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Coordination Chemistry in the Solid State

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Coordination chemistry in the solid state

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Salts, e.g. $LiPF_6$, may be dissolved in solid polymers, e.g. $(CH_2{-}CH_2{-}O)_n$. Dissolution is driven by the complexation of the cations by the donor groups on the polymer chains. The resulting solids are coordination compounds with infinite ligands. They form a vital bridge between coordination chemistry in solution and more classical solid-state chemistry. The solid coordination compounds are often referred to as polymer electrolytes. In this paper I present a view of the coordination chemistry of these fascinating compounds which yield elegant structures as well as forming the basis of high technology devices for the 21st century. Topics covered include: the forces driving complexation; the major ligands and complexes; the structures of several model systems; and the physical properties and applications of the materials.

1. Introduction

Macrocyclic chemistry is one of the cornerstones of coordination chemistry. Its significance was recognized by the award in 1987 of the Nobel Prize in Chemistry to Jean-Marie Lehn, Charles Pedersen and Donald Cram. Such complexes exhibit a wide range of structures and considerable diversity in their physical properties. By the simple act of covalently linking individual macrocyclic complexes together in one dimension, polymeric chains may be formed which, when sufficiently long, yield solid polymers capable of coordinating cations within the individual macrocycles. Therefore, in a natural way, macrocyclic chemistry straddles what is often seen as a great divide between the liquid and the solid state.

Recently, Lehn (1990) has shown that by linking bipyridine molecules together with $-CH_2{-}O{-}CH_2-$ units, helical structures can be formed in one dimension when these ligands coordinate certain cations (figure 1). If we dispense with the bipyridine molecules and simply allow ethylene oxide units to condense together to form poly(ethylene oxide) $[(-CH_2{-}CH_2{-}O-)_n]$, we obtain long-chain molecules which coil up into a helix. Each turn of the helix provides a macrocyclic ligand with regularly spaced ether oxygens capable of coordinating cations. The resulting solids are infinitely long one-dimensional coordination complexes (figure 2) (Lightfoot *et al.* 1993). We are not restricted to poly(ethylene oxide), many other polyether systems, and indeed many systems that are not based on ether oxygens but other coordinating groups, can also form polymer complexes. Such polymer–salt complexes are often referred to as polymer electrolytes (Bruce *et al.* 1993). They were first reported by Fenton, Parker and Wright in Sheffield (Fenton *et al.* 1973) and have been extensively developed by Michel Armand in Grenoble (Armand *et al.* 1989). These compounds are a fountain from which a rich variety of new structural coordination chemistry

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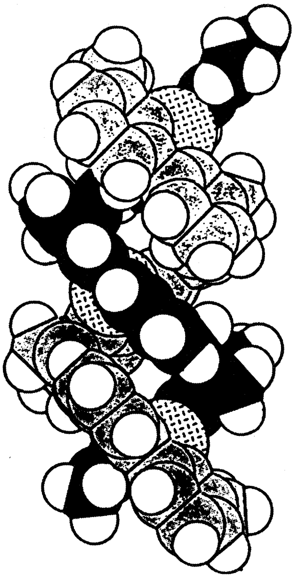

Figure 1. Part of the crystal structure of a silver trihelicate. The two ligand chains forming a double helix are composed of bipyridine groups separated by $-CH_2-O-CH_2-$. (Reproduced by permission of VCH from Lehn (1990, p. 1312).)

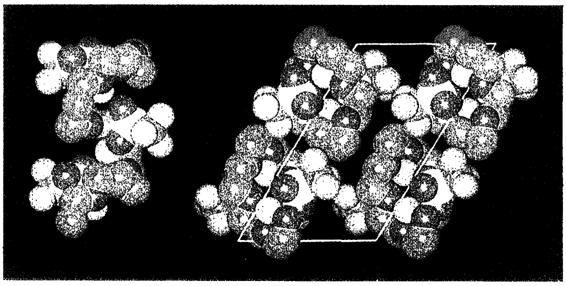

Figure 2. Part of the crystal structure of poly(ethylene oxide)$_3$:$LiCF_3SO_3$: one PEO chain with its associated ions (left); projection down the *b*-axis (fibre axis) of the unit cell showing four helical chains (right): green, carbon; red, oxygen; blue, lithium; yellow, sulphur; and pink, fluorine.

springs. Furthermore, they lead to a fascinating range of physical properties, including the ability to transport cations or anions, or both, rapidly through a solid medium. They can also act as flexible phosphors, or as electronic conductors. These unique materials are of considerable interest because of their potential applications. Their combination of solid yet flexible properties with ionic conductivity make them ideally suited for the development of all-solid-state electrochemical devices such as rechargeable lithium batteries, SMART windows and electrochromic display devices. An entire industrial technology is already developing based around these materials and will be one of the foundations of high-technology industry in the 21st century. In depth reviews of polymer electrolytes are available in the following: Bruce 1995*a*; Armand 1986; MacCallum & Vincent 1987, 1989; Ratner & Shriver 1988; Vincent 1989; Tonge & Shriver 1989; Cowie & Cree 1989; Bruce & Vincent 1993; Gray 1991; Linford 1987, 1990.

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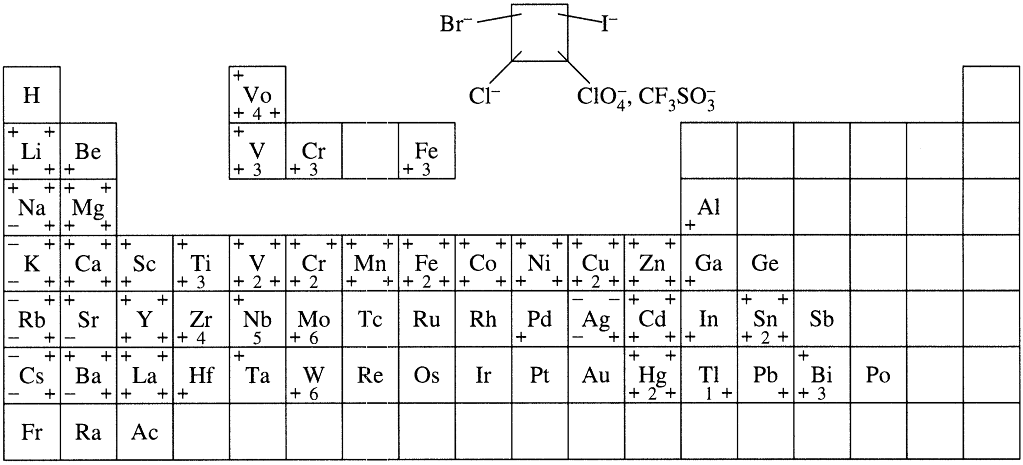


Figure 3. Part of the periodic table in which the elements marked with + form salts that are complexed by poly(ethylene oxide) and those with − do not. (Reproduced by permission of World Scientific from Armand & Gauthier (1989).)

The purpose of this article is to present, for the first time from a coordination chemistry viewpoint, the science of polymer–salt complexes. In the subsequent sections we will describe the thermodynamics controlling coordination of cations by the polymer ligands, the nature of the salt–polymer interactions, the structures of these coordination compounds, some of the exciting physical properties yielded by such materials and, finally, a brief treatment of the applications of such novel coordination compounds.

2. Why do polymers complex salts?

(*a*) *Thermodynamics of complexation*

Many salts may be coordinated by polymers (figure 3). Before considering in greater detail some of these salts and polymers, it will be helpful to develop a little of the physical principles behind the coordinations of cations by polymers. As with the coordination of cations by macrocyclic ligands, the driving force is a lowering of the free energy in the complexed state compared with the free energy of the individual salt and polymer. There are, of course, both enthalpic and entropic contributions to be considered; $\Delta G_{T,P} = \Delta H_{T,P} - T\Delta S_{T,P}$. Considering first the entropy contribution, this will be positive with respect to the salt since the ions will be more disordered when coordinated by the polymer than they are in the crystalline salt itself. It is well known that when ligands coordinate around a cation their entropy is reduced. One of the established advantages of macrocyclic ligands is that this ordering has already been introduced into the ensemble of ligating groups and therefore formation of a coordination complex involving a macrocycle costs less in entropic terms than would otherwise be the case. This is to some extent also true for polymeric ligands, however it is still the case that the entropy of the polymer chains is reduced compared with the free polymer, since complexation stiffens and thus restricts the degree of freedom available to the chains. Studies have now shown that in many cases the overall change in entropy on coordination of a salt by a polymeric ligand is negative. By implication, the driving force for complexation must be a negative enthalpy of formation. Before, however, considering the contributions to the enthalpy term, it is worth noting that since a negative ΔG of formation demands

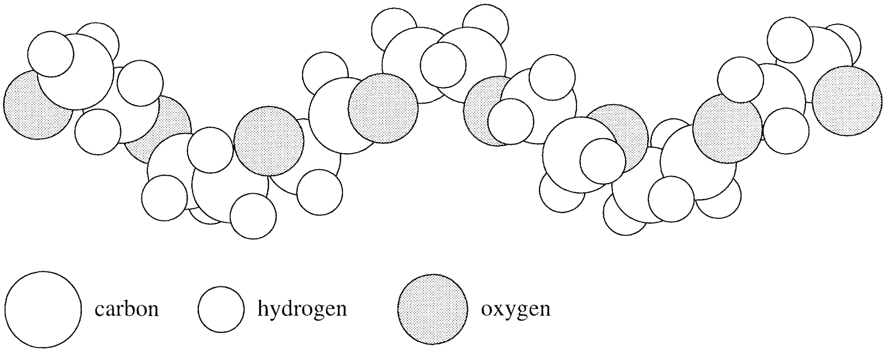


Figure 4. The structure of crystalline poly(ethylene oxide) showing the contents of one unit cell.

a negative ΔH and a positive value for $-T\Delta S$, on increasing the temperature the $-T\Delta S$ term will become a larger positive number until eventually a temperature will be reached at which dissolution will not occur. This has now been observed in many cases where upon raising the temperature of a polymer complex a point will be reached at which the salt precipitates out—a clear signature for a negative entropy of dissolution (Mehta *et al.* 1993; Cameron *et al.* 1989). We are, however, in this section, mainly concerned with the factors that promote complexation of salts by polymers and it seems clear that the dominant term controlling such a process is ΔH. The contributions which go to make up the change in enthalpy on complexation of a salt by a polymer are as follows:

(1) the lattice energy of the salt—positive ΔH^{s};

(2) the creation of suitable sites in the polymer—positive ΔH^{p};

(3) cation solvation, formation of coordinate bonds between the cations and suitable coordinating atoms on the polymer, e.g. ether oxygens—negative $\Delta H^{\mathrm{s-p}}$.

