Macrocyclic ligand–ion interactions as models for ion–polymer interactions in solid polymer electrolytes

J.W. Lorimer

Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada

Abstract - This review discusses the structure, conductivity and related properties of solid polymer electrolytes, especially those based on polymers containing ether linkages in the main polymer chain or as side chains. The emphasis is on the correlation of properties with structure, and the analogies in structure between ion-polymer complexes and ion-macrocyclic ligand complexes. It is suggested that the two types of system are complementary, in that studies of polymer-salt systems can give information about interactions in macrocyclic ligand-salt systems, and *vice versa*.

INTRODUCTION

Solid polymer electrolytes are solid ionic conductors formed by the dissolution of salts in polymers of suitably high molecular weight (ref. 1). The polymers contain, usually, ether linkages as part of the main chain or as side chains. A few examples of the use of thia-alkane polymers (the sulphur analogues of PEO) (ref. 2) and poly(ethyleneimine) (ref. 3) as the host polymer have also been described. The mixture may be homogeneous or heterogeneous depending on the temperature and salt content. The first solid polymer electrolyte was discovered in 1973 by Wright and co-workers (ref. 4). In 1978, Armand and co-workers (ref. 5) reported that such conductors were excellent candidates for electrolytes in all solid state lithium batteries; a mixture of lithium chloride and poly(ethylene oxide), at temperatures above 80°C, was homogeneous and had a conductivity of the same magnitude as the high-temperature, solid state *fast ion conductors*; i.e., its conductivity was about 10^{-6} S cm^{-1} at room temperature. This practical application, as well as related applications for electrochromic devices and ion sensors, has led to an enormous number of publications over the past almost 20 years. Good summaries of the literature can be found in the *Polymer Electrolyte Reviews* volumes edited by MacCallum and Vincent (up to 1989; ref. 6) and in the recent book by Gray (ref. 7; references to 1990). A recent Faraday Discussion (ref. 8) on "Charge Transfer on Polymeric Systems" contains much material on solid polymer electrolytes, as do two series of conferences: the International Meeting on Lithium Batteries and the Symposium on Polymer Electrolytes. The proceedings of the IMLB meetings are published as special issues of *Journal of Power Sources*. While the emphasis in the many publications is on some aspect of the use of solid polymer electrolytes in batteries, there are also numerous papers concerned with more fundamental aspects. Even here, the emphasis has been on experiments and theory to elucidate the nature of electric conduction, while other important aspects, such as the thermodynamics of the salt-polymer mixtures, have received scant attention, in part because of difficulties in finding appropriate experimental techniques for their study.

In this review, the general nature and structure of solid polymer electrolytes will be described. Next, the phenomenology and theories of conduction will be discussed briefly. Finally, some

observations will be made on the few instances of use of macrocyclic ligands as additives in solid polymer electrolytes, and the similarity in structure between the two classes of materials: solid polymer electrolytes and macrocyclic ligand-ion complexes. The emphasis is on understanding the properties of solid polymer electrolytes; macrocyclic ligand-ion interactions are dealt with specifically in other contributions to this Symposium. The approach is necessarily somewhat idiosyncratic, given the large extent of the available published work and the author's particular point of view and experience. For a recent and brief review of the many problems involved in realization of practical solid-state lithium batteries with polymer electrolytes, see (ref. 9).

CHEMICAL NATURE OF SOLID POLYMER ELECTROLYTES

The most widely-studied polymer for use in preparation of solid polymer electrolytes has been poly(ethylene) oxide, PEO. Unfortunately, all commercial samples are contaminated with catalyst residues, especially CaO and SiO_2. While the concentrations of impurities can be decreased markedly by a complex and lengthy purification procedure (refs. 10, 11), this has been used only rarely, and in fact may actually be undesirable for some purposes. Thus, Jacobs et al. (ref. 11) found that $PEO-LiClO_4$ mixtures decomposed explosively above 185°C for pure PEO, decreasing to 100°C at higher salt contents, in contradiction to other work that the mixtures were thermally stable up to 270°C. It has been suggested that the ion-exchange procedure, despite care in using both cation and anion exchange, removes metal cation impurities, but adds H^+ which catalyzes thermal decomposition (ref. 12). Poly(ethylene oxide) also has also the disadvantage that it is partially crystalline and partially amorphous, the extent depending on temperature and salt composition.
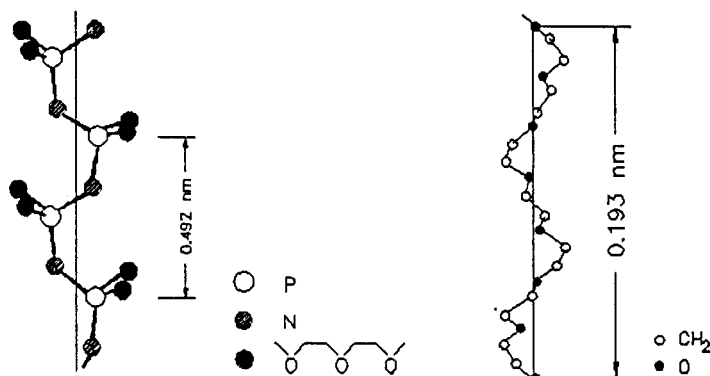

