Lithium-7 NMR and Ionic Conductivity Studies of Gel Electrolytes Based on Poly(acrylonitrile)

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Composite gel electrolytes prepared from mixtures of poly(acrylonitrile) (PAN), ethylene carbonate (EC), propylene carbonate (PC), and $LiClO_4$ or $LiAsF_6$ have been investigated by complex impedance, differential scanning calorimetry (DSC), and ^{7}Li nuclear magnetic resonance (NMR) spectroscopy. The ionic conductivity of a gel containing $LiAsF_6$ reaches 10^{-2} S/cm at 60 °C. Although the conductivity of the gels approach that found in EC/PC liquid electrolytes, NMR line width, and spin–lattice relaxation time (T_1) measurements indicate that even *short-range* ionic mobility is impeded by the presence of the PAN. As in the case of amorphous polyether–salt polymer electrolytes, the onset of ^{7}Li motional line narrowing in the gels is strongly correlated with the DSC-determined glass transition temperature.

Introduction

Solid polymeric electrolytes are currently receiving a great deal of attention because of their proposed large-scale use in secondary lithium batteries and electrochromic "smart windows".[1,2] The most extensive efforts have, thus far, been focused on polyether-based electrolytes. While these materials have favorable mechanical properties, their ambient temperature ionic conductivities are too low for many of the applications envisioned. Several approaches have been taken in attempting to overcome this limitation without sacrificing mechanical integrity, including the use of flexible, low glass transition (T_g) polymer hosts,[3,4] and the addition of plasticizing agents to polyethers.[5] A third strategy involves the immobilization of a liquid electrolyte in a rigid polymeric matrix. Two distinct methods of achieving the necessary macroscopic immobilization have been reported: (i) loading the liquid electrolyte into a microporous matrix (e.g., porous polyethylene);[6] (ii) increasing the viscosity of the liquid electrolyte by adding a soluble (in the electrolyte) polymer until a gel consistency is achieved. Two of these polymer additives which appear to yield materials with the requisite mechanical and electrical properties are poly(methyl methacrylate) (PMMA)[7] and poly(acrylonitrile) (PAN).[8,9]

Present speculation regarding the ion transport mechanism in PMMA/propylene carbonate (PC)/$LiClO_4$ gel invokes a model of connected liquid electrolyte regions, based primarily on the observation that the conductivity of the gel is not much lower (within a factor of 2) than that of the liquid electrolyte constituent.[7] Because of the dearth of microscopic characterization techniques reported for the gel electrolytes thus far, we have undertaken an investigation of ^{7}Li NMR line widths and spin–lattice relaxation times (T_1) in conjunction with complex impedance and differential scanning calorimetry (DSC) measurements of several PAN-based gels. One of the principal goals of this study is to determine whether or not the PAN acts as an inert matrix for the liquid electrolyte, thus testing the assertion described above for PMMA-based electrolytes. In particular, although the ionic conductivity suffers only a slight decrease upon addition of the "matrix" polymer (which produces a very large increase in viscosity), the sensitivity of NMR to the immediate environment of the Li^+ ions can reveal the presence of interactions with the PAN chain. Such interactions, if found, would necessitate a more sophisticated description of the ion transport mechanism in the gel electrolytes than currently exists.

Experimental Section

Gel electrolytes were synthesized from reagent-grade PC (Burdick and Jackson), ethylene carbonate (EC, Fluka AG), PAN (Polyscience, Inc.; average molecular weight of 150 000), and $LiClO_4$ (Alfa), or $LiAsF_6$ (Lithco "Lectro-salt"). The EC was purified by distillation under vacuum; the PC was dried with type 4A molecular sieves for 48 h and then distilled under vacuum. Karl-Fischer titrations for both EC and PC indicated water contents of less than 18 ppm. The Li salts were dried under vacuum at elevated temperature for at least 24 h (60 and 150 °C for $LiAsF_6$ and $LiClO_4$, respectively). The PAN was dried under vacuum at 60 °C for 48 h. The components were mixed together at room temperature to ensure wetting of the PAN, and the

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(1) Gray, F. M. *Solid Polymer Electrolytes*; VCH Publishers Inc.: New York, 1991.

(2) MacCallum, J. R., Vincent, C. A., Eds.; *Polymer Electrolyte Reviews*; Elsevier Applied Science: London, 1989; Vol. 2.

(3) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, *18*, 258.

(4) Bouridah, A.; Dalard, F.; Deroo, D.; Cheradame, H.; LeNest, J. F. *Solid State Ionics* **1985**, *15*, 233.