The lattice energy will vary a great deal from salt to salt. Highly charged ions with small ionic radii will lead to large lattice energies. The enthalpy required to create suitable sites for the ions within the polymer will depend on the strength of association between the groups on the polymer chains. ΔH^{p} is expected to be a less significant factor than ΔH^{s}. In the case of polymer electrolytes, the polymer acts both as the source of ligands and as the solvent, both cations and anions are embedded in the polymer matrix; however, the anions are barely coordinated by the polymer chains. They are stabilized in the polymer electrolyte mainly by their attraction to the cations. In contrast, the cations are strongly coordinated by the donor atoms of the polymer host. It is therefore clear that the principal contribution to $\Delta H^{\mathrm{s-p}}$ (the enthalpy of complexation) arises from the coordination of the polymer chains around the cation. It is the competition between this and the lattice energy of the salt which primarily determines whether a given salt will be coordinated by a given polymer.

Having considered the basic energetics involved in complexing cations by polymeric ligands, we will now look in more detail at how the chemistry, of first the ligands and then the cations, influences whether or not a complex can form and, if so, the nature and stability of that complex.

(*b*) *Polymeric ligands*

In order to coordinate cations the polymer must contain suitable donor groups, for example atoms with at least one lone pair of electrons. Many different heteroatoms

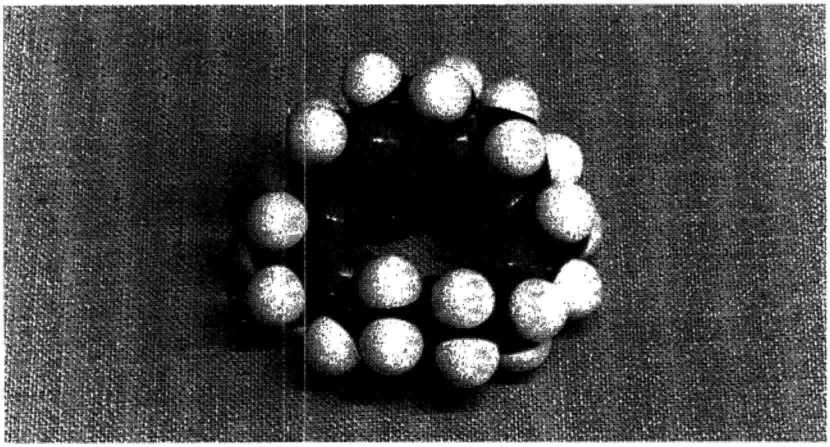


Figure 5. Molecular model of poly(ethylene oxide) showing the ability of the polymer to adopt a structure with an internal oxygen-lined environment. (Reproduced by permission of the Annual Reviews, from Cowie & Cree (1989, p. 85).)

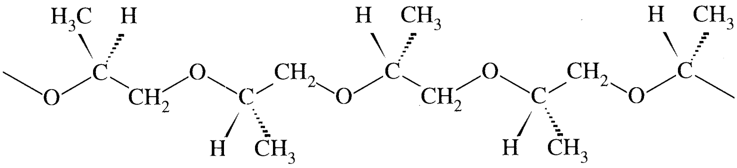


Figure 6. Molecular structure of atactic poly(propylene oxide).

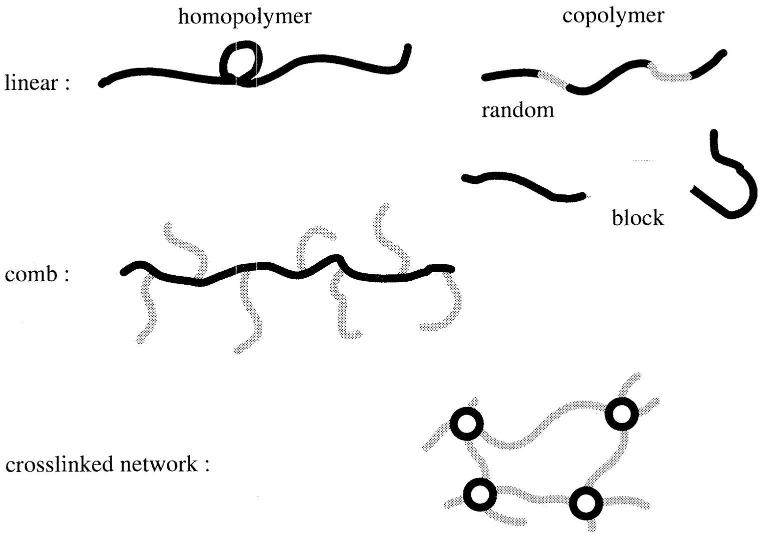


Figure 7. Possible architectures for polymer ligands.

are suitable as coordinating sites but to date by far the most common has been the ether oxygen, and of these systems high molecular weight poly(ethylene oxide) [PEO] has received the most attention. It is a semicrystalline polymer which melts at around 60 °C to produce an amorphous material. PEO can be prepared in a variety of molecular weights ranging from systems with only one ethylene oxide unit up to

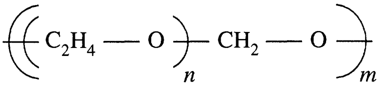


Figure 8. Methoxy linked poly(ethylene oxide).

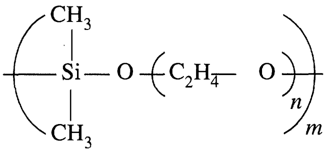


Figure 9. Dimethyl siloxy linked poly(ethylene oxide).

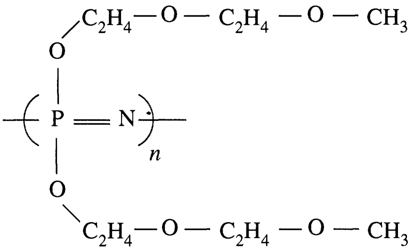
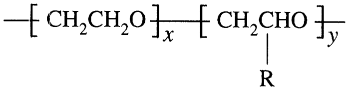


Figure 10. MEEP (poly(bis-methoxyethoxyethoxy)phosphazene)).

molecular weights in excess of 5 million. The structure of poly(ethylene oxide) is shown in figure 4. In its most stable configuration it adopts a helical conformation which provides, in each turn of the helix, a ring lined internally by ether oxygens that can accommodate cations. We can see why PEO is such a common ligand in the field of polymer electrolytes. Studies have shown that complexation by polyethers in the same family but with different repeat units, e.g. $-CH_2-CH_2-CH_2-O-$ or $-CH_2-O-$ do not provide the highly favourable coordination environment of PEO (Cowie *et al.* 1989). It appears that PEO has just the right repeat distance between the coordinating ether oxygens to provide a near ideal environment for simple cations (figure 5). A close analogue of PEO is PPO or poly(propylene oxide) (figure 6), which is also a suitable ligating polymer, but the complexes formed are less stable than the corresponding PEO systems. This is probably a result of the additional steric hindrance arising from the presence of the $-CH_3$ group on the α-carbon adjacent to the ether oxygen; its presence forces the polymer chain to adopt a more open helical structure which is less satisfactory for complexing cations. It is clear therefore that, as in the case of the crown ethers, the ethylene oxide repeat unit is an optimized building block for the formation of multidentate ligand structures with ether oxygen donor atoms. Many such systems, involving a variety of polymer architectures, have been synthesized over the last 15 years and some of the most important ones will be discussed here. The different possible architectures are illustrated in figure 7. We consider first the linear chain polymers. By introducing $-CH_2-O-$ groups between randomly variable-length segments of $(-CH_2-CH_2-O-)_n$ (n is usually between 6 and 8), the regular helical structure which promotes crystallization of the pure PEO polymer may be inhibited, thus yielding an all-amorphous linear chain polyether which, because of its similarity to PEO, is often referred to as aPEO (amorphous PEO). This amorphous polymer has a glass transition temperature of around $-65\,^{\circ}C$. After PEO, it is one of the most important polymer ligands which



$$-[\mathrm{CH_2CH_2O}]_x-[\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\mathrm{HO}]_y-$$

Figure 11. Comb-branched copolymer in which the backbone and side chains are based on ethylene oxide. R is an ether of varying chain length, typically 5 EO units.

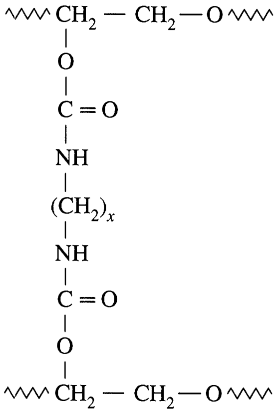


Figure 12. Urethane linked poly(ethylene oxide) chains.

has been synthesized in the last few years (Wilson *et al.* 1990). Although this polymer and its complexes with salts can crystallize below room temperature, it appears always to be amorphous above room temperature and this endows the complexes with high ionic conductivity. The structure of methoxy-linked poly(ethylene oxide) is shown in figure 8. Another important linear chain random copolymer is dimethylsiloxy linked poly(ethylene oxide) (figure 9). Here again the strategy for disruption of the regular helical structure is the same except that the $-\mathrm{CH_2}-\mathrm{O}-$ group has been replaced by a $-\mathrm{Si(CH_3)_2O}-$ unit. Turning to the comb-branched polymers, there are two systems of particular note. Amorphous comb-branched polymers with short polyether chains attached to a polyphosphazene backbone have been found to be excellent hosts for alkali metal salts (figure 10) (Blonski *et al.* 1984). This polymer host known as poly(*bis*-(methoxyethoxyethoxy)phosphazene) is fortunately abbreviated to MEEP! Important design features of such comb-branched systems are that they should possess a flexible backbone which enhances conductivity and may aid the side chains to adopt suitable conformations around the cations. The side-chains themselves can vary in length from approximately two to seven ethylene oxide units. Longer side-chains will usually permit crystallization of that part of the polymer structure which has an undesirable effect on the ionic conductivity of the materials. A second and interesting comb polymer system consists of a backbone of poly(ethylene oxide) with poly(ethylene oxide) side-chains, i.e. it has a very similar chemical composition to PEO but a comb-branched polymer architecture (figure 11) (Ballard *et al.* 1990). Simply by changing the structure from a linear chain PEO to a branched chain PEO, we inhibit crystallization while retaining good ligating properties. As an example of the final class of host polymers, we may consider the urethane-linked polyoxyethylene chains (figure 12). The urethane linkage provides an easily formed bridge between chains that yields an amorphous three-dimensional network within which salts may be dissolved.

