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applicable to alkaline-earth-metal and lanthanide compounds of reduced early transition metals.

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Supplementary Material Available: Details of the X-ray structure determinations and list of positional and anisotropic thermal parameters (7 pages); listing of observed and calculated structure factors (30 pages).

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^{7}Li NMR Study of Polymer Electrolytes Based on Composites of Poly[bis((methoxyethoxy)ethoxy)phosphazene] and Poly(ethylene oxide)

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Polymer electrolytes consisting of mixtures of poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP) and poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) complexed with $LiClO_4$ or $LiBF_4$ have been studied by differential scanning calorimetry (DSC) and ^{7}Li nuclear magnetic resonance (NMR) spectroscopy. Both types of measurements demonstrate that the MEEP/PEO composites are multiphase in that amorphous MEEP-like and crystalline PEO-like phases are present in the samples. The NMR results show that significant Li^+ ion mobility in the MEEP-like phase occurs only above the lowest temperature glass transition as indicated by DSC measurements. Strong cation–anion association effects are suggested by dipolar broadening in BF_4^- containing materials and by precipitation of salt crystallites from the MEEP/PPO composite at elevated temperature.

Introduction

Poly(ethylene oxide) (PEO) and its alkali metal salt complexes have played an important role in the development of polymeric solid electrolytes intended for use in high-energy-density batteries.[1-3] PEO complexes are generally multiphase with regard to the coexistence of crystalline and amorphous phases in the same sample. A serious limitation of PEO–alkali metal salt complexes that is related to the presence of the crystalline phase is their relatively low ionic conductivity below approximately 60 °C. Recognition of the fact that significant ion transport in polymer electrolytes occurs only in the rubbery phase of the amorphous component (above its glass transition temperature, T_g) has led to the synthesis of a variety of elastomeric complexes with low T_g's.[4-6] One such material is poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP), which combines the highly ion solvating property of its ethylene oxide side groups with the elastomeric character imparted by the flexible polyphosphazene backbone.[4]

Efforts to improve the mechanical stability of MEEP have included chemical[7] and radiation[8] crosslinking. Recently, two of us have described the synthesis and study of composites of MEEP and PEO complexed with lithium salts.[9] These materials were found to possess the mechanical integrity of PEO–salt complexes while offering significantly higher room-temperature conductivity.

Nuclear magnetic resonance (NMR) has been shown to be a powerful technique in probing the dynamical behavior of ions in solid electrolytes in general[10] and polymer electrolytes in particular.[11,12] This paper describes the use of ^{7}Li NMR to investigate both the distribution and temperature-dependent mobility of Li ions in MEEP/PEO

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Table I. Composition and Thermal Properties of the Materials Studied in the Present Work

sample	composition, wt % MEEP	PEO	PPO	$LiClO_4$	$LiBF_4$	ratio[a]	T_g, °C	T_m, °C
1	46	38	0	16	0	10	-73	65
2	60	26	0	14	0	12	-54	64
3	47	38	0	0	15	10	-54	65
4	62	26	0	0	12	11	-57	62
5	48	0	39	13	0	11	-35, +5	
6	92	0	0	8	0	16	-58	
7	0	0	81	19	0	8	0	

[a] This ratio is the ether oxygen/Li mole ratio. It was calculated by assuming that MEEP and PEO form complexes of the type $(MEEP)_4$-LiX and $(EO)_8$-LiX. Only four oxygen atoms per MEEP monomer are assumed to complex with Li^+. Samples 5–7 are fully amorphous electrolytes and thus exhibit no T_m.

composites containing lithium salts. Additional techniques employed in characterizing these multiphase materials include differential scanning calorimetry (DSC) and X-ray diffraction.

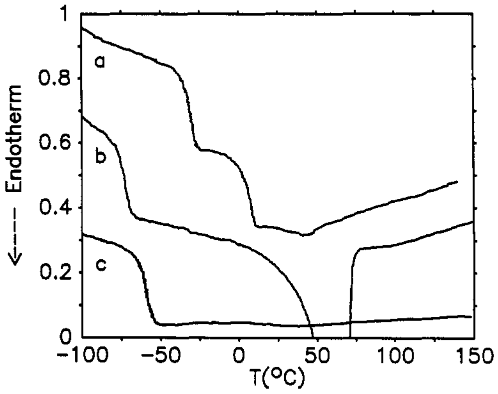

Figure 1. DSC thermograms for (a) MEEP/PPO:$LiClO_4$ (sample 5, Table 1), (b) MEEP/PEO:$LiClO_4$ (sample 1), and (c) MEEP:$LiClO_4$ (sample 6). The heating rate was 10 K/min.