(5) Huq, R.; Koksbang, R.; Tonder, P. E.; Farrington, G. C. *Electrochim. Acta* **1992**, *37*, 1681.

(6) Koseki, K.; Saeki, R.; Itoh, T.; Juan, C. Q.; Yamamoto, O. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier Applied Science: London, 1990; p 197.

(7) Bohnke, O.; Rousselot, C.; Gillet, P. A.; Truche, C. *J. Electrochem. Soc.* **1992**, *139*, 1862.

(8) Watanabe, M.; Kanba, M.; Nagaoka, K.; Shinohara, I. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 939.

(9) Abraham, K. M.; Alamgir, M. *J. Electrochem. Soc.* **1990**, *106*, 1657.

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Table I. VTF and Arrhenius Parameters[a]

electrolyte	(EC + PC):salt	A	T_0 (=T_g − 45)	T_g/K	E_a/eV (σ)	E_a'/eV (T_1)
EC:PC:LiClO$_4$	8.8:1	2.68	176		0.036	
EC:PC:PAN:LiClO$_4$	8.8:1	28.4	149	194	0.083	0.13
EC:PC:PAN:LiClO$_4$	17.6:1	3.73	138	183	0.083	0.10
EC:PC:PAN:LiAsF$_6$	17.6:1	27.7	139	184	0.081	0.17

[a] Gel electrolyte compositions are (in mole percents) 38 (EC):33 (PC):21 (PAN):8 (Li salt) for the 8.8:1 ratio and 40 (EC):34.75 (PC):21 (PAN):4.25 (Li salt) for the 17.6:1 ratio.

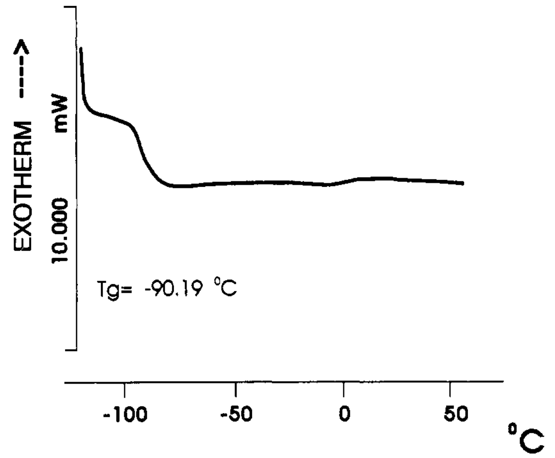

Figure 1. DSC thermogram of gel of composition PAN$_{0.21}$EC$_{0.40}$-PC$_{0.35}$(LiClO$_4$)$_{0.04}$. The heating rate is 10 K/min.

mixture was then placed in a preheated silicone oil bath at 100 °C and stirred until a clear viscous gel was formed. Films were fabricated by casting the hot gel between glass plates with spacers (to control thickness). Free-standing elastomeric electrolyte films were formed upon cooling to room temperature. All sample manipulations were performed in a drybox under argon. Specific gel compositions are given in Table I.

DSC measurements were performed on a Mettler TA3000 thermal analysis system. Electrical conductivities were determined from ac impedance measurements utilizing an EG&G PAR model 388 impedance analyzer with a SS/gel/SS cell configuration (SS = stainless steel). NMR measurements were performed on 500–1000-mg samples of gel contained in a sealed Pyrex 10-mm (outer diameter) NMR tube, with a JEOL GX-400 spectrometer operating at a ^{7}Li Larmor frequency of 155 MHz. Line widths reported correspond to the full width at half-maximum of spectra obtained from 4–16 averaged free induction decays, and T_1 values were extracted from recovery profiles of the steady-state single-pulse sequence. In all cases, the recovery profiles were observed to be exponential.