The ethylene oxide repeat unit, although common, is not ubiquitous in the field

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Table 1. *Some other coordinating polymers which have been used as solid solvents for polymer electrolytes*

Linear		
	poly(ethylene succinate)	$[OCH_2CH_2OC(O)CH_2CH_2C(O)]_n$
	poly(dioxolane)	$-[CH_2CH_2OCH_2O]_n-$
	polyesters	$-[(CH_2)mCO_2(CH_2)_p]_n-$
Comb polymers		
	backbone	pendant chains
	$-[Si(CH_3)O]_n-$	$CH_3(OC_2H_4)_rO-$
	$-[CH_2C(CH_3)CO_2]_n-$	$CH_3(OC_2H_4)_rO-$
	styrene$-[CH_2CH(C_6H_5)]_n$	$CH_3(OC_2H_4)_rO-CH_2-$
	styrene-block-butadiene	$CH_3(OC_2H_4)_rO-$
Networks		
	crosslink	chain
	γ rays	$-(CH_2CH_2O)_r$
	$-[Si(CH_3)O]_n-$	$-(OC_2H_4)_rO-$
	$PO_4 \equiv$	$-(OC_2H_4)_rO-$

of polymer electrolytes. Other donor groups can also coordinate cations, and polymers based on these have been investigated as ligands for a variety of systems. In particular, polyethylene imines in which the ether oxygens of poly(ethylene oxide) are replaced by $-\ddot{N}H-$ or $-\ddot{N}R-$ groups $[(-CH_2-CH_2-NR-)_n]$, have received some attention (Armand *et al.* 1989). In these cases the lone pair on the nitrogens act as a suitable donor coordinating the cations. As well as the poly(ethylene imines), which are quite closely related to the poly(ethylene oxides), sulphur-based polymer ligands, $-\underset{\cdot\cdot}{\ddot{S}}-$, have been prepared, e.g. poly(alkylene sulphides) $[-(CH_2)_p-S-]$. These, by analogy with the thio crown ethers, can also form polymers which are capable of coordinating a variety of cationic species (Shriver *et al.* 1995). Some other examples of polymeric ligands which have been studied are given in table 1.

Since the strength of interaction between cations and the heteroatoms of the polymer chain is the main factor determining whether complexation will occur for any given combination of cation and polymer, the hard–soft acid base (HSAB) theory developed originally by Pearson (1963) is of considerable value (Bruce *et al.* 1988). In this classification, ether oxygens are regarded as hard bases and will interact most strongly with hard cations, whereas sulphur is a soft base and will form strong interactions with the softer cations. In the next section the cationic species which are coordinated by the polymer hosts will be discussed and the interactions between them and the polymers will be considered further in the light of the HSAB theory.

(*c*) *Cations suitable for coordination*

A very wide range of cations may be complexed by polymeric ligands as is demonstrated by reference to figure 3. The salts of only a few anions are represented in the figure, many more are possible although monovalent polyatomic anions are favoured. So far the majority of salts which are known to interact with polymers containing heteroatoms are based on monatomic cations. The variety of monatomic cations is rich and includes mono-, di- and trivalent cations from the s, p, d and f blocks of the periodic table. Because of the range of such cations that may be complexed by polymers, the resulting systems exhibit diverse physical properties, as discussed in a later section. A brief examination of figure 3 illustrates that, provided one confines attention to monatomic cations, there are few restrictions on the possible choices of system. Evidently, size is not a factor which limits the coordination of cations by the polymer host; furthermore, this process is not limited by the electronic structure of the ions. As eluded to in the previous section, we can use the HSAB model to understand and systematize the interaction between cations and their various polymer hosts. Hard cations (acids) such as Mg^{2+} will be complexed most strongly by hard donor atoms (bases) such as ether oxygens, and indeed magnesium salts such as $Mg(CF_3SO_3)_2$ or $Ca(CF_3SO_3)_2$ can be incorporated up to a high concentration in poly(ethylene oxide). In contrast, soft acids such as Ag^+ are likely to be more strongly complexed by the thio ethers. This is not to say that soft cations cannot be complexed by hard ligands. An important example is the ability to complex $Hg(ClO_4)_2$ containing the soft Hg^{2+} cation by poly(ethylene oxide) (Bruce *et al.* 1988); however, in general, the HSAB theory has proved a very useful means of classifying the coordination of cations by polymeric ligands.

Direct evidence for the coordination of cations by polymers has been obtained by a variety of spectroscopic techniques, in particular infrared and Raman spectroscopy have played an important part in studying the local coordination environment (Torell *et al.* 1989; Frech *et al.* 1988). In these studies, low frequency vibrational modes in the region 660–670 cm^{-1} (which are associated with cation to ether oxygen interactions) have been observed. These are absent in the pure PEO host itself. Undoubtedly, the most detailed information concerning the coordination of cations by the polymer hosts has come from specific structural studies of these systems, as discussed in the following section.

3. The structure of polymer–salt complexes

In the case of polymer–salt complexes, as in many areas of chemistry, a knowledge of structure is the foundation on which our understanding of the chemical and physical properties of such compounds must be based. Despite this, the structures of polymer complexes have remained frustratingly elusive since they were discovered over 20 years ago. These compounds can be prepared as either crystalline or amorphous solids, frequently with the same composition. The crystalline solids melt at a relatively low temperature to form liquids which are more usefully regarded as amorphous solids since they have the bulk mechanical properties of solid materials. In general, investigation of the crystalline state of matter is easier than studying the amorphous state, also far more detailed and precise information may be gained from crystal structures. To take an example from the field of solid state inorganic chemistry, it would be unthinkable to attempt an investigation of the structure of amorphous SiO_2 without first establishing the crystal structure of quartz. Therefore, our quest for a knowledge of polymer electrolyte structure should begin with the crystalline complexes, despite the fact that it is the amorphous complexes which conduct. PEO forms crystalline complexes with many salts. Unfortunately, the established techniques based on single-crystal X-ray diffraction are not well suited to the investigation of polymer–salt complexes. The data is almost invariably of low quality and difficult to analyse. A breakthrough has recently been made by the application of state-of-the-art high-resolution powder X-ray crystallography to this problem. It is now possible to prepare samples of polymer–salt complexes which give high quality powder X-ray diffraction data and, as a result, the crystal structures of several important complexes have now been established using this technique. These studies have revealed a wealth of structural information and it is therefore appropriate that we examine some of these crystal structures.

(*a*) Poly(ethylene oxide)$_3$: $LiCF_3SO_3$

The archetypal polymer–salt complex is $LiCF_3SO_3$ coordinated by PEO. More papers have been published on this material than on any other polymer electrolyte, due largely to its use as a lithium-ion conducting electrolyte in rechargeable lithium batteries (MacCallum *et al.* 1987, 1989). The crystal structure of the complex formed with a composition of three ether oxygens per lithium ion is shown in figure 1 (Lightfoot *et al.* 1993). Starting first with figure 1*a*, which consists of just one part of one PEO chain with its associated ions, we can see that the PEO chain in this crystalline complex retains a helical conformation. Within each turn of the helix is located a lithium ion. The analogy with a stack of crown ethers covalently bonded together is obvious! The lithium ions fit neatly into the helix and are coordinated directly by three ether oxygens from the chain. The coordination environment is completed by two further oxygens, one from each of two triflate anions, thus forming a five-coordinate arrangement around the lithium ions in approximately a trigonal bipyramidal geometry. The distances from the Li^+ ion to its five nearest-neighbour oxygens are given in table 2. Interestingly, the triflate anions bridge neighbouring lithium ions along the chain by donating one of their oxygens to each of two lithiums. The remaining oxygen of each triflate group is uncoordinated. It is evident that the $-CF_3$ groups of the triflate anions sit outside the dimensions of the helix. Figure 1*b* shows a projection down the *b*-axis of the unit cell, which coincides with the fibre axis and is also coincident with the 2_1 screw axis of the helix. A number of important consequences arise from the information contained in this figure. First, it is evident that 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 one-dimensional coordination complex. Interchain interactions are of second order compared with the intrachain interactions. This structure already suggests that melting will involve the loss of the weaker interactions between the chains before any dissociation of the ions from their PEO chains. Recent results, which we have obtained by combining crystallographic and spectroscopic studies, appear to reinforce these views.

We have carried out variable temperature X-ray powder diffraction and infrared spectroscopy on the $PEO_3 : LiCF_3SO_3$ composition from room temperature passing through the melting transition at 179 °C, and on up to 250 °C (Bruce *et al.* 1995). These results indicate that there is no change in the structure of the individual chains on melting. The infrared spectroscopy probes, in particular, the vibrational states of the triflate anions; it is able to distinguish between triflate anions that are free and those that have lithium ions directly attached to the oxygens of the anion. Only one triflate species is evident in the spectrum of the crystalline state, and from the crystal structure data it is clear that this is a triflate ion with one lithium ion attached to each of two oxygens of the triflate. On melting no other triflate species are detected suggesting that the triflate ions remain attached to two lithium ions simultaneously and that, furthermore, short chains of $-Li^+-CF_3SO_{3^-}-Li^+-$ must be present in the amorphous state! Thus, by combining the crystallography and

Table 2. *Nearest-neighbour contact distances around* Li^+ *in* $PEO_3 : LiCF_3SO_3$

(O1–3 represent ether oxygens, whereas O5 and O6 represent triflate oxygens. ESDs are given in parenthesis.)

	bond length /Å
Li1—O1	2.38(9)
Li1—O2	2.01(8)
Li1—O3	1.72(7)
Li1—O4	2.21(8)
Li1—O5	2.14(8)

spectroscopy, unpresidented insight has been gained into the structural chemistry of these materials which has not been possible by extensive studies over the last 20 years using spectroscopic techniques alone. This greater insight into the structure of the amorphous materials, in particular, is of considerable importance since ionic conductivity is confined largely to these phases.