Experimental Section

The synthesis of the samples has been described previously.[9] Additional samples utilizing poly(propylene oxide) (PPO) in place of PEO have been included in this investigation. For the present work, the materials were prepared so that the ratio of the ether oxygens to lithium is 8:1 for the PPO and 16:1 for the MEEP portion.

The DSC measurements were performed with a microprocessor-controlled Du Pont 990 thermal analysis console equippped with a 910 DSC module. X-ray diffraction data were obtained with a Rigaku X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The polymer electrolyte films were covered with tape to protect them from reactions with air and moisture.

The NMR measurements were conducted on a JEOL GX400 NMR spectrometer (at a ^{7}Li frequency of 155 MHz). Spin–lattice relaxation times (T_1) and associated recovery profiles were measured for some samples at selected temperatures by either saturation recovery or steady-state pulse sequences.[13]

Results and Discussion

DSC thermograms for pure MEEP, a 55 MEEP/45 PEO composite (hereafter denoted as sample 1) and a comparable MEEP/PPO composite (sample 5), all containing $LiClO_4$ in roughly equivalent ether oxygen/Li ratios (details listed in Table I), are displayed in Figure 1. The MEEP–$LiClO_4$ material (sample 6) is characterized by a strong glass transition at approximately -58 °C (Figure 1c), in agreement with previously reported results.[4] The MEEP/PEO–$LiClO_4$ complex (Figure 1b) exhibits several interesting features that include a glass transition that is some 15 °C *lower* than that of the pure MEEP complex, a second and much weaker glass transition at about -25 °C, and a very prominent melting endotherm occuring at approximately 60 °C. This result implies that the composite material is multiphase with at least two distinct phases associated with the individual MEEP and PEO components. The weak glass transition at -25 °C occurs at a somewhat higher temperature than the T_g reported for pure PEO[14] and is therefore attributed to the PEO phase complexed with ions. This is reasonable since T_g for $PEO_9NaCF_3SO_3$, for example, occurs at -22 °C.[14] The 60 °C endotherm, commonly observed in PEO complexes,[3] results from the melting of the crystalline phase of PEO. For the strong glass transition, the slightly lower (than the MEEP complex) T_g associated with the composite suggests that the MEEP complex is more salt-rich than the MEEP phase of the MEEP/PEO composite. For the ether oxygen (in both MEEP and PEO)/salt ratios given in Table I, this result can be explained on the basis of a possible preference of the ions to associate with the PEO rather than the MEEP phase.

This conclusion is consistent with the variation in the low-temperature glass transition observed for different MEEP/PEO ratios. In particular, the slightly higher T_g (listed in Table I) of sample 2 relative to sample 1, which contains more PEO than sample 2 but which has nearly the same ether oxygen/Li^+ ratio, suggests that fewer ions are complexed in the MEEP phase of sample 1 than sample 2. This results directly from the reduced availability of PEO for ion solvation in the latter sample. A similar effect on the low temperature T_g's, however, is not seen for samples 3 and 4 (whose T_g's differ by only about 3 K). These samples have almost the same MEEP/PEO content as samples 1 and 2, but they contain $LiBF_4$ instead of $LiClO_4$. The effect of changing the anion on T_g of the complex may occur by alteration of the relative solubility of Li^+ ions in the MEEP and PEO phases or more simply by "stiffening" the polymer complex through the strong cation–anion interaction. Details concerning the latter mechanism will be discussed later. Note that the DSC results concur with the X-ray data, which indicate the possible presence of MEEP/PEO mixed complexes of Li salts.