Fig. 1. Structures of (right) poly(ethylene oxide) and (left) MEEP, poly[bis(methoxyethoxyethoxide)phosphazene] (based on refs. 14, 15).

Introduction of disorder into the polymer chains decreases crystallinity. An example is provided by introducing alkoxy side chains into poly(phosphazene) to give the polymer MEEP [poly [bis(methoxyethoxy-ethoxide)phosphazene] (ref. 13), which is completely amorphous over a wide range of temperature, -100 to at least 100°C (see below). However, amorphous polymers tend to flow even at room temperature, which limits the practical use of the unmodified polymer.

The salts and the polymer must be scrupulously anhydrous for use in alkali metal batteries, and must interact with the polymer to produce homogeneous mixtures, at least over some range of temperature and composition. The commonest salts used contain alkali metal cations (especially lithium) and anions such as ClO_4^-, $CF_3SO_3^-$ ("triflate"), SCN^-, BF_4^- and Br^-.

Figure 1 shows the structure of two common polymers: PEO and MEEP. The structure of PEO and poly(dichlorophosphazene) have been established by conventional X-ray methods (refs. 14, 15); it is assumed that the structure of MEEP, which differs from poly(dichlorophosphazene) in replacement of each -Cl by $H_3COCH_2CH_2OCH_2CH_2O-$, is similar. One characteristic feature of these structures is the ethylene oxide unit, $-CH_2CH_2O-$, as part of the main chain in PEO, and as a side group in MEEP.

PHASE BEHAVIOUR AND THERMODYNAMICS OF POLYMER ELECTROLYTES

Figure 2 shows the phase diagram for a typical polymer-salt system, in this case PEO-NaSCN (ref. 16). These diagrams are determined by differential scanning calorimetry, with support from optical microscopy and X-ray diffraction data. The phase diagram is actually a pseudo phase diagram, because only the crystalline portions take part in melting, so that the true compositions along the various melting curves are not known. In fact, measurements of the extent of crystallinity by NMR (ref. 17) indicate that the crystallinity of PEO-LiClO$_4$ mixtures increases sharply just below the apparent melting curve on the phase diagram, and reaches its full value somewhat above the melting curve. The equilibrium curves cannot, as a rule, be used to extract thermodynamic information; they can be represented equally well by assuming that the liquid phase is a completely-ionized electrolyte in the solvent PEO, or that the solid compounds NaSCN + (PEO)$_3$·NaSCN are
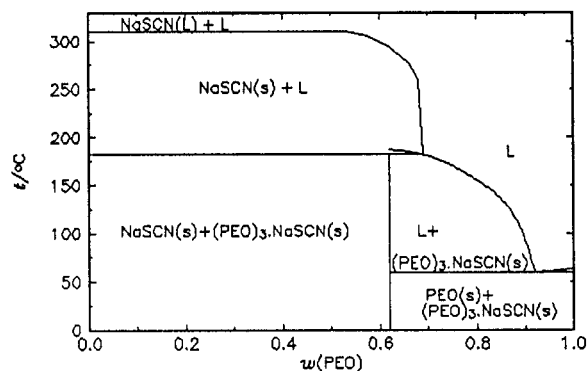

Fig. 2. Phase diagram of the system: PEO-NaSCN (after ref. 16).

in equilibrium with polymeric (PEO)$_3$·NaSCN in the liquid. One exception is found in the system NaSCN-PEO, where the nearly vertical liquidus curve for solid NaSCN suggests that complex formation also takes place in the liquid above the melting point of the solid binary compound. X-ray studies on samples taken from appropriate regions of the phase diagram, however, reveal the presence of definite solid compounds (see the review, ref. 12), with stoichiometries of n = 1, 2, 4 and 6 (in (PEO)$_n$·salt) being found.