A knowledge of the crystal structures is not only useful in its own right and as an essential element in building an understanding of the structure of amorphous phases, it also helps us to design new polymer electrolytes in which the crystallinity is supressed and, as a result, conductivity maximized. In figure 1 it is clear that the $-CF_3$ groups are located outside the dimensions of the helix and within the interchain space. By selecting anions which satisfy the coordination requirements of the Li^+ ion, but at the same time place more atoms in the interchain space, it should be possible to disrupt the crystallinity of the material (which depends on achieving a regular crystallographic register between the chains), hence promoting the formation of an amorphous phase. This is exactly what is found in practice. We can replace the $CF_3SO_{3^-}$— anion in $PEO_3 : LiCF_3SO_3$ by the imide anion $[(CF_3SO_2)_2N]^-$. The latter may be derived from the former by replacing one of the oxygens of the $-SO_3$ group by a nitrogen with a $-CF_3SO_2$ group attached. The additional $-CF_3SO_2N$ along with the original $-CF_3$ group are now located in the interchain space, which thus places far more atoms in this space than is the case for the analogous triflate complex. As a result, it is more difficult for the chains to line up and therefore crystallization is inhibited. Consequently, the melting temperature drops from 179 °C, in the case of the lithium triflate complex, to around 80 °C, in the case of the imide complex. Furthermore, it is much easier to quench amorphous polymer electrolytes at compositions other than 3:1 when formed using the lithium imide salt. This example demonstrates clearly the power of crystallographic studies in developing strategies for the design of new polymer electrolytes which are highly amorphous. The improved conductivities obtained using the imide system are shown in figure 17.

(*b*) Poly(ethylene oxide)$_4$: $K(NH_4)SCN$

The crystallographic studies have been extended to other polymer–salt complexes with larger cations. It is worth considering two specific examples in more detail: $PEO_4 : KSCN$ and $PEO_4 : NH_4SCN$. The crystal structures of both these complexes are similar, the structure of the KSCN system is shown in figure 13 (Lightfoot *et al.* 1994). The cations are again located in each turn of the helix but, as a result of the larger size of the potassium and ammonium cations compared with lithium, they are

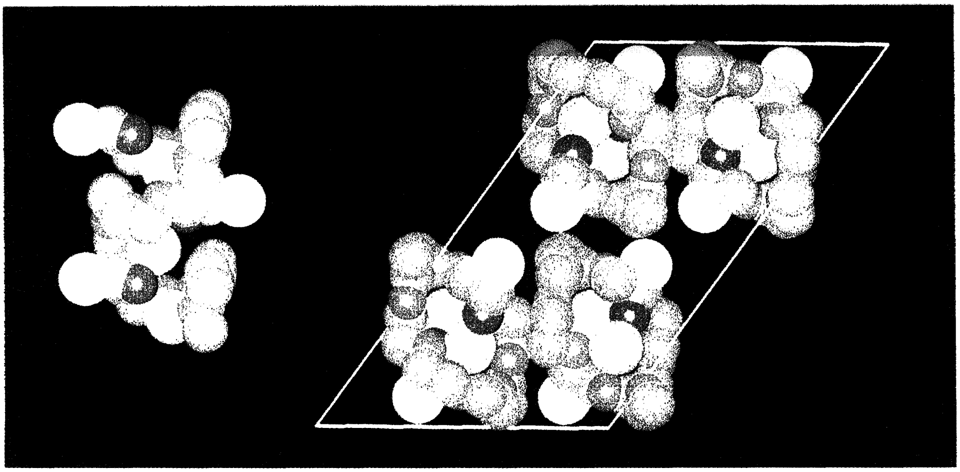

Figure 13. Part of the crystal structure of $PEO_4 : KSCN$: one chain with its associated ions (left); a projection down the *b*-axis (fibre axis) of the unit cell (right): green, carbon; red, oxygen; light blue, potassium; dark blue, nitrogen: yellow, sulphur.

each now coordinated by five ether oxygens. Three of the ether oxygens are coordinated to only one cation, whereas the remaining two bridge between neighbouring cations. This is in contrast to the structure of the $PEO_3 : LiCF_3SO_3$ complex in which the three ether oxygens coordinating each lithium were not coordinated to any other species (figure 1). In order to accommodate these larger cations, the PEO chain, which remains helical, changes its conformation. Within the basic repeating unit, $CH_2{-}CH_2{-}O$, the C—O bonds are in all cases *trans*, but the C—C bonds can adopt a gauche or gauche minus conformation. In the case of the $PEO_3 : LiCF_3SO_3$ complex, the conformational repeat is ttgttgttḡ, whereas in the case of complexes with the larger K^+ and NH_4^+ cations the repeat unit is ttgttgttḡttḡ. The latter conformation provides a wider helix with a larger pocket, lined with five ether oxygens, necessary to accommodate the larger cations. A further consequence of the alternate configuration is that four ethylene oxide units are contained within the fibre repeat distance, as opposed to three such units in the case of the 3:1 complex. Coordination around the cations is completed by one nitrogen from each of the two thiocyanate groups providing a seven-coordinate environment for the cations. Again, each anion bridges two neighbouring cations. Although the crystal structures of $PEO_4 : KSCN$ and $PEO_4 : NH_4SCN$ are identical, the dimensions are, of course, different, since the ammonium ion is somewhat larger than the potassium ion (see table 3).

(*c*) *General structural principles of polymer–salt complexes*

Reliable crystal structures have also been determined for four other complexes: $PEO_3 : NaClO_4$ (Lightfoot *et al.* 1992), $PEO_3 : NaI$ and $PEO : NaSCN$ (Chatani *et al.* 1987, 1990) as well as $PEO_4 : RbSCN$ (Bruce 1995*b*; Thomson *et al.* 1995). In the case of $PEO_3 : NaClO_4$, the structure is similar to that of $PEO_3 : LiCF_3SO_3$ with ClO_{4^-} replacing $(CF_3)SO_{3^-}$ except that the coordination around the Na ion is six, i.e. four ether oxygens plus one oxygen from each of two perchlorate ions. Two oxygens from each ClO_{4^-} bridge two neighbouring Na^+ ions. In the case of $PEO_3 : NaSCN$ the coordination around Na^+ is again six (four ether oxygens plus two anions) with each anion bridging two neighbouring Na^+ ions. The structure of

Table 3. *Nearest-neighbour contact distances around* K^+ *and* NH_4^+ *in, respectively,* $PEO_4 : KSCN$ *and* $PEO_4 : NH_4SCN$.
(Note that the H atoms on NH_4^+ could not be located by powder X-ray diffraction.)

$PEO_4 : KSCN$		$PEO_4 : NH_4SCN$	
	bond length /Å		bond length /Å
K1—O1	2.79(2)	N1—O1	3.11(2)
K1—O2	2.63(2)	N1—O2	2.88(2)
K1—O3	2.83(3)	N1—O3	3.04(2)
K1—O4	2.96(2)	N1—O4	3.16(2)
K1—O4′	3.09(2)	N1—O4′	2.91(2)
K1—N	3.05(4)	N1—N2	2.96(2)
K1—N′	2.74(2)	N1—N2′	2.68(2)

the $PEO_4 : RbSCN$ complex is very similar to the potassium and ammonium systems with the same local coordination and chain conformation.

Although the structural studies are, as yet, limited, we may tentatively examine the general trends which are emerging. Crystal structures are now available for cations ranging in ionic radius from 0.76 Å (Li^+) to 1.52 Å (Rb^+). The basic structural details for the main systems studied so far are summarized in table 4. In all cases the polymer–salt complex consists of isolated infinitely long one-dimensional coordination complexes, each composed of a helical PEO chain with a dedicated set of ions. Average cation–ether oxygen bond lengths for the alkali metal PEO complexes vary from 2.04 Å in the case of Li^+ to 3.01 Å in the case of Rb^+. It has long been held that cations larger than sodium could not be accommodated inside the helix but were instead located in the interchain space. The recent crystallographic studies demonstrated unequivocally that this view is entirely erroneous and that even cations which are double the size of lithium can be located inside the helix, albeit with a change in chain conformation. This demonstrates the crucial impact crystallographic studies are having on the field.

It is interesting and informative to compare the local coordination around the cations in polyether complexes with those in the simple crown ethers, since the latter are the macrocycles most closely analogous to polyethers. Consider the sodium complexes. Na^+ achieves the highest stability in 18–crown–6, in which the cation exhibits a coordination number of six involving complexation by the six oxygens of the crown. In the polyether, Na^+ is coordinated by only four ether oxygens, the preferred coordination of six being completed by two anions. PEO can provide a pocket with more than four ether oxygens in the coordination sphere as demonstrated by the $PEO_4 : KSCN$ complex, but in that case the cation to ether oxygen distance would be too large for Na^+, hence the adoption of the $(4 + 2)$-configuration for sodium. It is evident that the structures of the polymer–salt complexes are governed by the desire to adopt a helical conformation for PEO as well as the need to achieve a preferred cation to ether oxygen bond length, with the anions making up the desired coordination number. Potassium ions are stable in 18–crown–6, but in addition anions occupy the apical positions. In the case of ligation by PEO, the structure is similar but with only five ether oxygens in the ‘ring’. Finally, it is important to note that

Table 4. *Basic structural details of some polymer–salt complexes*

(Ionic radii are taken from Shannon & Prewitt (1969, 1970), and are based on a six-coordinate oxygen environment.)