Results

Initial evidence for chemical interaction between the liquid electrolyte and PAN was ascertained from the observed irreversibility of the increase in viscosity; i.e., upon reheating the gel to 100 °C, the gel does not recover its initial flowing consistency. Attempts to lower the viscosity by heating to higher temperature (above 100 °C) were hindered by sample decomposition, manifested by color change from clear to brown. Gel electrolytes prepared in the manner described above were reported to be free of crystallinity,[8] an observation which was verified in our laboratory by X-ray diffraction. Figure 1 displays a DSC thermogram of a sample of composition (molar) 40% EC, 34.75% PC, 21% PAN, and 4.25% LiClO$_4$ (with a 17.6:1 EC/PC:Li molar ratio). A strong glass transition centered at 183 K is observed. The only other prominent thermal features in the DSC which have been confirmed by thermogravimetric analysis occur at significantly higher temperature (i.e. > 450 K, not shown in the figure) and are attributed to solvent loss and, eventually, PAN decomposition. The glass transition temperatures for the three gel electrolytes investigated in this work are listed in Table I. It is noteworthy that, of the two LiClO$_4$-containing gels, the one with the higher salt concentration has a higher T_g. This is a well-known phenomenon in polyether-based polymer electrolytes which is attributed to the effective cross-linking of polyether segments by the salt cations.[1,2] As will be discussed in more detail later, the elevation of T_g in the gel is attributed primarily to interaction between PAN and the salt. It is, however, quite likely that some contribution to the difference in T_g's is due to the slightly different (EC + PC):PAN ratios of the gels; 75:21 for the more dilute salt gel and 71:21 for the concentrated salt gel (see Table I). Electrical conductivity data for the 8.8:1 EC/PC:LiClO$_4$ gel and a reference liquid electrolyte with an identical EC/PC:LiClO$_4$ (without PAN) ratio are shown in the Arrhenius plots in Figure 2. Throughout the entire temperature range of the measurements (238–338 K), the conductivity of the liquid never exceeds that of the gel by more than a factor of 4, and, in fact, the conductivities are nearly equal at 338 K. In addition, the Arrhenius plots exhibit significant curvature, which is characteristic of Vogel–Tammann–Fulcher (VTF) behavior.[1] Arrhenius behavior (straight lines in the semilog reciprocal T plot) reported previously[9] for gel electrolytes can be ascribed to the limited temperature range over which the conductivity was measured. Figure 3 shows Arrhenius plots of all three gel samples. The ionic conductivities above room temperature are quite high, reaching 10^{-2} S/cm at 60 °C in the most conductive sample studied, containing an EC/PC:LiAsF$_6$ ratio of 17.6:1. The solid lines are best-fit curves corresponding to the

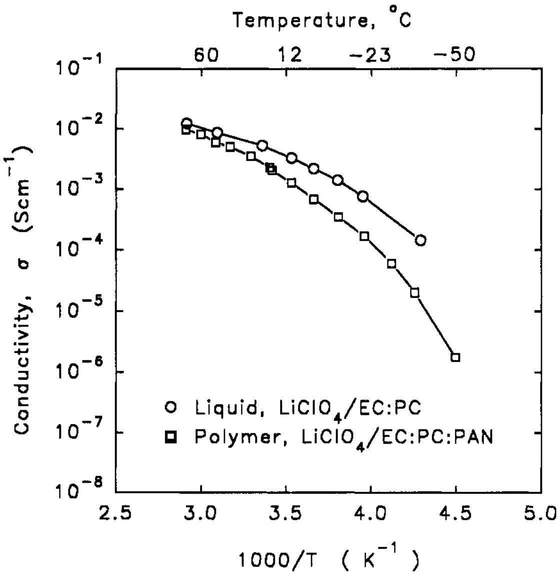

Figure 2. Arrhenius plots of electrical conductivity of high LiClO$_4$ content gel (Table I) and reference liquid electrolyte having the same PC/EC:salt ratio.

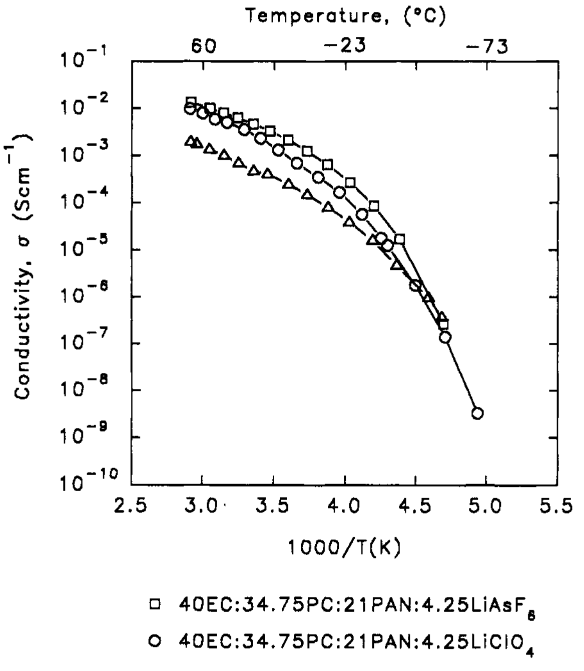

Figure 3. Arrhenius plots of electrical conductivity of the three gel samples. The curves are best fits of the VTF equation, with T_0 set equal to 45 K below the DSC-determined T_g.