Eutectic mixtures of PEO-NaSCN, PEO-LiClO$_4$ and other systems can be supercooled down to the glass transition temperature, suggesting that the cation-polymer interactions produce sufficient disorder that crystallinity is almost absent. On heating to just below the eutectic temperature, however, sudden crystallization occurs, indicating rearrangement on increased thermal motion of the polymer chains.

Figure 3 shows the glass transition temperatures of PEO-LiClO$_4$ (ref. 11) and MEEP-LiClO$_4$ (ref. 18) as functions of composition, as obtained from differential scanning calorimetry. The mixtures with MEEP are amorphous over at least the range 0 - mole fraction LiClO$_4$ and -100 to 100°C. The composition is given as $1/n$, where n is the mole ratio of polymer to salt, based on the polymer repeat unit. This quantity is proportional to the molality, m: the relation is $m = 1/nM_r$, where M_r is the molar mass of a polymer repeat unit. Note that the glass transition temperature is constant for small additions of salt, or may even undergo a shallow minimum. The glass transition temperature is considered to be a measure of the micro viscosity of the polymer chains, and shows a general increase with increasing salt content. One possible explanation is that, at low salt contents, cations are bound to O-sites on the polymer. As the salt content increases, cations act as crosslinks between binding sites on adjacent polymer molecules.

Unfortunately, direct measurement of the thermodynamic properties of polymer-salt complexes has only been possible in a few cases, mostly because of the lack of reversible electrodes for the unusual anions used in polymer electrolytes, such as ClO$_4^-$, SCN$^-$ and BH$_4^-$. Some measurements have been reported on the cells Li/polymer-LiI/PbI$_2$/Pb (ref. 19) and Li/polymer-LiClO$_4$/P(DVG)ClO$_4$ (ref. 20), where P(DVG) is poly(decaviologen), the second oxidation state of which is reversible to perchlorate ion. However, the data have not been reported in a form
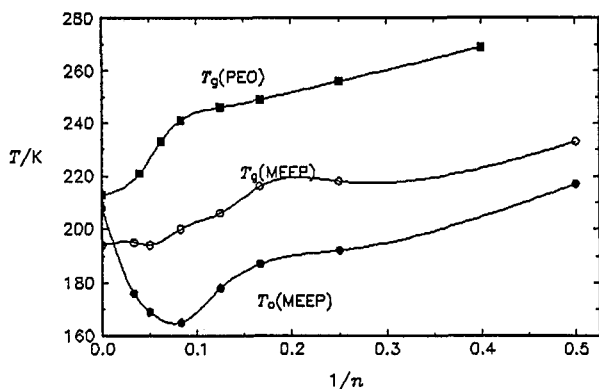
Fig. 3. Dependence of glass transition temperature, T_g, for PEO and MEEP and VTF parameter T_o for MEEP for polymer-LiClO$_4$ mixtures on $1/n$, n the mole ratio of polymer to salt, as in (polymer)n·LiClO$_4$) (from ref. 11, 18).

from which thermodynamic data can be extracted easily, the aim being to combine data from these cells and from concentration cells to obtain transport numbers.

CONDUCTIVITY – PHENOMENOLOGICAL ASPECTS

We shall consider four important aspects of the conductivity: high frequency dependence; low frequency dependence; dependence on temperature and on composition.

