

MECHANISM OF ION CONDUCTION IN ALKALI METAL-POLYMER COMPLEXES

DUWARD F. SHRIVER, RYAN DUPON and MATTHEW STAINER

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, IL 60201 (U.S.A.)

(Received June 7, 1982)

Summary

Polymer electrolytes have many materials properties which are attractive for applications in advanced electrochemical devices. However the ionic conductivities are still too low for widespread utilization. One avenue for the improvement of the conductivity is the delineation of the factors which influence ion transport in polymers. The most successful models for alkali metal ion transport in polymers are based on the concept that ions are passed between polymer segments by large amplitude polymer motions, and that relatively few interactions between the ion and polar polymer groups are broken in the transition state. Evidence for the contribution of polymer segmental motion to ion transport is obtained from the form of the temperature-dependent conductivity, from the higher conductivity for amorphous than for crystalline polymers, from the decrease in conductivity with increasing pressure, and from doping experiments. Simple energy estimates indicate that the ion motion probably occurs with the breaking of at most one or two cation-polar group interactions, rather than the hop of an ion from one polymer chain to the next.

Introduction

A variety of polyelectrolyte polymeric materials is known to exhibit high ion transport when swollen with solvent. There is, however, another class of ion-containing materials based on complex formation between polar polymers and alkali metal salts, which does not require the presence of solvent to achieve substantial ionic conductivities [1 - 6]. Owing to a variety of desirable properties, these materials are of interest for use as electrolytes in high energy density batteries: the flexibility and conformability of polymers should facilitate the construction of completely solid state batteries in which the electrolyte can maintain contact with the electrodes despite volume changes in the latter. The light weight and ease of fabrication in thin-film configurations are also attractive features of the polymer. Finally, one can

envison the chemical bonding of polymer electrolytes to electrode materials as a means of maintaining continuity at the critical electrode-electrolyte interface. At present however, the conductivity of the polymer electrolytes is too low for wide adoption of these materials in electrochemical devices. The preparation of new polymer electrolytes having higher conductivity should be facilitated by recent studies which indicate the factors which promote polymer-salt complex formation and ion transport. These principles will be discussed in the present paper. The bulk of the studies have been performed on poly(ethylene oxide), $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n = \text{PEO}$, complexes of alkali metal salts, but recent results with other host polymers will be presented.

Discussion

Polymer-salt complex formation

The factors influencing polymer-salt complex formation can be summarized as follows [6]: (1) A high concentration of polar groups facilitates complex formation. The types of polar polymers used so far include ethers, esters, amines, and sulfides. (2) Chain flexibility facilitates polymer-salt interaction. (3) Polymers with high cohesive energy densities do not readily form alkali metal salt complexes. (4) Similarly, salts with very high lattice energies do not form complexes.

Fortunately, one of the factors which favors polymer-salt complex formation, chain flexibility, also promotes ion transport. Many commercial engineering plastics based on polar polymers appear to be poor complexing agents for alkali metal salts. This unfavorable polymer-salt interaction can be attributed to the high cohesive energy density and polymer chain inflexibility of these materials.

Temperature-dependent conductivity and the Gibb's model

The temperature dependent conductivity of amorphous polyether-salt complexes reveals curved plots of $\ln(\sigma T)$ vs. $1/T$, which are linear when the temperature variable $1/(T - T_0)$ is employed [4, 5]. This functional dependence of the ion transport has previously been observed for small molecule diffusion through polymers, and one possible interpretation is that cooperative polymer conformation fluctuations are responsible for the transport process. The empirical constant T_0 represents the temperature below which the polymer motions responsible for ion transport are frozen out and therefore it is approximately equal to the glass transition temperature, T_g . The $1/(T - T_0)$ dependence is reproduced by the configurational entropy model of Gibbs and co-workers [7, 8], which gives eqn. (1) for the conductivity [10].