VTF equation

$$\sigma = AT^{-1/2} \exp[-E_a/(T - T_0)] \qquad (1)$$

where T_0 is taken as the idealized temperature corresponding to zero configurational entropy.[10] In accord with previous work on polyether-based polymer electrolytes, in which T_0 was found to be approximately $T_g - 45$,[11] T_0 is fixed at $T_g - 45$ for the three gels resulting in the best-fit parameters A and E_a listed in Table I. The data for the liquid electrolyte were fitted to the VTF equation with T_0 treated as an adjustable parameter (due to there being no glass transition in this sample). The three gels exhibit very similar values of E_a, although the 17.6:1 EC/PC:$LiClO_4$ sample is characterized by a somewhat low preexponential factor.

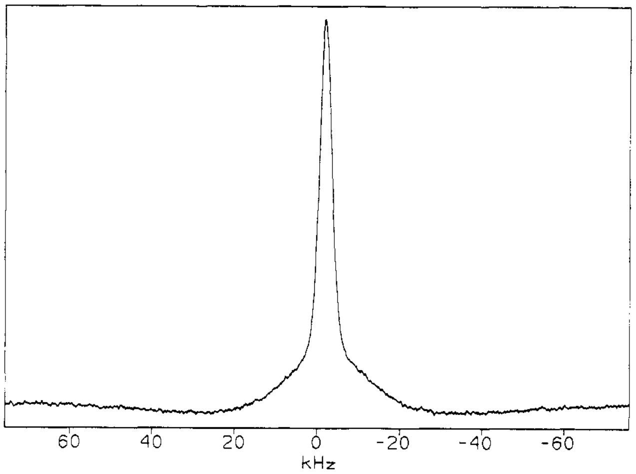

Figure 4. ^{7}Li NMR spectrum of $PAN_{0.21}EC_{0.38}PC_{0.33}(LiClO_4)_{0.08}$ at 195 K.

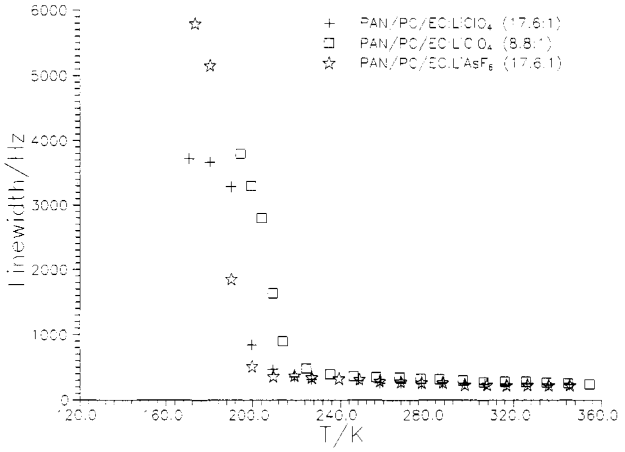

Figure 5. Temperature dependence of the ^{7}Li NMR central linewidth (full width at half maximum) for the three gel samples.

A low temperature (195 K) ^{7}Li NMR absorption spectrum for the 8.8:1 EC/PC:$LiClO_4$ sample is shown in Figure 4. The broad shoulders flanking the main spectrum are attributed to a distribution of quadrupole satellite transitions associated with a heterogeneous Li nearest-neighbor configuration in the composite material. In appearance, this spectrum is similar to that observed in Li salt/polyether complexes.[12,13] The main source of broadening of the central portion of the spectrum is attributed to nuclear dipole–dipole interactions, again in accord with previous results for polyethers. Upon raising the temperature, the broad satellites abruptly collapse and the central line undergoes motional narrowing. The ^{7}Li central line widths of the three gel samples are plotted as a function of T in Figure 5. At the lowest temperature accessible with the spectrometer probe utilized in this investigation (~175 K) the central line width of the 17.6:1 PC/EC:$LiClO_4$ gel sample shows signs of reaching its rigid limit (about 4 kHz). In fact, the onset of line-narrowing, which heralds the presence of Li^+ ion motion on a time scale comparable to the reciprocal of the line width (~10^{-3} s), occurs at a temperature very close to the value determined for T_g. The close correspondence between the glass transition and the onset of cation (i.e., ^{7}Li or ^{23}Na) motional narrowing in polyether–salt polymer electrolytes is well established and highlights the coupling between ionic and polymer segmental mobility.[14] Although the data for the 8.8:1 PC/EC:$LiClO_4$ gel sample does not, unfortunately, extend to a low enough temperature where it is clearly evident that the line width is leveling off, comparison between the two $LiClO_4$-containing samples does suggest that the main features of the T-dependent line-width behavior of the more salt-concentrated gel are shifted to higher temperature by some 10 K. From Table I it can be noted that this shift is correlated with the difference in T_g between the two materials. Although the data for the $LiAsF_6$-containing gel are also consistent with the T_g results, it is interesting to note that the low temperature line widths reach values nearly 50% higher than the $LiClO_4$-containing samples.

