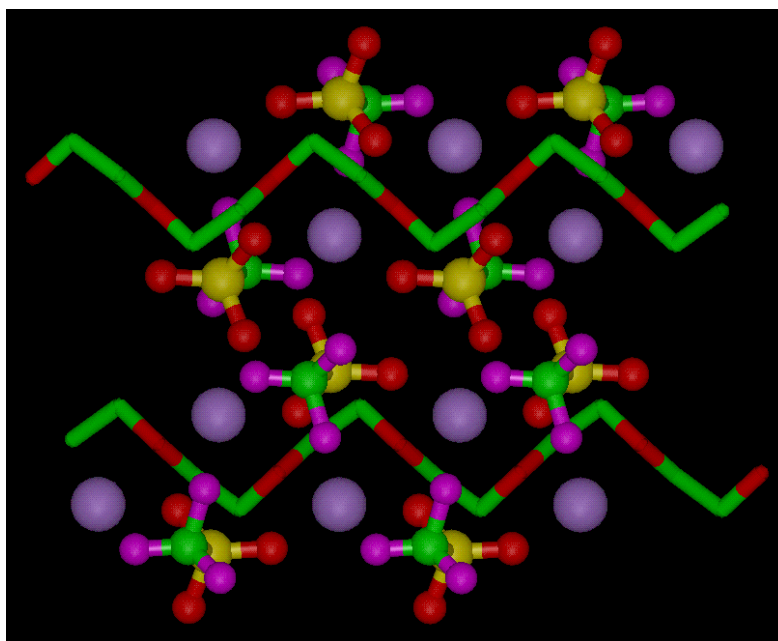


Figure 4. The structure of PEO:NaCF₃SO₃. Thick green lines represent carbon in the PEO chain and thick red lines represent oxygen. Violet spheres, sodium; green, carbon; magenta, fluorine; yellow, sulphur; red, oxygen. Hydrogen atoms are not shown.

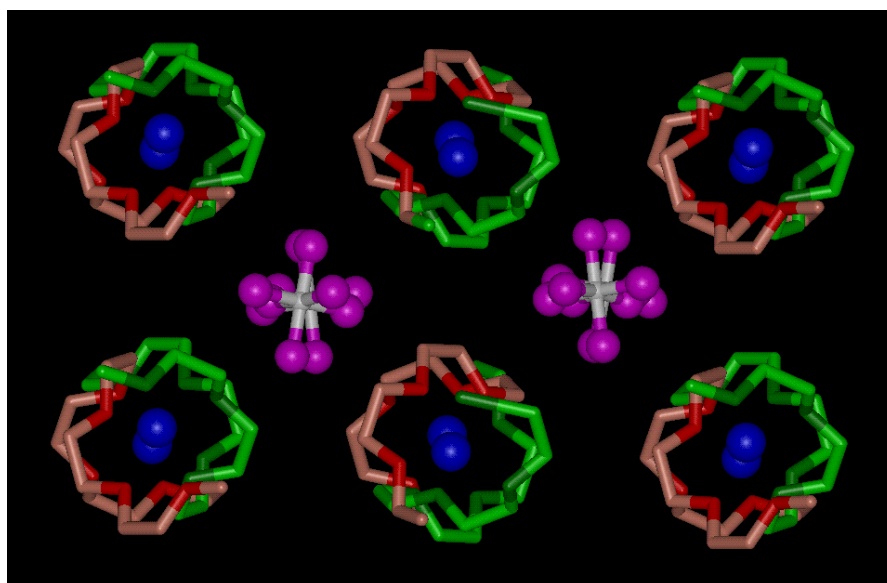


Figure 5. View of the PEO₃:LiAsF₆ structure along the fibre axis. Blue spheres, lithium; white, arsenic; magenta, fluorine; light green, carbon in chain 1; dark green, oxygen in chain 1; orange, carbon in chain 2; red, oxygen in chain 2. Hydrogen atoms are not shown.