$$\sigma = AT^{-1/2} \exp\{-K/T - T_0\} \quad (1)$$

where

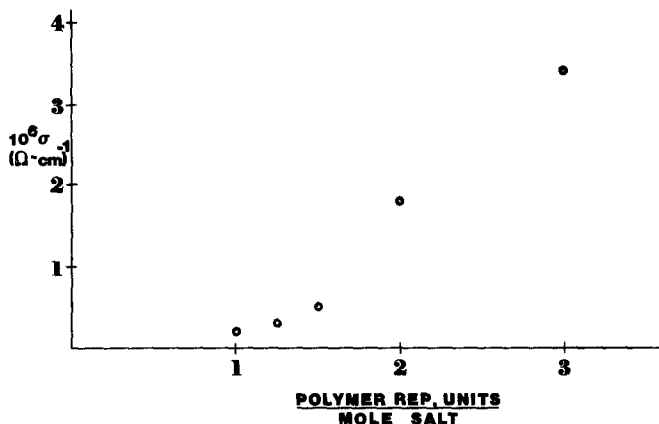


Fig. 1. Conductivity vs. polymer to salt ratio for poly(ethylene succinate)·Li[BF₄].

$$K = T_0 \Delta \mu S_c^* / k_B B. \quad (2)$$

A , T_0 , and B are constants, S_c^* is the minimum configurational entropy required for rearrangement, and k_B is the Boltzmann constant. The exponential term, A , is proportional to carrier concentration, so this factor will yield an increase in conductivity with increasing salt concentration in the polymer-salt complex. By contrast to this simple prediction we have observed decreasing conductivity with increasing salt concentration for poly(ethylene succinate)-lithium salt complexes, Fig. 1 [9]. This behavior correlates with the increasing stiffness and apparent increase in glass transition temperature T_g as the salt concentration of that material is increased. This behavior is fairly common; so it appears likely that many polymer-salt complexes will exhibit a maximum in conductivity with an increase in salt concentration [10]. Another consequence of the Gibbs treatment is that the conductivity should decrease markedly with increasing pressure, and this type of behavior has been recently observed for the 4.5:1 PEO·NaSCN complex [11].

Structural model and conductivity paths

Pure PEO consists of an extended helix having a fiber repeat distance of 19.48 Å [12]. X-ray diffraction on oriented PEO·KSCN indicated a much shorter fiber repeat distance, 8.1 Å [1]. Detailed infrared and Raman data provide a variety of structural information including the conformation of the polymer backbone, and the general lack of contact ion pairing [13]. A structural model which is consistent with the vibrational data, the X-ray fiber repeat distance, and structures of short-chain polyether complexes of alkali metal ions [14 - 16], is a compressed helix having an interior channel lined with oxygen atoms [13]. The interior channel is large enough to accommodate a K⁺ ion, but space filling molecular models indicate that the larger Rb⁺ and Cs⁺ ions would require frequent kinks in the helix. These predictions of the structural model agree with the observation that PEO complexes with

lithium, sodium, and potassium salts are crystalline, but those with rubidium and cesium salts are not. Recent X-ray unit cell measurements have led to a somewhat different proposal for the structural model of these complexes, involving a double helix [17].

It is tempting to postulate that ion transport occurs down the helical channels in one or the other of these proposed structures. Indeed, the structural study of inorganic solid electrolytes often provides useful information on conductivity paths and an earlier discussion of the PEO complexes presented the possibility of linear chain conductivity paths [3]. An experiment was devised to determine whether ion motion down the proposed helical channels dominates the conductivity in these materials. This experiment was based on the spectroscopic observation that, unlike most anions, the BH_4^- ion forms a tight ion pair with Na^+ . This ion pairing is associated with a far lower conductivity of the $\text{PEO}\cdot\text{NaBH}_4$ complexes. Therefore, small levels of substitutional doping by BH_4^- for other anions should block ion transport down a channel and therefore greatly reduce the conductivity of ion transport along the helical channel dominates. This line of argument is illustrated in Fig. 2.

Figure 3 presents the results of conductivity studies on $\text{PEO}\cdot\text{NaBF}_4$ which has been substitutionally doped with NaBH_4 , [18]. In contrast to the predictions for conduction down the helix a substantial doping level, 25%, has little influence on the conductivity. It thus appears that the ion transport is occurring in the amorphous regions of this highly crystalline polymer or that inter-helix ion paths are important. As with the amorphous polymer-salt conductors discussed in the last section, the ion transport in these crystalline polymer materials is probably dominated by polymer chain fluctuations.