	PEO	PEO conformation	ionic radius of cation /Å	no. of ether oxygens	no. of anions	total coordination number
$PEO_3 : LiCF_3SO_3$	helix	ttgttgttḡ	0.76	3	2	5
$PEO_3 : NaClO_4$	helix	ttgttgttḡ	1.02	4	2	6
$PEO_4 : KSCN$	helix	ttgttgttḡttḡ	1.38	5	2	7
$PEO_4 : NH_4SCN$	helix	ttgttgttḡttḡ	1.61[a]	5	2	7
$PEO_4 : RbSCN$	helix	ttgttgttḡttḡ	1.52	5	2	7

[a] There is considerable debate concerning the effective ionic radius of NH_4^+; it can vary substantially from solid to solid. Our lattice parameter measurements place it between K^+ and Rb^+ in polyethers.

in all the polymer systems studied so far there is clear evidence of direct-contact ion pairing between the cations and the anions. The conformational restraints of the PEO chains make it impossible for one PEO chain to saturate the coordination requirements of cations even as small as Li^+.

4. Properties of polymer electrolytes

(*a*) *Conductivity*

Unquestionably the most important property of polymer electrolytes is ionic conductivity. The ability to formulate polymer–salt complexes into thin films capable of transporting ions has already resulted in a massive worldwide effort geared to the development of devices based on these materials. It is important to contrast ionic transport in conventional liquid electrolytes from that in solid polymer electrolytes. Indeed the contrast comes into sharpest focus when one considers the changes which occur on dissolving a salt in a low molecular weight liquid ether and then permitting the molecular weight of the ether ligands complexing the salt to rise continuously so that we pass from the liquid state through the waxes to the solid. In liquids, ions move with their coordination spheres intact; however, in the solid state this cannot happen. The groups coordinating the ions are in the latter case attached to a polymer chain and cannot be transported over long distances; it is therefore necessary for the ions to dissociate, at least to some extent, from their coordination sphere in order to move through the polymer matrix. Evidently, in low molecular weight liquid ethers, or for that matter in complexes formed with crowns or cryptands, the strength of binding between the cation and its coordinating atoms has no direct influence on the mobility of the ion (more correctly the ion complex). The reverse is true in the case of polymer electrolytes, where strong binding would result in an immobile ion. The HSAB theory can provide a guide to the likely lability of a cation. In the case of polyether ligands, which are hard bases coordinating cations which are hard acids, such as Mg^{2+}, the strong binding gives rise to immobile cations. Of those magnesium complexes with polyethers which have been studied, the cations are invariably found to be immobile (Farrington *et al.* 1989). On the other hand, cations which are relatively soft acids coordinated by hard bases are likely to yield mobile cations. An example of this class are the complexes formed between poly(ethylene oxide) and Hg^{2+} salts, e.g. $Hg(ClO_4)_2$. In this case, the divalent cation is found to be highly mobile (Bruce *et al.* 1988). In general, with high molecular weight ligands, there is a delicate balance between sufficiently strong cation–ligand interactions required to promote formation of the complex and sufficiently weak interactions required to promote mobility of the cations.

So far we have concentrated on the mobility or otherwise of the cations. Since the anions interact relatively weakly with the polymer chains, in all cases they are generally mobile unless directly attached to the polymer backbone by a covalent linkage. Under this latter circumstance a transport number of unity for the cations would be anticipated. Such a material, in which the anions are directly linked to the matrix, is termed a polyelectrolyte, the classic example of which is Du Pont's NAFION, well known as a proton conducting membrane. These materials contain fluorosulphonate anions attached to the polymer backbone (Shriver *et al.* 1995).

Since the ability to exchange cations between coordinating sites on the polymeric ligands is essential for ion transport to occur in polymer electrolytes, it will not be surprising that the rate of ligand exchange reactions has a significant bearing on ionic conductivity. It is perhaps more surprising that there is a close correlation between the mobility of cations in polyether-based electrolytes and the rate of exchange of water molecules surrounding the same cations when dissolved in aqueous solutions. Figure 14 summarizes the rates of water exchange in the first coordination sphere around a series of cations. Also indicated in the table is the generally accepted view concerning the mobility of the same cations when coordinated by polyethers. It is evident that the cations which undergo fast water exchange are also mobile in poly(ethylene oxide), whereas the group of cations which undergo slow exchange of water molecules are found to be immobile in the polyethers. Cations such as Cu^{2+} are particularly interesting since it is anticipated that their Jahn–Teller activity is related to the rapid water exchange, since this can promote easy access to the activated state. Cu^{2+} salts in polyethers are notoriously difficult to study and exhibit rather anomalous behaviour; nevertheless, it seems generally agreed that Cu^{2+} ions are indeed mobile in polyethers (Bonino *et al.* 1988).

For ions to be transported in solid polymers it is necessary not only for there to be rapid exchange of the ions between the ligating groups, but, in addition, the polymer chains must move in order to create new coordination sites to which the cations may migrate (figure 15). The level of mobility, and therefore the level of conductivity, depends on the probability of creating suitable coordination sites adjacent to already occupied sites. The greater the polymer chain dynamics, then the higher the probability of creating such sites and hence the greater the mobility, provided the ligand exchange rate is also high and therefore not rate limiting. It is for this reason that ion transport is confined to the amorphous complexes above their glass transition temperature. More sophisticated theories have been developed in order to describe the process of ion transport through a dynamic polymer environment, such as the dynamic bond percolation model (Ratner *et al.* 1989). These have achieved some success in describing the basic processes of conductivity in polymer electrolytes.

It is interesting to consider the implications which the structural data presented in the previous section have for the nature of ionic conductivity in polymer electrolytes. In the early days of study in this field it was assumed that cation transport would occur by the ions moving along the one-dimensional channels formed by the helices

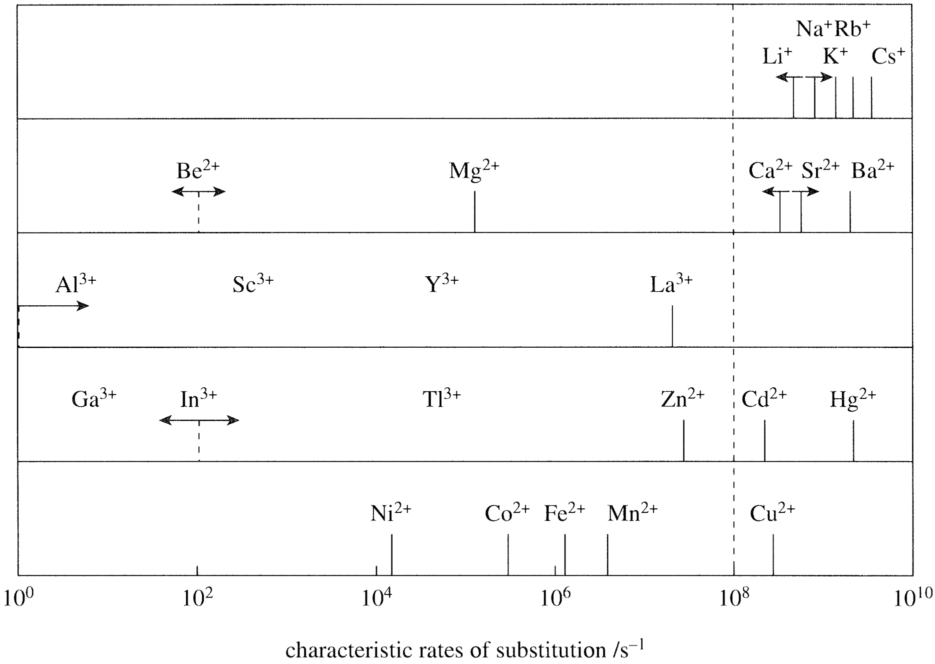

Figure 14. Characteristic rate constants for H_2O substitution in the inner coordination sphere of metal ions. The dotted line represents the division between mobile and immobile ions in PEO. (H_2O data reproduced with permission from IUPAC, Eigen (1963).)

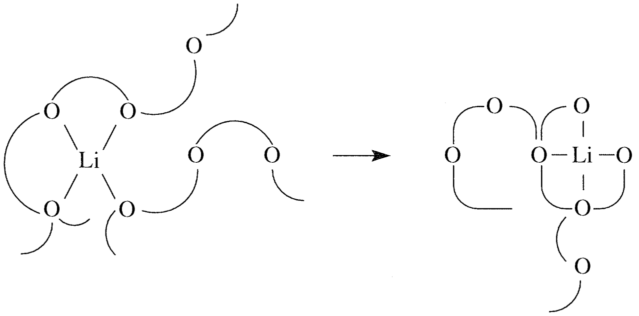

Figure 15. Cartoon of Li^+ ion motion illustrating the handing-on of the cation from chain to chain.

and that crystalline polymer electrolytes may therefore have the highest conductivity. These ideas were based on the established views of ion transport in ceramic materials such as sodium β-alumina. It was later shown that ionic conductivity is confined to the amorphous complexes. As a result, a picture of ions moving somewhat randomly through a totally non-structured environment prevailed. However, the recent structural results bring us back again to consider the view that cation transport may well occur along the helices, since in all the structures studies so far the cations appear to reside within the dimensions of the helix. Of course, such ion transport will be facilitated by the polymer chain dynamics and one may envisage concertina modes along the chains as being important here. These ideas have, at present, the status of a hypothesis which we may be sure will receive considerable examination over the next few years. It has also been known for a long time that on increasing the salt concentration in an amorphous polymer electrolyte, the conductivity would eventually decline and that this decline was associated with an increase in the glass transition temperature, indicative of a stiffening of the polymer chains. It had been widely believed that this was associated with ionic crosslinking between the chains. The recent structural results suggest that this is not the case and that the rise in Tg, and hence reduction in conductivity, is due to intrachain crosslinking. This view is consistent with recent results which probe the dynamics of the system with pulsed field gradient NMR (Ward *et al.* 1995).

(*b*) *Optical properties*

Ionic conductivity is not the only property that polymer–salt complexes possess. By dissolving suitable lanthanide salts in PEO it may be possible to prepare low-cost plastic phosphors or other luminescent materials. The ease with which such materials could be processed into a variety of (particularly curved) shapes makes this an attractive prospect and one worthy of further study. In fact, here again, we make contact with the coordination chemists since J.-M. Lehn has suggested a related approach using lanthanide complexes (e.g. europium cryptates containing N-oxide ligands) which could be embedded in polymers. The ligand absorbs the light more efficiently than the lanthanide ion, energy is then transferred to the ion and emitted (Lehn 1990).

