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Ionic Transport in Polymer Electrolytes: The Essential Role of Associated Ionic Species

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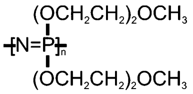
ABSTRACT: Polymer electrolytes based on poly(bis(methoxyethoxyethoxy)phosphazene) (MEEP) exhibit some of the highest room temperature ionic conductivities reported in a single-phase system. The mechanism of ionic transport in polymer electrolytes, particularly the nature of the charge-carrying species, has been poorly understood at the molecular level. Vibrational spectroscopy is used to determine the nature and relative amounts of ionic species present in MEEP−$LiCF_3SO_3$ as a function of salt concentration. The composition corresponding to the conductivity maximum is completely dominated by neutral cation−anion contact ion pairs and the triple anion species, $\{Li(CF_3SO_3)_2\}^-$. Furthermore, the conductivity changes only slightly at higher salt concentrations where triple cations dominate. These data require a dissociation−reassociation mechanism of ion transport in which dynamic equilibrium is established between the various ionically associated species by exchange of individual Li^+ and $CF_3SO_3^-$ ions. The individual ions migrate between associated ionic species through the liquidlike domains defined by the entangled ethylene oxide side chains.

Introduction

The mechanism of ionic transport in ion-conducting polymers is currently a subject of intense interest, primarily driven by numerous potential applications for these materials including utilization as electrolytes in rechargeable lithium batteries. However, it has proved difficult to develop lithium ion polymer electrolytes with sufficiently high room temperature conductivities (on the order of 10^{-4} S cm^{-1})[1] and the necessary mechanical properties to permit large-scale processing. Because the mechanism of ionic transport, particularly the nature of the charge-carrying species, is poorly understood in these materials at the molecular level, there are only very general outlines to guide the rational synthesis of new polymer electrolytes.

Much attention has focused on amorphous polymer electrolytes because studies have shown that the amorphous phases of polymer electrolytes generally exhibit markedly higher conductivity than ordered phases.[2,3] An important amorphous polymer electrolyte consists of salts dissolved in poly(bis(methoxyethoxyethoxy)-phosphazene) (MEEP), a polymer first synthesized and studied as a polymer electrolyte host by Shriver, Allcock, and their co-workers.[4,5] A MEEP monomer unit



$$\left[N{=}\underset{(OCH_2CH_2)_2OCH_3}{\overset{(OCH_2CH_2)_2OCH_3}{P}} \right]_n$$

consists of a phosphorus−nitrogen backbone with two ethylene oxide side chains that contain the sites which coordinate the lithium ions.[6] Polymer electrolytes based on MEEP exhibit some of the highest room temperature ionic conductivities reported to date.[7] This system is amorphous over a temperature range of at least −100 to 100 °C with room temperature conductivities that are at least 2 orders of magnitude higher than PEO−$LiCF_3SO_3$ at comparable compositions.[4,7]

In this paper, we describe a vibrational spectroscopic study of MEEP containing dissolved $LiCF_3SO_3$ (LiTf) and compare these data with conductivity measurements. This comparison enables us to identify the various ionic species present over a range of compositions and conductivities, thereby deducing those species playing a major role in charge transport.

Experimental Section

The materials used in the polymer synthesis were purchased from Aldrich and used as received unless otherwise noted. The precursor methoxyethoxyethoxyethanol was distilled from CaH_2 prior to use. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled prior to use. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from heptane and sublimed at 40 °C (0.05 mmHg).

The synthesis of MEEP follows the literature procedure with only slight modifications.[8] The general synthesis is described here. Poly(dichlorophosphazene) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C. Methoxyethoxyethoxyethanol was added slowly to a suspension of sodium hydride in THF, and the mixture was stirred overnight until a clear solution resulted. Then a solution of poly(dichlorophosphazene) in THF was added dropwise to the resultant sodium alkoxide, and the reaction was monitored by ^{31}P NMR. After ~24 h of stirring at 25 °C the reaction was complete, and the reaction mixture was placed in dialysis against water for purification. Two weeks of dialysis in water was followed by 1 week of dialysis in methanol. Precipitation of the polymer into hexanes yielded the final product. The absence of water in the product was confirmed by NMR and FT-IR. The absence of NaCl in the product was confirmed by flame atomic absorption spectroscopy. The resultant polymer was characterized by multinuclear NMR and GPC.