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(10) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.

(11) Wintersgill, M. C.; Fontanella, J. J. In *Polymer Electrolyte Reviews*, MacCallum, J. R., Vincent, C. A. Eds.; Elsevier Applied Science: London, 1989; Vol. 2, p 43.

(12) Chung, S. H.; Jeffrey, K. R.; Stevens, J. R. *J. Chem. Phys.* **1991**, *94*, 1803.

(13) Greenbaum, S. G.; Panero, S.; Scrosati, B. *Electrochim. Acta* **1992**, *37*, 1533.

(14) Greenbaum, S. G.; Pak, Y. S.; Adamic, K. J.; Wintersgill, M. C.; Fontanella, J. J. *Materials Research Symposium on Solid State Ionics II*; Materials Research Society: Pittsburgh, 1991; Vol. 210, p 237.

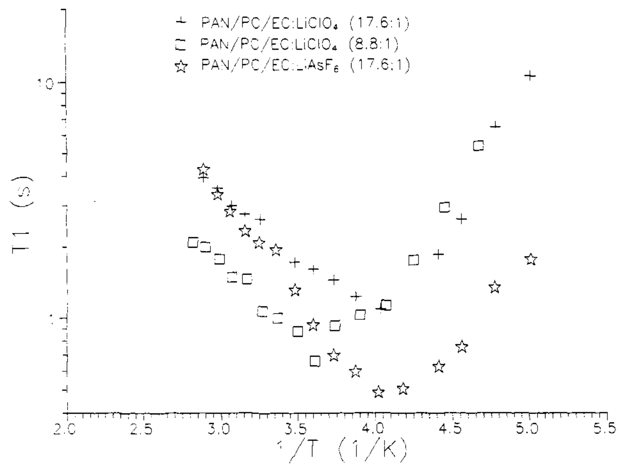

Figure 6. Arrhenius plots of spin-lattice relaxation time T_1 for the three gel samples.

Similar behavior has been previously reported in comparisons between polyethers complexed with $LiClO_4$ and $LiBF_4$, in which the larger line width of the $LiBF_4$ complex was attributed to heteronuclear ^7Li–^{19}F dipolar interactions.[13] This conclusion has important implications for polymer electrolytes because, by virtue of the short-range nuclear magnetic dipole–dipole interaction, it demonstrates that the Li^+ ions are not well-separated from their counterions.

From the point of view of one of the principal goals of this study, perhaps the most significant information contained in the data in Figure 5 concerns the high temperature line widths of the samples. In particular, all three of the gels exhibit a common line width which levels off around ~300 Hz above 300 K. This line width is comparable to that observed in polyether–lithium salt complexes (at temperatures significantly higher than their glass transitions),[12] and more than an order of magnitude larger than that of the reference liquid electrolyte (~15 Hz at 295 K). Given the short-range nature of the nuclear magnetic dipole–dipole interaction which, as described above, is the principal source of broadening of the central line, comparison between the gel and liquid electrolyte results clearly demonstrates that even short-range ionic motion is restricted in the gel. That is, the interpretation of the high conductivity of the gel in terms of microscopic "pockets" of liquid electrolyte separated by regions of inert PAN matrix is not the correct one. Additional information regarding the local environment of the Li^+ ions can be obtained by examining the spin–lattice relaxation (T_1) results. Figure 6 displays Arrhenius plots of T_1 for the three gel samples. All three samples exhibit well-defined T_1 minima which, according to $\omega\tau \sim 1$, indicates the temperature at which the motional correlation time is comparable to the reciprocal of the angular resonance frequency (~10^{-9} s).[15] Thus T_1 measurements probe much higher frequency motions than those that characterize the onset of line-narrowing. Straight lines fitted to the high-T portions (above the T_1 minima) of the T_1 curves, usually referred to as the "extreme narrowing limit" imply activation energies in the range of 0.10–0.17 eV (values listed in Table I). It is interesting to note that these values are comparable to those extracted from straight line fits to the conductivity data in Figure 3. That is, temperature-dependent Arrhenius activation energies can be computed from the instantaneous slope of the conductivity curve, according to the approximation