(*c*) *Mixed conduction*

Another intriguing possibility is to combine, on the nanoscopic scale, electronically conducting polymers with covalently attached polymer–salt complexes, leading to elegant systems with ionic and electronic conductivity. This has recently been taken to new and imaginative heights by M. Armand who has constructed electronically conducting lamella with polymer–salt complexes located between the planes (Armand 1995).

5. Applications

An article such as this would not be complete without some brief discussion of the applications to which polymer electrolytes may be put since this represents a considerable driving force for research in the field. Polymer electrolytes combine, almost uniquely, the properties of a solid but flexible material with high ionic conductivity. As a result, these complexes may be used to replace conventional liquid electrolytes, leading to the fabrication of all-solid-state electrochemical devices. The three main applications of polymer electrolytes presently under investigation are, lithium batteries, smart windows and electrochromic displays. Let us consider first lithium batteries.

(*a*) *Lithium batteries*

A schematic representation of a rechargeable lithium polymer battery is shown in figure 16. This application dictates that, in addition to the above requirements, polymer electrolytes must possess excellent stability towards the highly reducing environment at the negative electrode and highly oxidizing environment at the positive electrode, the ability to be processed as a thin film, and of course it must be cheap (Gauthier *et al.* 1989). Conductivities for the three basic classes of polymer electrolyte which have been considered for applications in lithium batteries are shown in figure 17. Early technological developments concentrated on the simplest systems based on poly(ethylene oxide) which has acceptable conductivities only above about 80 °C. The enhanced conductivity possible by switching to salts which inhibit crystallization, such as lithium imide (discussed in § 3), is evident. However, even this material will probably confine the use of the batteries to temperatures of around 50–100 °C. In order to achieve high currents and, hence, high rates of discharge at room temperature and below, it is necessary to add low molecular weight solvents to the polymer electrolyte, forming plastercized materials such as the poly(acrylonitrile) (PAN)-based system shown in figure 17. The solvent is believed to play two roles. First, it acts to 'lubricate' the polymer chains, thus increasing their flexibility and local motion—as a result the ion mobility is greater than in the absence of plastercizer. Second, the solvent ion promotes the dissociation of ion pairs, thus increasing the concentration of charge carrying ions. The relative contribution that these two mechanisms make to enhancing ion transport will vary from system to system. These plastercized materials represent a fascinating class of compounds which, although not true solid polymer electrolytes, do exhibit some interesting coordination chemistry since the cations can be simultaneously ligated by the host polymer and the molecules of the plastercizer. Space does not permit us to discuss these materials in more detail here. It is worth just mentioning one new plastercized polymer electrolyte which is based on a kynar host polymer (a copolymer of vinylidene fluoride and hexafluoropropylene) in which $LiPF_6$ is dissolved along with a mixture of dimethyl carbonate and ethylene carbonate. This new polymer electrolyte appears to exhibit the most attractive compromise between the properties listed above (Tarascon 1994). As a result, it is likely to form the basis of the first commercial all-solid-state lithium polymer battery, which is currently at an advanced stage of development. A major attraction of the polymer electrolyte concept is that lithium batteries may be fabricated by a continuous rolling process in which a thin film of the cathode material can be rolled out on a metal substrate, a thin polymer film can then be applied to the cathode and a lithium metal or carbon anode applied on top of this, again with a metal backing such as nickel or copper foil. The thickness of the entire laminate can be as little as 30–50 μm. Large numbers of cells may be constructed in a highly automated and rapid manner, thus leading to a low cost of construction. In addition, the laminate can be rolled up in a 'Swiss-roll' fashion to produce a highly compact power source or prepared in a variety of other shapes as desired. Finally, the high proportion of active material in the entire cell construction ensures a high gravimetric energy density, higher than is possible with liquid electrolyte systems, leading to very light weight battery designs.

(*b*) *Electrochromic devices*

Like the lithium batteries, these are polymer-electrolyte-based all-solid-state electrochemical cells (figure 18). Two related technologies are under development. The first is a smart window, i.e. an electrochemical cell which when fully charged is transparent but when slightly discharged will convert to an opaque state; on recharging the cell the transparent state can be reclaimed and this process may be carried out hundreds of thousands of times. In the case of the example shown in figure 18, the device is transparent when lithium ions are located in the thin nickel oxide layer; however, on transfering the lithium ions across the polymer electrolyte and into the WO_3 layer, at the same time as the charge compensating electrons passed round the external circuit, a lithium tungsten bronze is formed and the device becomes opaque.

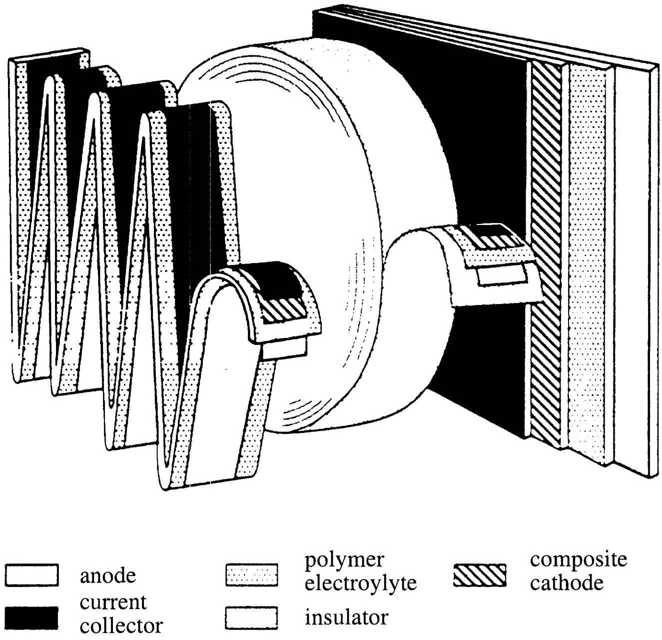

Figure 16. Various configurations for extended-area polymer electrolyte batteries. (Reproduced by permission of VCH from Gray (1991).)

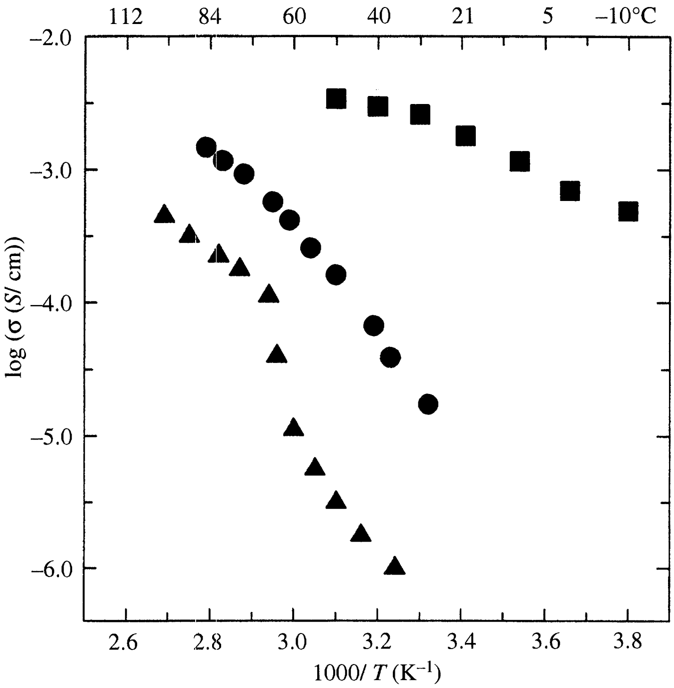

Figure 17. Temperature dependence of ionic conductivity for examples of the three main classes of polymer electrolyte: ▲, PEO$_8$: LiCF$_3$SO$_3$; •, PEO$_8$: Li[(CF$_3$SO$_2$)N]; ■, polyacrylonitrile containing a 1 : 1 ratio of ethylene carbonate to propylene carbonate and 3 mole % LiAsF$_6$.

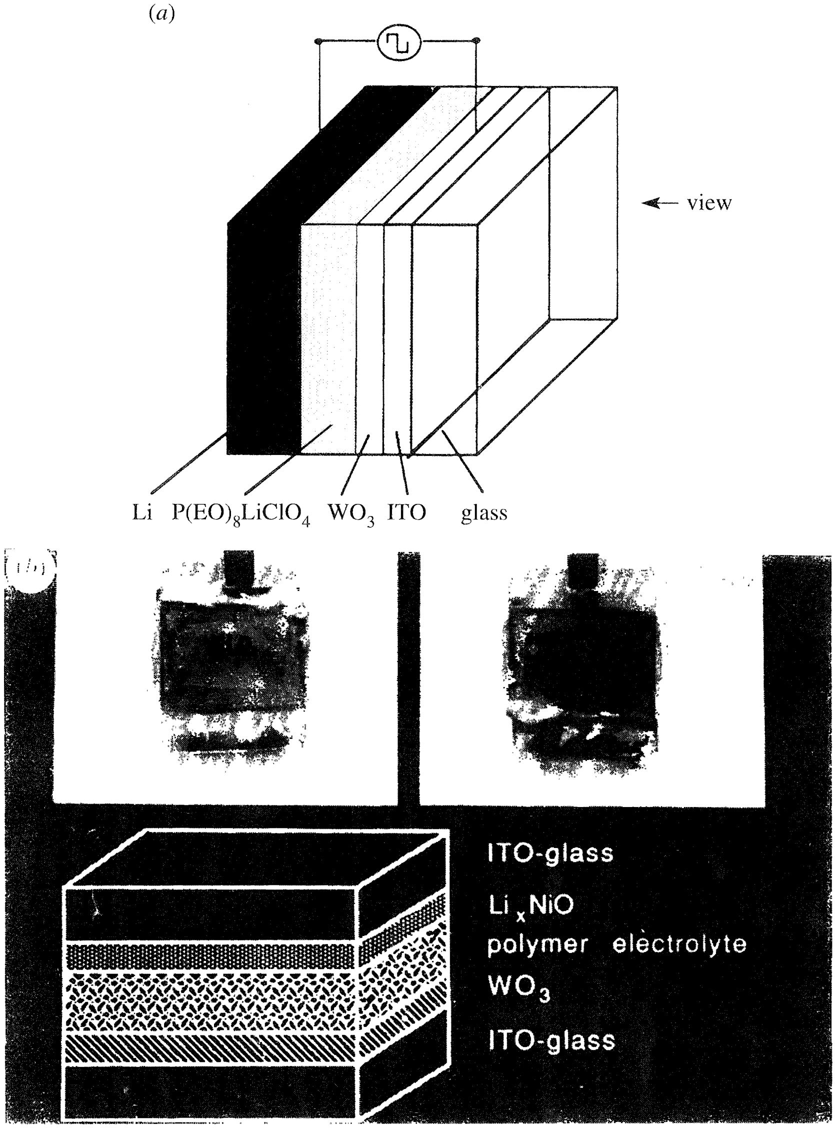

Figure 18. (*a*) Schematic diagram of a solid-state electrochromic display using a polymer electrolyte. (Reproduced by permission of VCH from Gray (1991).) (*b*) Bottom, schematic of an electrochromic (smart) window; top, a laboratory prototype showing the transparent (left) and opaque (right) states.