MEEP was dried under vacuum at ~45 °C for 24 h. Lithium triflate, $LiCF_3SO_3$ (LiTf), obtained from Aldrich was dried under vacuum at ~120 °C for 24 h. Tetrahydrofuran (THF) was stored over molecular sieves. All materials were stored

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Table 1. Conductivity and Ionic Species in the MEEP:LiTf System as a Function of Composition

P:Li	O:Li	EO:Li	conductivity[a] (S cm^{-1})	% speciation			
				"free"	pair/LiTf$_2^-$	agg	error
1.7:1	10:1	6.6:1	1.2×10^{-5}	0	4	96	16
4:1	24:1	16:1	2.7×10^{-5}	0	100	0	4
6.7:1	40:1	26.6:1	2.2×10^{-5}	12	88	0	4
8:1	48:1	32:1	2.2×10^{-5}	21	79	0	10

[a] Conductivity (at 30 °C) from ref 4.

in a nitrogen atmosphere glovebox with moisture less than 1 ppm. Desired ratios of MEEP and LiTf were dissolved in THF in the glovebox and stirred for 48 h. To obtain thin films of the samples, the polymer solutions were cast onto glass slides or Teflon sheets, and the THF was allowed to evaporate at room temperature in the glovebox. The resulting films were dried under vacuum for 48 h at ~35 °C. The absence of THF was confirmed by FT-IR.

Raman spectra were taken at room temperature using an ISA Jobin-Yvon T64000 Raman spectrometer, using the 514 nm line of an argon laser at a power of 300 mW at the laser head. Raman spectra were recorded in a backscattering geometry through the 80× objective lens of a microscope. Infrared spectra were recorded at room temperature with a Bruker IFS 66VFT-IR at a resolution of 1 cm^{-1} over a range of 500−4000 cm^{-1}. The MEEP−LiTf films were sandwiched between ZnSe windows. Curve fitting analysis of the spectra was accomplished using a commercial program (Galactic Grams version 5.05). Spectra were curve-fit to a straight baseline and one Gaussian−Lorentzian product function for each band using a nonlinear least-squares method.

Results and Discussion

The CF_3 symmetric deformation mode, $\delta_s(CF_3)$, of the $CF_3SO_3^-$ (triflate) ion has been used to study the nature and number of ionic species present in ethylene oxide−lithium triflate systems.[9−11] The mode frequency and intensity are highly dependent on interactions of cations with triflate oxygen atoms.[11,12] There are several ionic species that can be spectroscopically detected: "free" Tf^- ions (i.e., solvent-separated ion pairs), LiTf contact ion pairs, and the triple cation Li_2Tf^+. The contact-ion pair and the isolated triple anion species $LiTf_2^-$ are spectroscopically indistinguishable because the two triflate ions in $LiTf_2^-$ are vibrationally decoupled to the extent that each vibrates as an LiTf entity (with a common lithium ion). It is also not possible to distinguish an isolated triple cation from an Li_2Tf^+ entity vibrating as part of a more extensively associated species.[13] Table 1 compares the conductivities of several MEEP:LiTf compositions with an estimate of the relative concentration of the various ionic species present obtained from deconvolution of the $\delta_s(CF_3)$ band as measured in the Raman spectrum. (The ratio O:Li is the molar ratio of *all* side chain oxygen atoms to lithium ions (including P-O-C species), whereas EO:Li designates the molar ratio of just the side chain *ether* oxygen atoms to lithium ions.) The estimate of the relative concentrations is the ratio of the integrated band intensity for each species to the total integrated $\delta_s(CF_3)$ band intensity. The column headed by "agg" indicates Li_2Tf^+ and the Li_2Tf^+ entity vibrating as part of a higher aggregate species. The nature of such a species will be discussed below. To investigate the error in this analysis, the procedure was repeated several times for each composition, beginning with the preparation of a fresh sample. These errors are also listed in the table.