$$\sigma = \sigma_0 \exp(E_a'/kT) \qquad (2)$$

For example, analysis of the data for the $LiAsF_6$ sample yields E_a' = 0.37 and 0.11 eV at 278 and 328 K, respectively. In view of the different frequency motions probed by electrical conductivity and T_1 measurements, it is not surprising that the activation energies do not agree more closely. Nevertheless, it is interesting to note that while the two 17.6:1 PC/EC Li salt samples exhibit T_1 minima at about the same temperature, the more salt-rich gel has its T_1 minimum occurring some 20–25 K higher. Thus the high-frequency ionic motion is also somewhat impeded in the 8.8:1 PC/EC $LiClO_4$ gel. T_1 measurements of reference liquid electrolytes with 8.8:1 and 17.6:1 PC/EC:$LiClO_4$ ratios did not, in fact, exhibit a clear dependence on salt concentration.

Discussion

The correlation between the onset of ^7Li motional line-narrowing and T_g in the gels invites comparison with polyether–salt polymer electrolytes. However, while the glass transition in the latter material can be envisioned as large-scale segmental motion (the segments comprise ~4 or more repeat units) associated with the α relaxation,[11] the interpretation of specific molecular units contained within the composite gel that are set into motion at T_g is open to question.

In an early study of PAN/EC/$LiClO_4$ complexes, the increase of conductivity activation energy with increasing salt concentration was taken as evidence of interaction between the conducting ions and the PAN chains. It was also noted that, under certain circumstances, complex formation between PAN and Li salts is possible.[8] Recent infrared measurements of C≡N stretch modes as a function of salt concentration in PAN/PC/EC/Li salt composites, also imply some interaction between the Li^+ ions and the polar portion of the PAN backbone.[16] Interactions of this nature could be expected merely on the basis of the fairly high dielectric constant of PAN (around 6.5 at 25 °C[8]). In view of the above evidence taken together with the results cited in this investigation, in particular (i) irreversible increase in viscosity during sample preparation, (ii) single-phase behavior of the composite gel as evidenced by DSC and NMR line-narrowing associated with T_g, and (iii) high-temperature NMR line broadening (compared to the liquid electrolyte); it is now clear that the picture of passive PAN chains providing only dimensional stability must be discarded. Interaction between Li salts and PAN may, in fact, contribute to dimensional stability of the composite, but the ion transport mechanism must now be regarded as more complex than that which occurs in the liquid. The degree to which salt–PAN interactions modify the ion-transport mechanism (in addition to merely increasing the macroscopic viscosity of the gel) is currently unknown, for lack of a microscopic model of competitive ion solvation by EC/PC and PAN. On the basis of the high conductivity of the gels it is, of course, tempting to conclude that the transport mechanism is not much different than in the liquid electrolyte, as discussed in the Introduction. That

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(15) Abragam, A. *The Principles of Nuclear Magnetism*: Oxford University Press: Oxford, 1961; Chapter VIII.

(16) Abraham, K. M., unpublished results.

is, the Li^+ ions are still solvated primarily by EC/PC molecules. However the central issue of this investigation is to point out that ion–PAN interactions cannot be neglected.

A simplified but nevertheless intriguing scenario concerning the role that PAN plays in ion solvation involves the contribution that PAN makes to the dielectric constant of the composite. In particular, the quoted value of 6.5 at 25 °C, well below T_g (107 °C for pure PAN[8]), may not be relevant to PAN in a highly plasticized state such as that which characterizes the gels above their T_g. That is, the mobility of the polar groups of PAN, which contribute to the dielectric constant and hence ion solvation, may be considerably enhanced in the gel. Dielectric measurements of mixtures of PAN, PC, and EC are currently in progress in order to test this hypothesis. Preliminary results indicate that the dielectric constant of the mixture is somewhat enhanced with respect to the value predicted from a weighted average of the constituents (assuming a value of 6.5 for PAN). Although this preliminary macroscopic result supports the assertion that plasticized PAN can compete, to some degree, with EC/PC for ion solvation, a detailed comparison between PAN–ion and EC/PC–ion interactions must await further spectroscopic studies (i.e., vibrational; double or triple resonance NMR, etc.).

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