Such devices are envisaged for applications such as car sun-roofs and as window glass in buildings in warm climates so that the degree of heating from natural sunlight can be controlled and therefore the need to burn fossil fuels in air conditioning systems may be greatly reduced. The latter is a vital environmental concern in the USA, where more fossil fuel is burned in running air conditioning in summer than in heating buildings in winter. The second related application is that of electrochromic displays. This is viewed in reflection rather than in transmission, but operates in a similar fashion to a smart window (figure 18). Again, on discharging the cell, lithium tungsten bronze is formed at the positive electrode, which gives rise to an intense blue colour in reflection. Display devices of this type require no power to remain in the on state and have excellent perceived contrast. They are envisaged for use as large area displays, such as indicator boards at railway stations (Monk *et al.* 1995).

6. Future directions

The inevitable limitations of space have precluded discussion of many interesting topics in the field of polymer–salt complexes. It is apposite to briefly mention some of those which are still embryonic but which will become major areas of research over the next few years. The first of these is the further combination of spectroscopic and crystallographic studies directed towards a better understanding of the structure of polymer–salt complexes in the amorphous (conducting) state. Techniques such as Raman and infrared spectroscopy, magic angle spinning NMR, and EXAFS, which have been exploited individually in the past, will be combined to yield major advances in our structural understanding in the future. Another vital area will be the use of computer simulation techniques to investigate the structural features of polymer electrolytes as well as the dynamics of both the chains and the ions. The challenge, as ever, is to find the most appropriate potentials, particularly for the interactions between the ions and the polymer chains; important progress is being made in this area (Mills *et al.* 1994). Some of the early studies have served to indicate the exciting possibilities (Xie *et al.* 1992). It is also hoped that the future will see a greater use of the wide range of other techniques which are common in coordination chemistry but have not been widely applied to polymer electrolytes. In particular, we may think of those techniques such as UV-visible spectroscopy, magnetic measurements and some laser spectroscopic methods, as well as electron spin resonance. These will be particularly useful in studying the transition metal-, lanthanide- and actinide-based systems which have received only limited attention. Some pioneering studies, particularly in the use of UV-visible spectroscopy, have been carried out by Farrington's group at the University of Pennsylvania (Mendolia *et al.* 1993).

I apologise to my colleagues in the field of polymer electrolytes for the many omissions in part arising from my desire to emphasize the coordination chemistry of polymer–salt complexes. However, if this article has served, even in a small way, to enthuse more coordination chemists to consider applying their talents to the field of polymer–salt complexes then, despite its flaws, it will have more than served a useful purpose.

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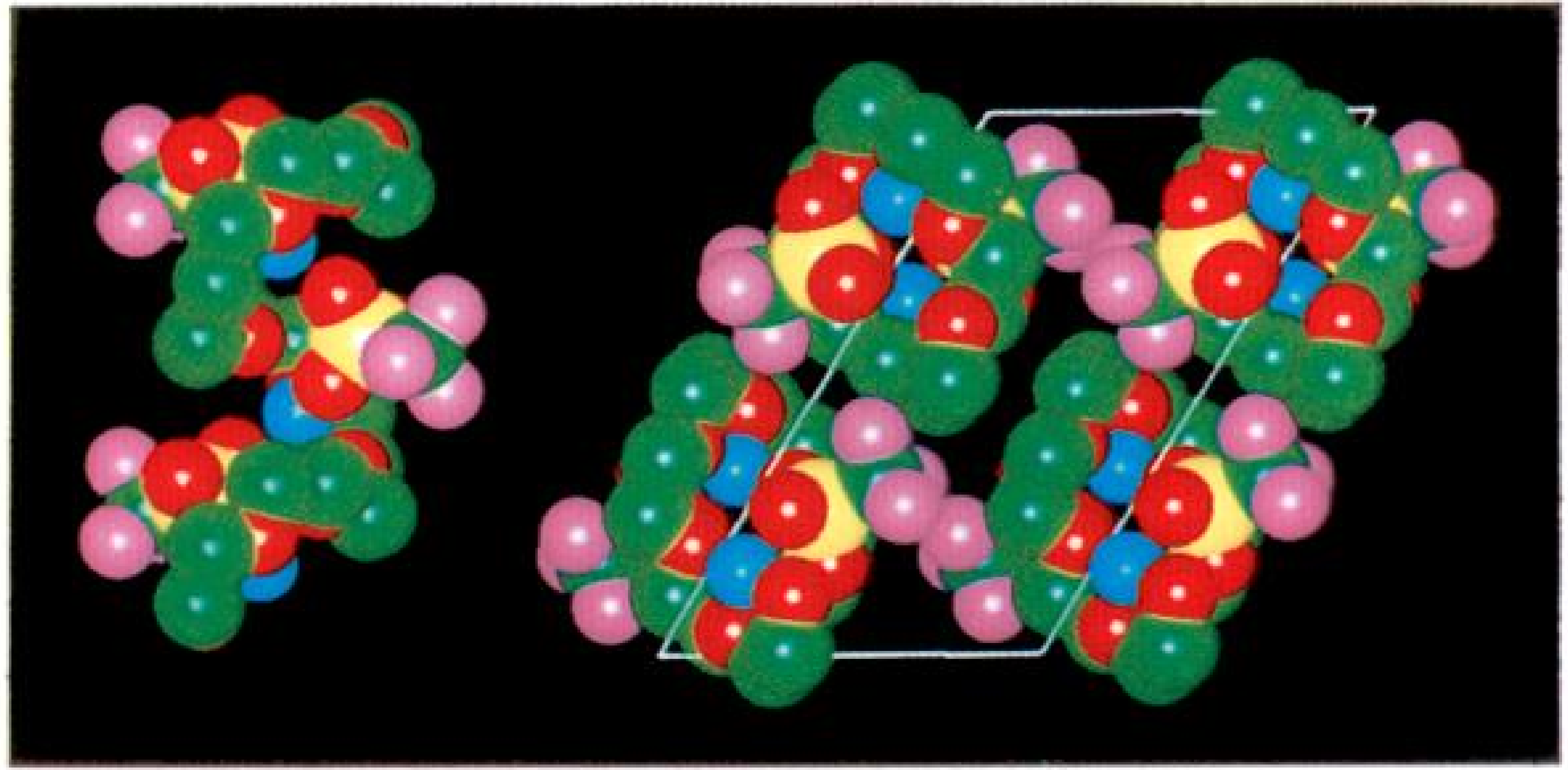
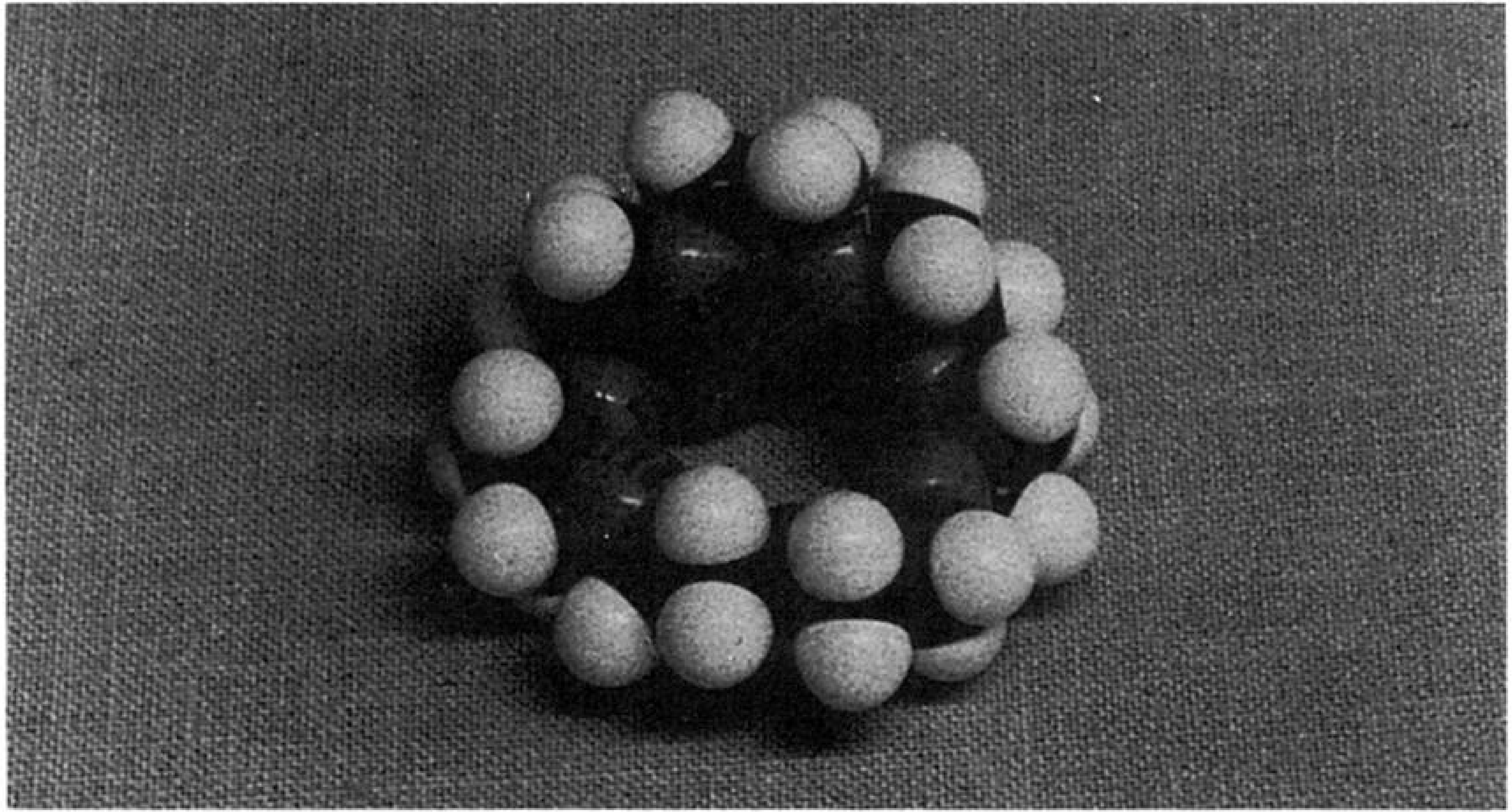
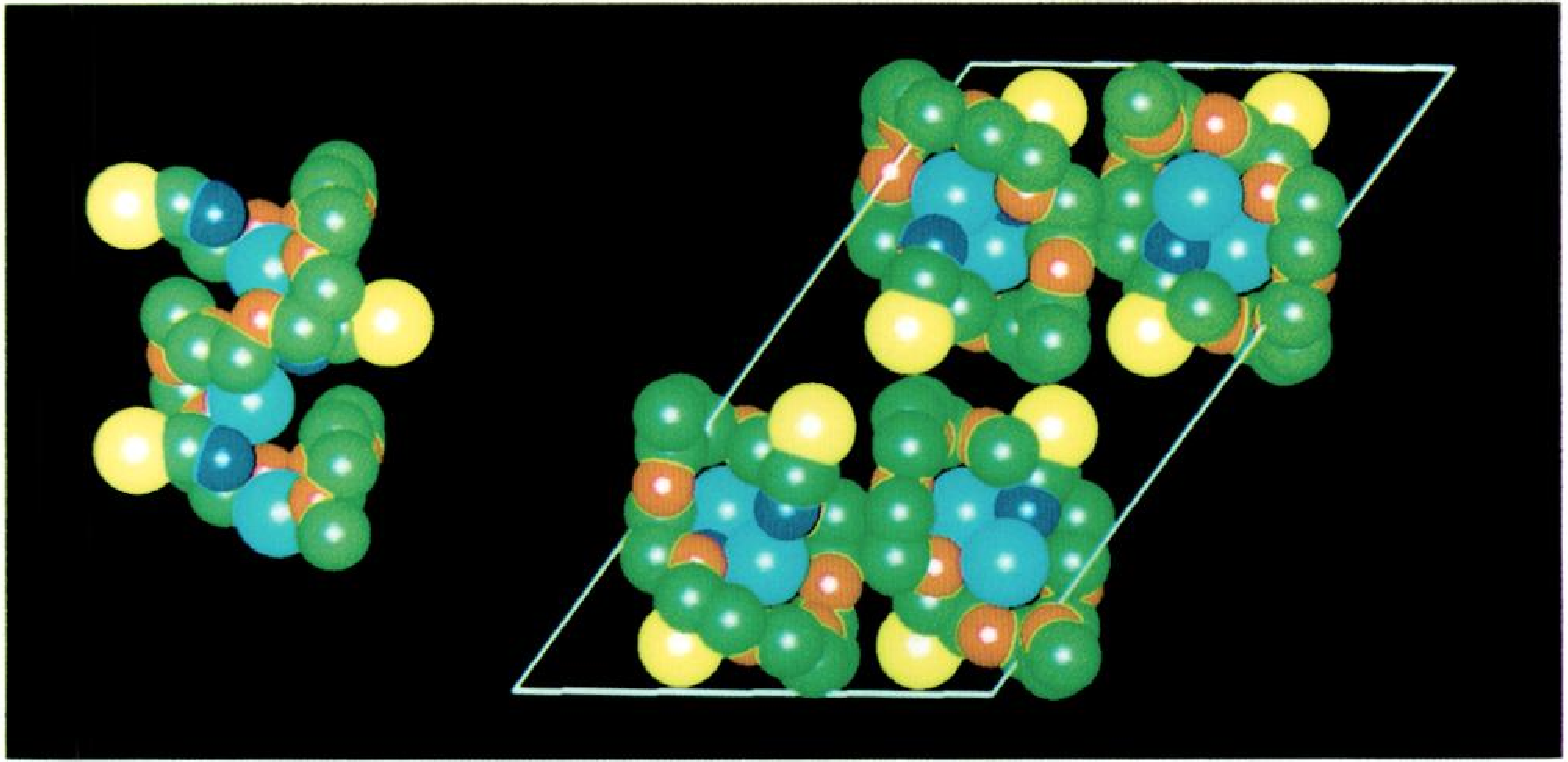