As expected, the relative amount of more highly associated species increases with increasing salt concentration, behavior that has been noted in other polymer−salt and glyme−salt systems.[14−16] At very high salt concentrations, i.e., EO:Li ≤ 10:1, the dominant species is triple cation Li_2Tf^+. On charge balance considerations, we would expect an equal concentration of "free" Tf^- ions, although very few are observed within experimental error. Therefore, the triple cation Li_2Tf^+ must be present as part of a more highly associated aggregate. We note that the concentration dependence of the ionic species present in MEEP−LiTf is similar to the behavior observed in solutions of LiTf dissolved in $CH_3(OCH_2CH_2)_2OCH_3$ (diglyme), where a dynamic equilibrium was postulated between contact ion pairs and Li_2Tf_2 dimeric species at high salt concentrations.[17] This parallel behavior is not surprising, given that the ethylene oxide interactions of the MEEP side chains can be modeled by diglyme. The existence of Li_2Tf_2 dimeric species in solution is made plausible by the fact that the crystalline phase of diglyme:LiTf consists exclusively of isolated $diglyme_2Li_2Tf_2$ dimers. In that system, each lithium ion is coordinated to the three oxygen atoms of a diglyme molecule and two triflate oxygen atoms, one from each of the two triflate ions in the dimer. The two triflate anions then link the two lithium ions together to form the dimeric structural unit. Consequently, each triflate ion vibrates as an Li_2Tf^+ entity although the anions are part of an Li_2Tf_2 dimer. We are aware that in the $P(EO)_3LiTf$ line compound all triflate ions vibrate as if they were Li_2Tf^+ triple cations.[13] However, a one-dimensional extended structure, such as is seen in the $P(EO)_3LiTf$ compound, is highly unlikely in MEEP−LiTf. Consequently, we suggest that the triple cation species that dominate the spectrum at high salt concentrations are really present as Li_2Tf_2 dimers with each lithium ion coordinated by two or three side chain oxygen atoms, not necessarily from the same side chain.

A striking observation emerges from the comparison of ionic conductivity with the ionic species present at various system compositions. Over a concentration range where the ionic speciation ranges from mostly contact ion pairs and triple anions, $LiTf_2^-$, with a significant amount of "free" ion to mostly Li_2Tf^+ aggregate with a small amount of ion pairs and $LiTf_2^-$ ions, the conductivity only changes by approximately a factor of 2. This is a remarkable result, considering that MEEP−LiTf exhibits one of the highest room temperature ionic conductivities known. It is particularly interesting that the maximum conductivity is found at a composition consisting exclusively of contact ion pairs and triple anions. The apparent indifference of the ionic conductivity (within a half order of magnitude) to the nature of the ionic species present at various concentrations, combined with occurrence of the maximum conductivity at a composition dominated by neutral contact ion pairs and triple anions, argues for a mechanism of ion transport that generates reasonable concentrations of highly mobile charge carriers in the presence of very large relative concentrations of ionically associated species. The critical questions are, what is the nature of these charge carriers and how are they produced?

We suggest that dynamic equilibrium is established between the various ionically associated species by exchange of individual Li^+ and Tf^- ions, with the net effect that the individual Li^+ and Tf^- ions are the primary charge carriers, migrating through the liquidlike domains defined by the entangled ethylene oxide side chains. We will justify this picture of liquidlike domains later. It has been previously suggested that associated ionic species play a role in the mechanism of ionic transport, although the associated species was assumed to transport charge.[18] An early mechanism involving intercluster hopping was suggested by Teeters and Frech[19] and expanded by other workers.[20] Ferry et al. proposed that the earlier dynamic bond percolation model[21] based on the movement of ions between ether oxygen sites be augmented by considering hopping between ions in pairs and dissolved ions.[10] Because only neutral contact ion pairs and bulky triple anions are present to any extent at the conductivity maximum, dissociation of these ionically associated species is the only mechanism that can significantly contribute to the conductivity.