Low-frequency conductivities are usually measured by determination of the impedance for thin-layer samples between blocking electrodes such as platinum (cf. ref. 21). Determination of the frequency dependence below 100 kHz, and down to as low as 1 mHz, is necessary in order to find the correct D.C. conductivity; the frequency dependency in this range is pronounced. At higher frequencies (in the MHz region and above), the conductivity is determined from dielectric loss measurements (ref. 22). Figure 4 gives a typical low-frequency impedance plot using blocking electrodes, which is characterized by a low frequency sloping line which is more-or-less independent of temperature, and is ascribed to micro roughness at the electrode-polymer contact, and a depressed and distorted arc which suggests occurrence of at least two relaxation processes with similar time constants. The frequency-independent cell resistance is found from the intersection of the sloping line with the axis of the imaginary part of the impedance, ImZ, and the conductivity is then calculated using the cell dimensions.
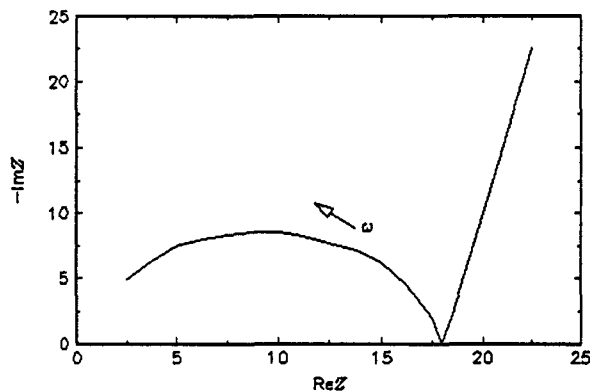

Fig. 4. Electrochemical impedance spectrum of a 100 μm film of (MEEP)$_{20}$·LiClO$_4$ at -20°C between Pt electrodes; frequency range 1.5 Hz - 65 kHz (schematic - after ref. 21).

Figure 5 gives the dependence of the conductivity of MEEP-LiClO$_4$ mixtures on temperature and composition (ref. 18, 21). The temperature dependence can be described accurately by a general form of the so-called VTF (Vogel-Tammann-Fulcher) equation,

$$\ln(\sigma T^\alpha) = \ln A - E/(T-T_o)$$

where T_o is an empirical temperature called the "ideal glass transition temperature", σ is the conductivity at temperature T, α is an empirical parameter related to the specific model which can

be used to rationalize the VTF equation (with possible values 0, 1/2 or 1) and A is a parameter which depends on composition.

The dependence on composition is much more complex. The general behaviour is that the conductivity divided by molality *increases* with molality, thus in a direction opposite to that expected for a completely-ionized electrolyte, then goes through a maximum and decreases to very low values. Data for $LiClO_4$ in amorphous oxymethylene-linked PEO of molecular weight 100 000 and from amount concentrations of 0.002 to 1.2 mol dm^{-3} show the same behaviour (fig. 6), but with a sharply rising conductivity at extremely high dilutions (ref. 23). Such high dilutions are impractical to reach experimentally with salt-polymer systems for several reasons: samples are typically a few hundred mg in order to achieve homogeneity and to fill the thin-layer cells which are used because of the rather high resistance, especially near and below room temperature. Thus, preparing small samples of accurately-known composition becomes more difficult as the salt concentration decreases, and no data have been obtained for high molecular weight polymers above about 0.1 mol kg^{-1}, a molality insufficiently low to exhibit anything approaching limiting behaviour. Another difficulty (alluded to already) is the presence of residual conducting impurities in the polymer. In fig. 5, the data for $1/n = 0$, corresponding to polymer with no added salt, show appreciable conductivity and the shape of the curve suggests that this conductivity arises from ionic, rather than electronic, conduction.
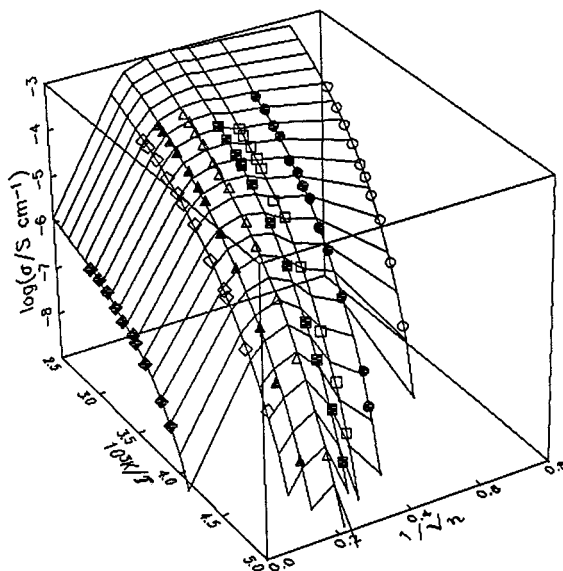

Fig. 5. Log(conductivity) as a function of reciprocal temperature and composition (as $1/\sqrt{n}$, with n the mole ratio of MEEP to $LiClO_4$, i.e., $(MEEP)n \cdot LiClO_4$) (ref. 18, 21).