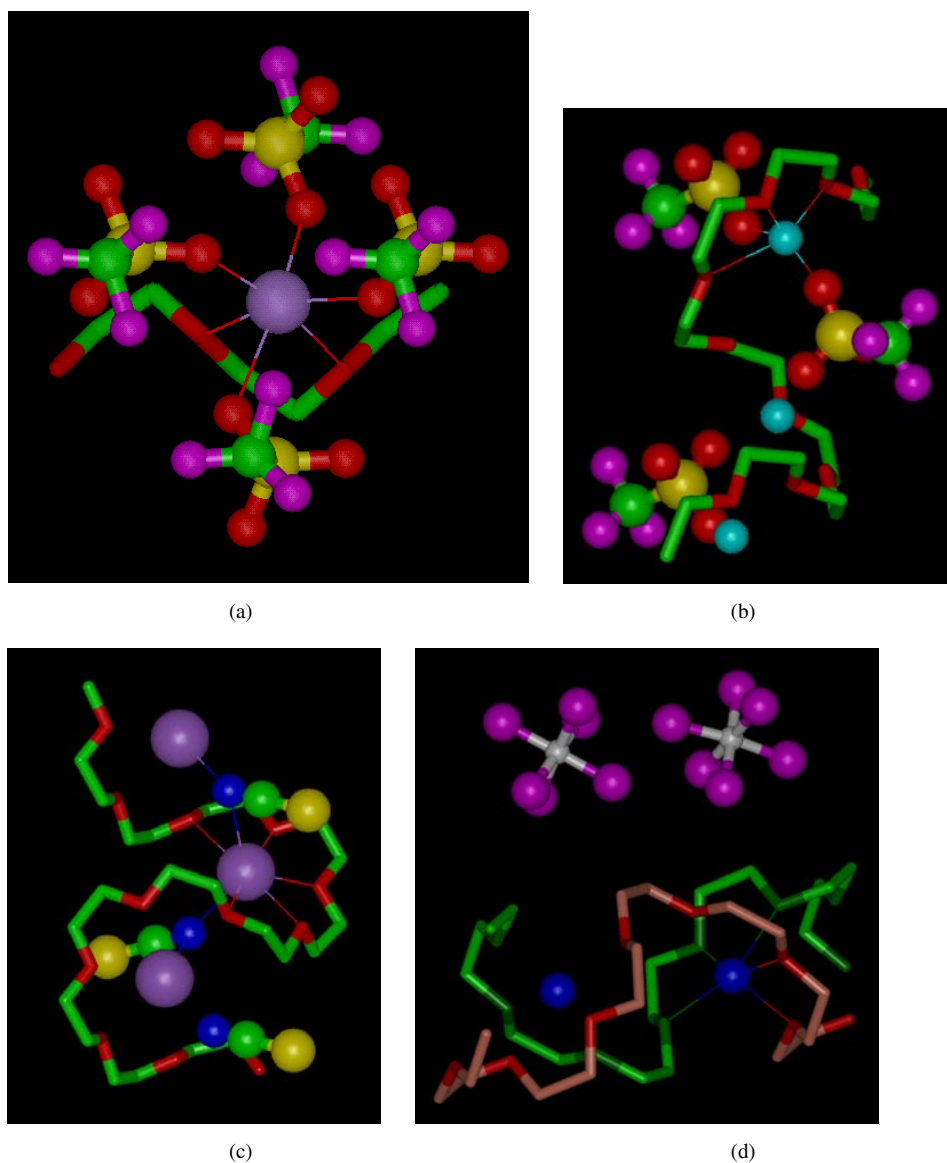


Figure 6. Fragments of the structures of (a) PEO:NaCF₃SO₃, (b) PEO₃:LiCF₃SO₃, (c) PEO₄:KSCN, (d) PEO₃:LiAsF₆ showing the relative position of the chains, their conformation and the coordination of the cations.

located in each turn of the helix and is coordinated by five oxygen atoms. Three of the five oxygens coordinating Li⁺ are from the chain while the other two belong to two imide anions. Each imide bridges neighbouring Li⁺ ions along the chain by donating one oxygen to each Li⁺. Both oxygens come from the same half of the imide; the other SO₂CF₃ moiety is not involved in coordination.

The solution of the crystal structure of PEO:NaCF₃SO₃ (Andreev *et al* 1997b) further emphasized the decisive role of molecular flexibility in successful *ab initio* structure determination in direct space. The true structure (figure 4) was found only after the triflate

anion had been treated as a fully flexible moiety, with all bond lengths and bond angles varied independently during the SA minimization. The structural model obtained after further refinement revealed a stretched zig-zag conformation of the PEO chain similar to that in PEO:NaSCN. The Na^+ ion is in a sixfold coordinate site comprising two oxygens from a single PEO chain and four from four different triflates with one of the triflate oxygens shared by two cations. The structure provided an excellent match between the observed and calculated patterns with $R_{wp} = 5\%$. The structure of PEO:NaCF₃SO₃ served as a starting model for elucidation by Rietveld refinement of the structure of another 1:1 complex, PEO:KCF₃SO₃. The structures are very similar with the only difference being the coordination of the cation. Unlike Na^+ , potassium is coordinated by seven oxygens. One of the four triflates donates two oxygens and two of the coordinating oxygens are shared between two cations.