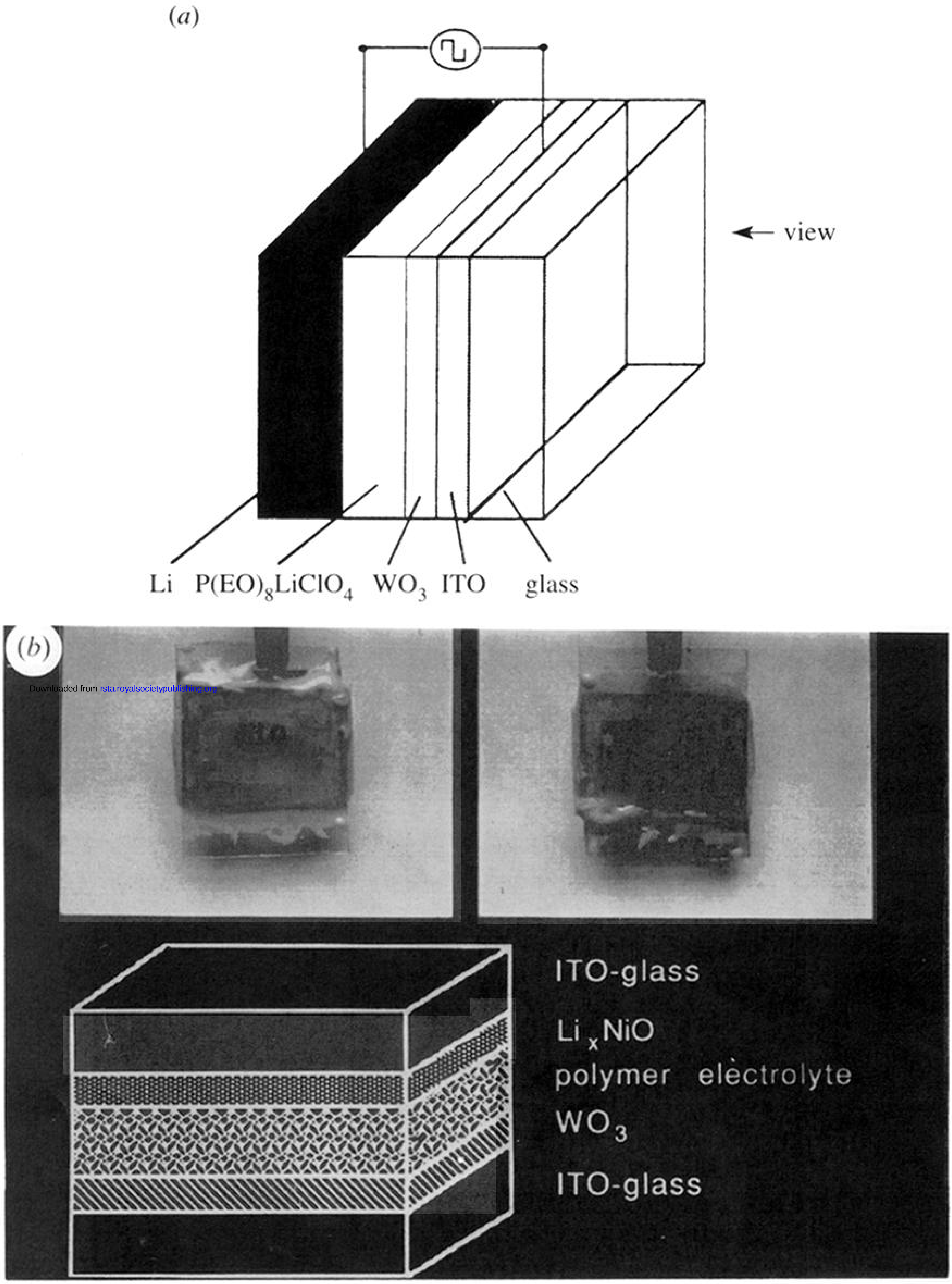
igure 2. Part of the crystal structure of poly(ethylene oxide)$_3$:LiCF$_3$SO$_3$: one PEO chain with s associated ions (left); projection down the *b*-axis (fibre axis) of the unit cell showing four elical chains (right): green, carbon; red, oxygen; blue, lithium; yellow, sulphur; and pink, fluone.



igure 5. Molecular model of poly(ethylene oxide) showing the ability of the polymer to adopt a tructure with an internal oxygen-lined environment. (Reproduced by permission of the Annual eviews, from Cowie & Cree (1989, p. 85).)



igure 13. Part of the crystal structure of PEO_4 : KSCN: one chain with its associated ions (left); projection down the *b*-axis (fibre axis) of the unit cell (right): green, carbon; red, oxygen; light lue, potassium; dark blue, nitrogen: yellow, sulphur.



igure 18. (*a*) Schematic diagram of a solid-state electrochromic display using a polymer elecrolyte. (Reproduced by permission of VCH from Gray (1991).) (*b*) Bottom, schematic of an lectrochromic (smart) window; top, a laboratory prototype showing the transparent (left) and paque (right) states.