CONDUCTIVITY – THEORETICAL ASPECTS

(a) Low-frequency region. Impedance data similar to those in fig. 4 can be interpreted, as least qualitatively, in terms of either ion association or ion binding to the polymer (refs. 24, 25). The theory, deduced by application of transport equations from non-equilibrium thermodynamics, assumes that a perturbation of the electric field in an impedance experiment creates a concentration gradient, which in turn induces a shift in ion pairing or ion binding equilibria. For this effect to be important, the relaxation times for ion pairing or ion binding must be in the tens of microseconds range, i.e., rate constants for recombination as slow as 10^5 dm^3 mol^{-1} s^{-1}, which well may be the case in media of such high viscosity as polymer electrolytes. The theory has yet to be applied systematically, but does agree with the interpretation of the dependence of conductivity on salt concentration (see below).

(b) High-frequency region. The frequency dependence of conductivity at high frequencies has been the subject of a theory called by Ratner and his colleagues the *dynamic bond percolation theory* (refs. 26-28). This theory assumes that cation motion occurs through breaking of coordinate bonds and a hopping motion between neighbouring coordinate sites; anion motion occurs by hopping between an occupied site and a sufficiently large void. The polymer chains are in motion, so that sites move relative to each other, and hopping probabilities renew their values in a characteristic

time τ_r. The probability of a jump is f, and the frequency of hopping from a filled to a vacant site is w, or zero for hopping between two filled sites. Of the three characteristic parameters, f can be identified with the fraction of available free volume, w with a reduced ion velocity, and τ_r with the relaxation time of configurational or orientational changes. The theory predicts: at frequencies << $1/\tau_r$ (or for small renewal times), ions drift in an applied electric field without hindrance by polymer chain rearrangements; if τ_r is large, the effective hopping rate is fw, as in a static bond percolation model. An increase in τ_r thus enhances the conductivity through cooperative chain motions. The theory accounts reasonably successfully for conductivities in the MHz and above range, where above about 10 GHz conductivity can be ascribed as arising from chain motions alone. At lower frequencies, the conductivity of PEO and PEO-NaBH$_4$ decreases, suggesting that strong ion pairing exists for the latter, as also indicated by NMR measurements. By contrast, the conductivity of NaSCN-PEO decreases, but much less rapidly, which is ascribed to long-range diffusive motion of the ions.

Subsequent modifications of the dynamic bond percolation theory (ref. 29) have also taken into account ion pairing and cross-linking of polymer chains by cations; the original theory contains the essential features of ion binding.

(c) Frequency-independent conductivity. The dynamic bond percolation theory does not address the problem of the dependence of conductivity on composition. In a theory that might be expected to be appropriate for very low frequency behaviour, Cheradame and co-workers (ref. 30, 31) have proposed explicit expressions in terms of ion pair and ion multiplet equilibria. Ion binding has not received similar treatment. Molar conductivities, $\Lambda = \sigma/c$ of typical salt-polymer mixtures are
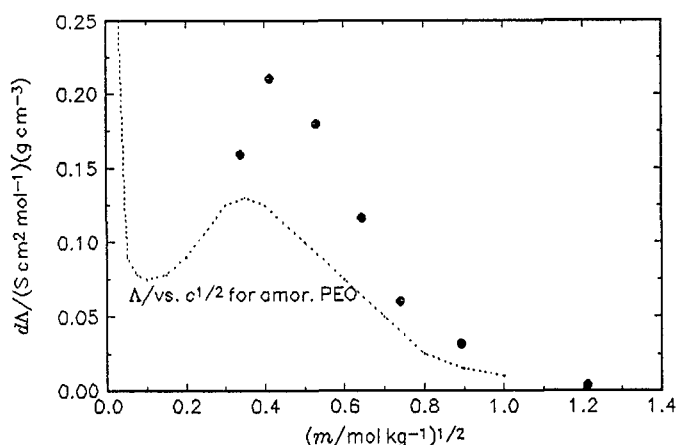

Fig. 6.   Closed circles: molar conductivity - density product of LiClO$_4$-MEEP mixtures as a function of square root of molality of salt. For comparison (dotted curve): molar conductivity of LiClO$_4$-oxymethylene-linked PEO mixtures as a function of square root of amount concentration of salt (after ref. 23; scales same). Temperature = 25°C.

shown in fig. 6. The values for MEEP-LiClO$_4$ are interpolated from the VTF fitting equations for the data in fig. 5. For MEEP-LiClO$_4$, the density, d, of the mixtures is unknown. The relation between amount concentration and molality is

$$c = d/(M_s + 1/m)$$

where M_s is the molar mass of the salt. Thus the only quantity that can be calculated is the product of molar conductivity and density:

$$d\Lambda = \sigma/c = \sigma(M_s + 1/m)$$

As mentioned above, the molar conductivity for LiClO$_4$ in amorphous oxymethylene-linked PEO resembles the molar conductivity-density product of MEEP-salt mixtures, so that the mechanism of conduction is probably the same in both cases.