In the composition regime where contact ion pairs/triple anions dominate, a mechanism describing the conductivity might begin with a step in which a LiTf contact ion pair dissociates according to

$$\mathrm{LiTf} \rightarrow \mathrm{Li}^{+} + \mathrm{Tf}^{-} \tag{1}$$

The lithium ion of the contact ion pair is assumed to be coordinated by a single triflate oxygen atom and several side chain oxygen atoms, although not necessarily from the same side chain. After dissociation, the triflate ion is relatively free although the lithium ion retains some degree of coordination with the side chain oxygen atoms. However, the potential energy environment of the cation is now considerably less deep than in its original coordinated state, and that environment is dynamically disordered through the thermal motion of the side chains. Hence, the cation is also mobile, although its contribution to the charge transport is smaller than that of the anion. Blonsky et al. measured the transference number of lithium as 0.32 at a 24:1 EO:Li composition.[4] It is reasonable to assume that the transference number is not significantly different at room temperature.[22] At a 24:1 EO:Li composition, contact ion pairs and triple anions are the dominant species present. The triflate ion can encounter a contact ion pair in its immediate vicinity, forming the triple anion species

$$\mathrm{Tf}^{-} + \mathrm{LiTf} \rightarrow \mathrm{LiTf_2}^{-} \tag{2}$$

Of course, the triflate anion could also reassociate with the lithium ion that resulted from step 1, the reverse of process (1). However, the reassociation step would not contribute to the dc conductivity. Alternatively, the conductivity might begin with the dissociation of an immobile $\mathrm{LiTf_2}^{-}$ species according to

$$\mathrm{LiTf_2}^{-} \rightarrow \mathrm{Tf}^{-} + \mathrm{LiTf} \tag{3}$$

The triflate ion can then associate with an ion pair in the vicinity, in a step that formally looks like the reverse of step (3), i.e.

$$\mathrm{Tf}^{-} + \mathrm{LiTf} \rightarrow \mathrm{LiTf_2}^{-} \tag{4}$$

In this picture, the dissociation of LiTf or $\mathrm{LiTf_2}^{-}$ produces "free" Tf^{-} as a transient species in its role as the principal charge carrier. "Free" Tf^{-} may also be present as a long-lived species (spectroscopically detected at ≤4% relative concentration) that can also contribute to the conductivity. In the very short time scale defined by the movement of highly mobile, individual Tf^{-} ions from a dissociation site (e.g., LiTf or $\mathrm{LiTf_2}^{-}$) to a reassociation site (e.g., a nearby LiTf), the more highly associated species serve as relatively "immobile" sites for ionic association/dissociation reactions such as those described in eqs 1−4. The associated species are relatively immobile in this time scale because the lithium ion in the species is coordinated with the oxygen atoms of the side chain(s). Although it is possible that isolated triple anions are also charge carriers here, the expected low mobility of this rather bulky species leads us to conclude that a dissociation−reassociation mechanism such as suggested above is the only reasonable mechanism that accounts for the unusually high room temperature conductivity exhibited in MEEP−LiTf.

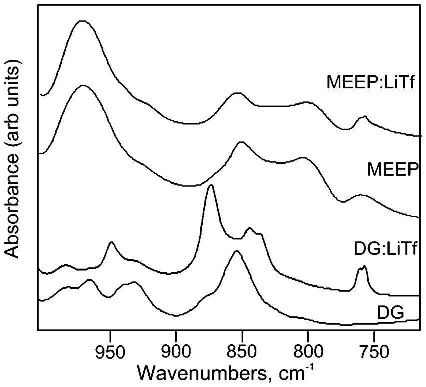

Figure 1. FT-IR of MEEP, MEEP:LiTf 2:1, diglyme, and diglyme LiTf 5:1 (EO:Li) in the region from 1000 to 725 cm^{-1}.