The comparison of crystalline poly(ethylene oxide) complexes with the analogous poly(propylene oxide) complexes, which are amorphous, indicates that amorphous polymers have higher conductivity [4]. A more rigorous comparison of the influence of crystallinity would be possible if a crystalline polymer-salt complex could be quenched from the melt into an amorphous state which would persist long enough to permit conductivity measurements. Our initial attempts to prepare metastable amorphous phases were unsuccessful, but recent observations by Stainer have shown that the ammonium ion conductor, $\text{PEO}\cdot\text{NH}_4\text{SO}_3\text{CF}_3$, can exist for a matter of hours around room temperature in an amorphous state. The conductivity curves, Fig. 4, which have been obtained on the amorphous and crystalline forms of this material clearly show much higher conductivity of the former [19]. The increased conductivity of the amorphous salt complexes finds a ready explanation in the higher, large amplitude chain motions in amorphous polymer. The polymers having greater than 60% crystallinity display significant polymer motion, as shown by the microwave measurements [6]. A comparison of $\text{PEO}\cdot\text{NaSCN}$ at 22 °C with the pure polymer in the microwave region indicates that ion motion dominates the conductivity response below 0.1 GHz, but above 1 GHz the conductivities for the two materials are nearly the same, indicating that polymer motion may dominate at the high frequencies.

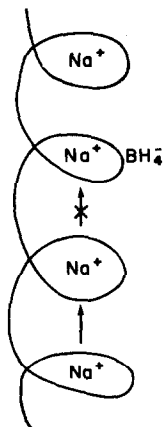


Fig. 2. Schematic representation of the blockage of Na motion down the helical PEO tunnel by an NaBH_4 ion pair.

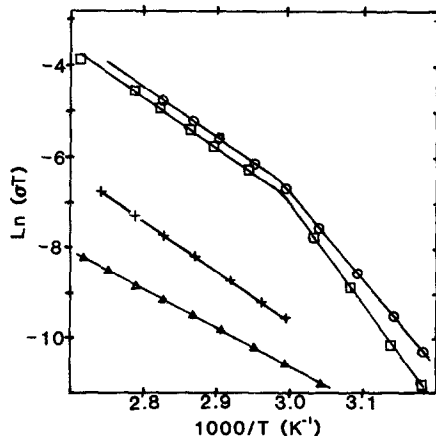


Fig. 3. Variable temperature conductivity plots for: $\text{PEO} \cdot \text{NaBF}_4$, 4:1, (\circ); $\text{PEO} \cdot \text{Na}[(\text{BF}_4)_{0.75}(\text{BH}_4)_{0.25}]$ ca 4:1, (\square); $\text{PEO} \cdot \text{Na}[(\text{BF}_4)_{0.49}(\text{BH}_4)_{0.51}]$, ($+$); and $\text{PEO} \cdot \text{NaBH}_4$, 3.4:1, (\triangle).

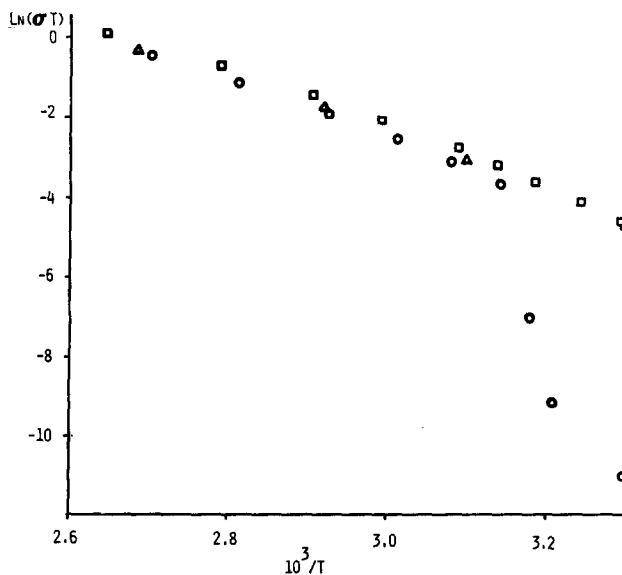


Fig. 4. Variable temperature conductivity plots for $\text{PEO} \cdot \text{NH}_4\text{SO}_3\text{CF}_3$, 8:1. First data set obtained by heating the crystalline polymer (\circ). Second and third data sets obtained by heating the quenched amorphous polymer (\triangle and \square). The transition from low to high conductivity observed with the first data set (\circ) represents a transformation from crystalline to amorphous forms.