The explanation of the data in fig. 6 is that (ref. 23) ion pairing begins at very low salt concentrations, causing a much sharper decrease in conductivity than would be predicted on the basis of complete ionization. As the salt concentration increases, charged ion triplets form, which lead to an increase in conductivity. At still higher salt contents, higher uncharged ion aggregates predominate, and the molar conductivity decreases. This explanation ignores two factors: the increase in viscosity with increasing salt content, which would tend to lower the conductivity, and the effects of ion binding to the polymer. Thus the interpretation of conductivities, while probably correct in general outline, is far from quantitative. Thermodynamic properties, including activity coefficients and partial molar volumes, would be of considerable help in interpretation.

MACROCYCLIC LIGANDS AND POLYMER ELECTROLYTES

The above description of the structure of solid polymer electrolytes suggests analogies with crown ethers. In fact, Kaplan et al. (ref. 32) showed that addition of 12-crown-4, 15-crown-5 or 18-crown-6 to Li triflate in poly(vinylene carbonate) led to an increase in conductivity by a factor of at least 1000, and increasing with cavity size of the crown ether. They explained the increase by assuming that the crown ether acted as an ionophore with a non-polar exterior which assisted transport of the cation through the polymer. Ratner and Shriver and co-workers (ref. 33) found that addition of cryptand-2,2,2 to the sodium salts of poly(phosphazene sulfonate) or poly(alkoxyaluminate) polyelectrolytes caused increases of conductivity up to ten times, which they attributed to a decrease in ion pairing. Addition of 15-crown-5 had a much smaller effect, which was attributed to a lower affinity for the cation and a more open structure.

In fig. 7, the structures of 18-crown-6, the side chains of MEEP, and pentaglyme (pentaethylene glycol dimethyl ether) are compared. The side-groups in MEEP can be considered to be equivalent to either (a) immobilized pentaglyme or (b) immobilized 18-crown-6 with a broken c-c link, either with a phosphorus atom in the phosphazene chain replacing one $-CH_2CH_2-$ group.

Breaking the crown ether ring (as in pentaglyme) would be expected to decrease ion binding and increase oxymethylene chain mobility, and thereby increase the conductivity. Similar effects might be expected with tetraglyme or hexaglyme. Comparison of the conductivity of tetraglyme-$LiClO_4$ with MEEP-$LiClO_4$ at the same temperature and O:Li ratio indicates that, indeed, the tetraglyme system has the higher conductivity, by about one power of ten compare to MEEP (ref. 34), supporting the view that ion binding plus the nature of the anchor of the binding group is of importance in determining the magnitude of the conductivity.
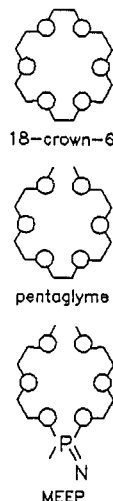

18-crown-6

pentaglyme

MEEP

Fig. 7. Comparison of ether side-chains in MEEP, pentaglyme and 18-crown-6.

CONCLUSIONS

Despite almost two decades of intensive work on solid polymer electrolytes, experimental data on their thermodynamic properties are almost non-existent. While extensive data on conductivities is available, and interpretation of the dependence of conductivity on frequency and temperature is reasonably well understood, quantitative understanding of the dependence on composition is still in a relatively primitive stage. Analogies between polymer-ion interactions in solid polymer electrolytes and macrocyclic ligand-ion interactions complexes may provide information of mutual value to both fields, and may indicate the way towards new materials of interest.