The power of the SA method has been further proven by the *ab initio* solution of the first 6:1 complex, PEO₆:LiAsF₆ (MacGlashan *et al* 1999). With 26 non-H atoms in the asymmetric unit, 79 variable parameters including 15 torsion angles, this structure remains the most complex to be determined from powder diffraction data. The structure of PEO₆:LiAsF₆ is different from all known crystal structures of PEO:salt complexes and could not have been predicted based on analogy with other known structure or by any model-building/refinement procedure. It is the most powerful example of the need for a new *ab initio* approach to structure solution such as we have implemented and described here. In this structure the Li^+ cations are arranged in rows with each row located inside a cylindrical surface formed by two PEO chains (figure 5). Each chain adopts a non-helical conformation that defines a half-cylinder with the two half-cylinders interlocking on both sides. The cation is coordinated simultaneously by both chains, involving three ether oxygens from one and two from the other, giving a total coordination around Li^+ of five. Each of the five ether oxygens is coordinated to only one Li^+ ion while the sixth ether oxygen is not involved in cation coordination. In contrast to other known PEO complexes, the anions do not coordinate the cations but instead are located outside the dimensions of the cylinder in the interchain space. The correctness of the structural model is ensured not only by an excellent fit to the experimental data ($R_{wp} = 6\%$) but also by the fact that the established structure served as a valid starting model for elucidating the structures of the isomorphous complexes, PEO₆:LiPF₆ and PEO₆:LiSbF₆ by Rietveld refinement (Gadjourova *et al* 2000).

5. Discussion

The studies we have conducted on polymer electrolytes revealed the following trends in the crystal structure of these complexes with increasing PEO:salt ratio. The conformation of the polymer chain gradually changes from a stretched zig-zag in 1:1 (figure 6(a)) complexes through a helix in 3:1 (figure 6(b)) which increases in diameter in 4:1 (figure 6(c)) and finally splits into two interlocking half-cylinders when the ratio reaches 6:1 (figure 6(d)). The changes in the chain conformation are accompanied by changes in coordination. While the coordination number for the same type of cation does not depend on the polymer:salt ratio the balance between the number of ether oxygens and the number of anionic species involved in coordination of the cation changes gradually. In 1:1 complexes cations are coordinated by two ether oxygens and four or five, depending on the size of the cation, atoms from the anions. The relative number of coordinating ether oxygens increases to 3/2 (Li^+) or 4/2 (Na^+) in 3:1 complexes reaching 5/2 in 4:1. Each cation in the 6:1 complexes is coordinated solely by ether oxygens. Some of the anions in 1:1 complexes are shared between neighbouring cations forming cross-links and a three-dimensional network. The cross-linking disappears

in 3:1 and 4:1 complexes where each PEO chain is associated with a dedicated set of cations and anions. Ion-pairing disappears completely in 6:1 complexes with anions existing freely in the interchain space. In addition, one of the ether oxygens in the most dilute (6:1) complexes is not involved in coordination which may assist cationic transfer along the cylindrical tunnel formed by polymer chains.

The unusual structural features of the crystalline 6:1 complexes promoted conductivity studies of these compounds. The investigation is currently under way. We have pointed out previously that our structural studies imply significant order in the amorphous state and have predicted that by enhancing such organization higher ionic conductivity can be achieved (Bruce 1996, Andreev and Bruce 2000). The beneficial effect of structural ordering on ionic conduction of polymer electrolytes is supported by the recent findings of Golodnitsky and Peled (2000), who reported a fivefold enhancement in conductivity of PEO:LiI films upon mechanical stretching. NMR studies of the stretched material (Chung *et al* 1999) showed that a non-axial stress promotes the alignment of the crystalline regions in the direction of the applied stress and reduces the segmental motion of the host polymer, which is usually considered as the main driving force of ionic conductivity (Druger *et al* 1983). It is likely that in both dilute crystalline complexes and mechanically stretched amorphous and crystalline mixtures the enhancement of conductivity is caused by an orderly alignment of the tunnels, cylinders and helices respectively, which provide efficient pathways for charge carriers.

Acknowledgment

PGB is indebted to the EPSRC for financial support.

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