At compositions where the triple cation is the majority species (although probably present as the $\mathrm{Li_2Tf_2}$ dimer as previously discussed), a simple dissociation process leads to a free triflate ion

$$\mathrm{Li_2Tf_2} \rightarrow \mathrm{Li_2Tf}^{+} + \mathrm{Tf}^{-} \tag{5}$$

that can then recombine with another $\mathrm{Li_2Tf}^{+}$ ion in the immediate vicinity

$$\mathrm{Tf}^{-} + \mathrm{Li_2Tf}^{+} \rightarrow \mathrm{Li_2Tf_2} \tag{6}$$

The dissociation of $\mathrm{Li_2Tf_2}$ can also produce a lithium ion

$$\mathrm{Li_2Tf_2} \rightarrow \mathrm{Li}^{+} + \mathrm{LiTf_2}^{-} \tag{7}$$

Of course, it is possible to devise other schemes involving more elaborate association/dissociation steps. However, the overall concept remains the same: ionic transport consisting of highly mobile Tf^{-} and Li^{+} ions moving over short distances between proximate, relatively immobile, ionically associated species.

The role of the MEEP host is also important in understanding the mechansim of ionic transport. As noted earlier, diglyme−LiTf systems provide a useful model for the lithium ion−ethylene oxide interactions of the MEEP side chains. Figure 1 shows a comparison of the IR spectra of MEEP, MEEP:LiTf 2:1, diglyme, and diglyme:LiTf 5:1. (A 2:1 solution of diglyme:LiTf cannot be prepared because a crystalline compound forms at a 3:1 ratio.) This spectral region from 800 to 1000 cm^{-1} contains modes that are a mixture of $\mathrm{CH_2}$ rocking and CO stretching motions.[23−25] The frequencies and intensities of these bands are sensitive to the conformation of the EO chain.[16,17,26] The collapse of the four bands in diglyme between 900 and 1000 cm^{-1} into a broad, slightly structured feature in MEEP coupled with a comparison of the bands primarily due to CH_2 rocking motion (particularly the breadth of the features at 804 and 851 cm^{-1} and the absorption due to unresolved bands between these two features) indicates that the side chain conformations are distributed over a much wider range of dihedral angles in MEEP than in diglyme despite the fact that diglyme is a liquid. Even more interesting is the observation that the addition of LiTf to MEEP produces almost no change in these and other regions of the spectrum sensitive to changes in ethylene oxide conformation, even at very high salt concentrations. These data suggest that there is no distinctive change in the conformation of the side chains upon interaction with the lithium ions. This is in sharp contrast to diglyme−LiTf solutions, where the striking frequency shifts and changes in band intensities are observed upon addition of salt. These spectral changes originate in the growth of local structures (e.g., ionic coordination and conformation of the ethylene oxide units) at increasing salt concentrations and closely resemble analogous local structures in the diglyme−LiTf crystal.[17]

We infer that the formation of a MEEP−LiTf polymer electrolyte must occur with the dissolution of salt in the highly disordered ethylene oxide side chains as if those side chains constituted a liquidlike phase surrounding the polyphosphazene backbone. The highly entangled nature of the polyphosphazene backbone and the resulting close proximity of the ethylene oxide side chains leads to a conformationally disordered system despite the presence of isolated, ordered, ionic dimers. The high mobility in part arises through the thermal motions of disordered ethylene oxide side chains, producing a locally disordered potential energy environment for the ions.

Conclusions

The data presented in this study argue that the mechanism of ionic transport in MEEP−LiTf at moderate to high salt concentrations necessarily involves a series of ionic dissociation and reassociation steps. Specifically, transient triflate anions (and to some degree lithium cations) are generated through the dissociation of relatively immobile, associated ionic species and migrate via stepwise processes through regions of relatively immobile, associated species contained in a matrix of highly disordered ethylene oxide side chains. The ionically associated species playing a major role in this mechanism have been identified as contact ion pairs, triple cations, and (possibly) triple anions. Although this study has focused on the MEEP−LiTf system, the relatively high concentration of ion pairs and more highly associated species in other polymer−salt systems (such as PEO−LiTf) at compositions with large values of ionic conductivity strongly argues that an dissociation/reassociation mechanism such as we propose here is essential in a wider variety of polymer electrolytes. We recognize that in a number of polymer−salt systems there are relatively large amounts of "free" ion at salt concentrations where the conductivity is significant. In such systems, it is possible that processes involving solvent-separated ion pairs or triples which are analogous to a dissociation/reassociation mechanism play a significant role in the transport of ions.