REFERENCES

1. C.A. Vincent, Prog. Solid St. Chem., 17, 145 (1987).
2. Y. Chatani, T. Kobatake, H. Takadoro and R. Tanaka, Macromolecules, 15, 170 (1982).
3. S. Clancy, D.F. Shriver and L.A. Ochrymowycz, Macromolecules, 16, 170 (1986).
4. D.E. Fenton, J.M. Parker and P.V. Wright, Polymer, 14, 589 (1973).
5. M.B. Armand, J.M. Chabagno and M.J. Duclot, in Fast Ion Transport in Solids, P. Vashista, J.M. Mundy and G.K. Shenoy, eds. Elsevier North-Holland, Amsterdam, 1979; Second International Conference on Polymer Electrolytes, St. Andrews (1978).
6. J.R. MacCallum and C.A. Vincent, *Polymer Electrolyte Reviews-1,* (1987); -2, (1989). Elsevier, London.
7. F.M. Gray, *Solid Polymer Electrolytes.* VCH, Weinheim, (1991).
8. Faraday Discussions of the Chemical Society, No. 88, (1989).
9. J.W. Lorimer, 34th International Power Sources Symposium, Proceedings, 77 (1990).
10. R. Dupon, D.H. Whitmore and D.F. Shriver, J. Am. Chem. Soc., 128, 715 (1981).
11. P.W.M. Jacobs, J.W. Lorimer, A. Russer and M. Wasiucionek, J. Power Sources., 26, 503 (1989).
12. D. Fauteux, *in* J.R. MacCallum and C.A. Vincent, *Polymer Electrolyte Reviews-2,* 121 (1989). Elsevier, London.
13. P.M. Blonsky, D.F. Shriver, P.E. Austin and H.R. Alcock, Solid State Ionics, 18 & 19, 258 (1986).
14. H. Tadokoro, J. Polymer Sci. C, 15, 1 (1966).
15. E. Giglio, F. Pompa and A. Ripamonti, J. Polym. Sci., 59, 293 (1962).
16. C. Robitaille, S. Marques, D. Boils and J. Prud'homme, Macromolecules, 20, 3023 (1987).
17. W. Gorecki, R. Andreant, C. Berthier, M. Armand, M. Mali, J. Roos and D. Brinkmann, Solid State Ionics, 18 & 19, 295 (1986).
18. P.W.M. Jacobs, J.W. Lorimer, A. Russer and M. Wasiucionek, unpublished,
19. A. Bouridah, F. Dalard, D. Deroo and M.B. Armand, Solid State Ionics, 18-19, 287 (1986).
20. A. Bouridah, F. Dalard and M. Armand, Solid State Ionics, 28-30, 950 (1988).
21. P.W.M. Jacobs, J.W. Lorimer, A. Russer and M. Wasiucionek, J. Power Sources., 26, 483 (1989).
22. T. Wong, M. Brodwin, B.L. Papke and D.F. Shriver, Solid State Ionics, 5, 689 (1981).
23. F.M. Gray, Solid State Ionics, 40/41, 637 (1990).
24. J.W. Lorimer, J. Power Sources, 26, 491 (1989).
25. J.W. Lorimer, Abstract C-7.5, 1st International Symposium on Electrochemical Impedance Spectroscopy, Bombannes, France (1989).
26. S.D. Druger, M.A. Ratner and A. Nitzan, Solid State Ionics, 9/10, 1115 (1983).
27. S.D. Druger, M.A. Ratner and A. Nitzan, Solid State Ionics, 9/10, 1115 (1983).
28. S.D. Druger, M.A. Ratner and A. Nitzan, Solid State Ionics, 9/10, 1115 (1983).
29. M.A. Ratner and A. Nitzan, Faraday Discuss. Chem. Soc., 88, 19 (1989).
30. H. Cheradame and P. Niddham-Mercier, Faraday Discuss. Chem. Soc., 88, 77 (1989).
31. J.F. Le Nest, H. Cheradame and A. Gandini, Solid State Ionics, 28-30, 1032 (1988).
32. M.L. Kaplan, E.A. Rietman, R.J. Cava, L.K. Holt and E.A. Chandross, Solid State Ionics, 25, 37 (1987).
33. K. Chen, K. Doan, S. Ganapathiappan, M. Ratner and D.F. Shriver, Solid State Ionics II, Proc. Mat. Res. Soc. Symp., 210, 722 (1991).
34. E. Andrukaitis, P.W.M. Jacobs, P. Kurek and J.W. Lorimer, Abstract 11, 177th Meeting, The Electrochemical Society, Montreal, (1990).