The DSC thermogram for the MEEP/PPO composite (sample 5, Figure 1a) shows the presence of two separate glass transitions of comparable intensity, at about -35 and 5 °C. The lower T_g is substantially higher than that associated with MEEP or the MEEP phase of the MEEP/PEO composites. This suggests a homogeneous MEEP/PPO amorphous phase, in contrast to the distinct thermal features associated with the separate components of the MEEP/PEO composites. The 5 °C T_g of the MEEP/PPO material may be attributable to a small

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Table II. X-ray Diffraction Data (d, Å) for $LiBF_4$, PEO, and Polymer Electrolytes

		PEO–$(LiBF_4)_{0.13}$		55^c MEEP/45 PEO–$(LiBF_4)_{0.10}$	
PEO	$LiBF_4$	unheated[a]	heated[b]	unheated	heated
		4.07_{31}	4.02_{50}		
		3.74_{44}	3.73_{100}	3.73_{40}	3.74_{30}
				3.49_{60}	3.51_{60}
		2.40_{100}	2.41_{45}		
2.31_{70}[d]			2.27_{24}	2.28_{60}	2.29_{80}
	2.18_{100}		2.16_{13}	2.17_{60}	2.18_{50}
					2.08_{30}
		2.01_{40}			2.01_{20}
	2.61_{65}				
1.92_{100}		1.96_{40}	1.96_{40}	1.94_{100}	1.94_{100}
1.80_{20}	1.84_{70}	1.88_{18}	1.88_{18}	1.88_{50}	1.92_{90}
1.73_{10}	1.74_{30}			1.71_{30}	1.85_{30}
	1.71_{90}				

[a] All the unheated electrolytes were X-rayed at least 4 weeks after they were prepared. [b] Sample heated for 2 h at 90 °C and then cooled to room temperature. [c] Weight ratio of polymers in percentage. [d] Subscript refers to the relative intensity of the X-ray lines.

amount of PPO complexed with ions on the basis of known T_g's of PPO–salt complexes.[12]

It should be mentioned that all values of T_g reported in Table I refer to the results of DSC measurements performed on samples that were held in a roughing vacuum for several hours prior to measurement. Samples held in vacuum or in a dry box (less than 1% relative humidity) for several weeks exhibited increases in T_g. All NMR data were taken on samples treated in vacuum for at least several hours and thus correspond to the DSC results listed in Table I.

The X-ray diffraction pattern of the $LiBF_4$ complex of the 55 MEEP/45 PEO composite (sample 3) is compared in Table II with the patterns of PEO, $LiBF_4$, and PEO–$(LiBF_4)_{0.13}$. The data were obtained for a sample that had been heated to 90 °C for 2 h followed by cooling to room temperature and for an unheated sample. The unheated electrolyte contains the principal line of PEO at 1.96 Å with additional lines at 4.07, 3.74, 2.40, 2.01, and 1.88 Å, most probably due to a crystalline PEO–$LiBF_4$ complex. When this sample is heated for 2 h at 90 °C and then cooled to room temperature, the most intense line of $LiBF_4$ appears at 2.16 Å, suggesting that heating the sample induces precipitation of $LiBF_4$. The multiphase nature of the MEEP/PEO composite electrolyte is indicated by its X-ray pattern. For example, unheated sample 3 contains the principal lines of PEO at 1.94 and 2.28 Å. The line at 3.73 Å in this sample is common with PEO–$(LiBF_4)_{0.13}$. However, the two strong lines of the latter electrolyte at 4.07 and 2.4 Å are not present in the composite. Instead, the composite exhibits a strong line at 3.49 Å. Consequently, the lines at 3.73 and 3.49 Å in sample 3 are most probably due to a mixed complex of $LiBF_4$ with PEO and MEEP. When the composite electrolyte is heated to 90 °C followed by cooling to room temperature, two new lines at 2.08 and 2.01 Å, of which the latter can be ascribed to precipitated $LiBF_4$, appear. It should be noted that because of its amorphous nature a MEEP–$(LiBF_4)_n$ complex would not exhibit any Bragg lines. The X-ray patterns of $LiClO_4$ complexes of the MEEP/PEO composite could also be explained in terms of a heterogeneous mixture comprised of crystalline PEO, a PEO–$LiClO_4$ complex, and a mixed MEEP/PEO–$LiClO_4$ complex. However, no evidence for precipitated $LiClO_4$ was found in samples heated to 90 °C. X-ray data also revealed that $LiClO_4$ and $LiBF_4$ complexes of MEEP/PPO composites were completely amorphous for all ratios of MEEP and PPO.