From energy estimates it appears unlikely that an ion will break all interactions with the polar host before forming interactions with another polymer segment [10]. For example, in a poly(ether) complex the average $\text{Na}^+ \text{--} \text{O}$ bond energy is about -66 kJ/mole so the breaking of four such inter-

actions would require an activation energy around 260 kJ/mole. Since the observed activation energies are in the range of 40 - 120 kJ/mole it appears likely that a maximum of one or perhaps two such interactions are broken in the activated complex, assuming that the ion motion proceeds by a dissociative mechanism. Another potential limiting mechanism for ion transport is association with a polar group from a new polymer segment before dissociation of the polar group from the old site. At the present time it does not appear fruitful to carry speculation about the intimate details of ion transport beyond this point, because experimental tests for the detailed mechanism are not readily available and theoretical models for handling polymer dynamics of this complexity have not been developed. The less specific ideas concerning the role of polymer chain motion and the associated concept of configurational entropy appear to be very useful guides to the properties of polymer electrolytes and thus provide fruitful avenues for the development of new materials.

Acknowledgments

This research was sponsored in part by the Office of Naval Research, and by the Northwestern University Materials Research Center, which is funded by the NSF DMR. We greatly appreciate the stimulating ideas and expertise of colleagues in the solid electrolyte group at Northwestern University: Professors Mark Ratner, Donald Whitmore, and Morris Brodwin and their students.

References

- 1 D. E. Fenton, J. M. Parker and P. V. Wright, *Polymer*, **129** (1982) 1694.
- 2 P. V. Wright, *Br. Polym. J.*, **7** (1975) 319.
- 3 M. Armand, J. M. Chabagno and M. Duclot, *Abstr. Second Int. Meeting on Solid Electrolytes, St. Andrews, Scotland, 1978*, Abstract 65.
- 4 M. Armand, J. M. Chabagno and M. J. Duclot, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, North-Holland, New York, 1979, p. 131.
- 5 D. Andre, L. F. LeNest and H. Cheradame, *Eur. Polym. J.*, **17** (1981) 57.
- 6 D. F. Shriver, B. L. Papke, M. A. Ratner, R. Dupon, T. Wong and M. Brodwin, *Solid State Ionics*, **5** (1981) 83.
- 7 J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28** (1958) 373.
- 8 G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43** (1965) 139.
- 9 R. Dupon, unpublished observations, Northwestern University, 1981.
- 10 B. L. Papke, M. A. Ratner and D. F. Shriver, *J. Electrochem. Soc.*, **129** (1982) 1694.
- 11 J. J. Fontanella, M. C. Wintersgill, J. Adams, R. Dupon, D. F. Shriver and C. G. Andeen, *Bull. Am. Phys. Soc.*, **27** (1982) 167.
- 12 Y. Takahashi and H. Tadokoro, *Macromolecules*, **6** (1973) 672.
- 13 B. L. Papke, M. A. Ratner and D. F. Shriver, *J. Phys. Chem. Solids*, **42** (1981) 493.
- 14 W. Saenger and H. Brandt, *Acta Crystallogr.*, **B35** (1979) 883, and references therein.
- 15 F. Vögtle and E. Weber, *Angew. Chem., Int. Ed. Engl.*, **18** (1979) 753.
- 16 S. Yanagida, K. Takahashi and M. Okahara, *Bull. Chem. Soc. Jpn.*, **51** (1978) 3111.
- 17 J. M. Parker, P. V. Wright and C. C. Lee, *Polymer*, **22** (1981) 1305.
- 18 R. Dupon, B. L. Papke, M. A. Ratner, D. H. Whitmore and D. F. Shriver, *J. Am. Chem. Soc.*, **104** (1982) 6247.
- 19 M. Stainer, unpublished observations, Northwestern University, 1982.