References and Notes

(1) Vincent, C. A.; Scrosati, B. *Modern Batteries: An Introduction to Electrochemical Power Sources*, 2nd ed.; John Wiley & Sons: New York, 1997.
(2) Berthier, C.; Gorecki, W.; Minier, M. *Solid State Ionics* **1983**, *11*, 91−95.
(3) Stainer, M.; Hardy, L. C.; Whitmore, D. H.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 784−790.
(4) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, 258−264.
(5) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854−6855.
(6) York, S.; Kellam, E. C., III; Allcock, H. R.; Frech, R. *Electrochim. Acta* **2001**, *46*, 1553−1557.
(7) Allcock, H. R.; Napierala, M. E.; Olmeijer, D. L.; Cameron, C. G.; Kuharcik, S. E.; Reed, C. S.; O'Connor, S. J. M. *Electrochim. Acta* **1998**, *43*, 1145−1150.
(8) Allcock, H. R.; O'Connor, S. J. M.; Olmeijer, D. L.; Napierla, M. E.; Cameron, C. G. *Macromolecules* **1996**, *29*, 7544−7552.
(9) Huang, W.; Frech, R. *Polymer* **1994**, *35*, 235−242.
(10) Ferry, A.; Jacobsson, P.; Torell, L. M. *Electrochim. Acta* **1995**, *40*, 2369−2373.
(11) Frech, R.; Rhodes, C. P.; York, S. S. *Mater. Res. Soc. Symp. Proc.* **1999**, *548*, 335−345.
(12) Huang, W.; Frech, R.; Wheeler, R. A. *J. Phys. Chem.* **1994**, *98*, 100−110.
(13) Frech, R.; Chintapalli, S.; Bruce, P. G.; Vincent, C. A. *Macromolecules* **1999**, *32*, 808−813.
(14) Schantz, S.; Sandahl, J.; Borjesson, L.; Torell, L. M.; Stevens, J. R. *Solid State Ionics* **1988**, *28−30*, 1047−1053.
(15) Schantz, S.; Torell, L. M. *Solid State Ionics* **1993**, *60*, 47−53.
(16) Frech, R.; Huang, W.; Dissanayake, M. A. K. L. *Mater. Res. Soc. Symp. Proc.* **1995**, *369*, 523−534.
(17) Rhodes, C. P.; Frech, R. *Macromolecules* **2001**, *34*, 2660−2666.
(18) Bruce, P. G.; Vincent, C. A. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 43−54.
(19) Teeters, D.; Frech, R. *Solid State Ionics* **1986**, *18 & 19*, 271−276.
(20) Arumugam, S.; Shi, J.; Tunstall, D. P.; Vincent, C. A. *J. Phys. C* **1993**, *5*, 153.
(21) Druger, S. D.; Ratner, M. A.; Nitzan, A. *Solid State Ionics* **1983**, *9 & 10*, 1115−1120.
(22) Kato, Y.; Watanabe, M.; Sanui, K.; Ogata, N. *Solid State Ionics* **1990**, *40−41*, 632−636.
(23) Matsuura, H.; Fukuhara, K.; Tamaoki, H. *J. Sci. Hiroshima Univ., Ser. A* **1985**, *49*, 89−113.
(24) Matsuura, H.; Fukuhara, K. *J. Polym. Sci., Part B* **1986**, *24*, 1383−1400.
(25) Matsuura, H.; Fukuhara, K.; Tamaoki, H. *J. Mol. Struct.* **1987**, *156*, 293−301.
(26) Huang, W.; Frech, R.; Johansson, P.; Lindgren, J. *Electrochim. Acta* **1995**, *40*, 2147−2151.

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