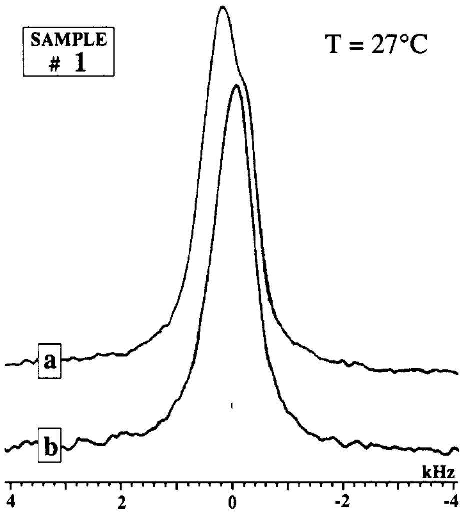

Figure 2. ^{7}Li NMR absorption spectra of MEEP/PEO:$LiClO_4$ (sample 1) at 27 °C: (a) after long-term storage (several weeks) at room temperature; (b) within 1 h of being maintained above 60 °C for more than 1 h.

The ^{7}Li NMR absorption spectrum of sample 1 is displayed in Figure 2. Both spectra a and b were recorded at 27 °C, the latter spectrum being obtained after the sample had been held at a temperature greater than 60 °C for more than 1 h. The asymmetry of spectrum a is attributable to the presence of two distinct local environments for the Li ions, the high-frequency shoulder corresponding to Li solvated within an amorphous network and the low-frequency component characteristic of ions in the crystalline phase. Above 60 °C, the low-frequency component vanishes and the high-frequency component grows in intensity (spectrum b), corresponding to the well-known melting of crystalline PEO at 60 °C (and the associated melting endotherm in Figure 1b). The slowness of the recrystallization kinetics ensures that the sample remains amorphous during the entire experiment and, in fact, for several days following its first elevated temperature excursion. Similar observations, as manifested by both NMR line width and ionic conductivity, have been reported for PEO–alkali metal salt complexes.[11]

It is noteworthy that besides being spectroscopically distinct, the two line-shape components of spectrum 1a have spin–lattice relaxation times (T_1's) differing by nearly 2 orders of magnitude, the longer T_1 (around 35 s at room temperature for the 60 MEEP/26 PEO sample, 2) being associated with the crystalline phase of the complex. Figure 3 illustrates the T_1 recovery profile corresponding to the above sample, without having allowed adequate time for recrystallization. Thus, the data reflect primarily the contribution of the amorphous component. Also shown is the profile obtained at temperature −73 °C, well below T_g. In addition to the considerably longer T_1 implied by the low-temperature recovery data, the difference in line widths obtained at −73 and 27 °C is striking.

Ionic mobility in solid electrolytes is usually reflected in motional line narrowing of the associated ion's NMR spectra in the temperature region of enhanced mobility.[10] For polymer electrolytes the onset of line-narrowing is just above the T_g of the material, corresponding to segmental motions associated with the rubbery phase which are necessary for ion transport.[11,12] Arrhenius plots of the ^{7}Li full widths at half-maximum (fwhm) line widths of all seven samples are displayed in Figure 4. All of the plots clearly show that the onset of motional narrowing corre-

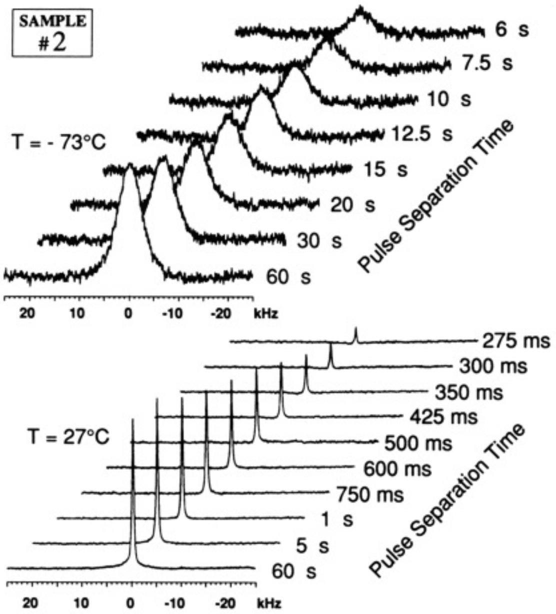

Figure 3. Stack plots of T_1 recovery profile in MEEP/PEO: $LiClO_4$ (sample 2) at −73 °C (top) and 27 °C (bottom).

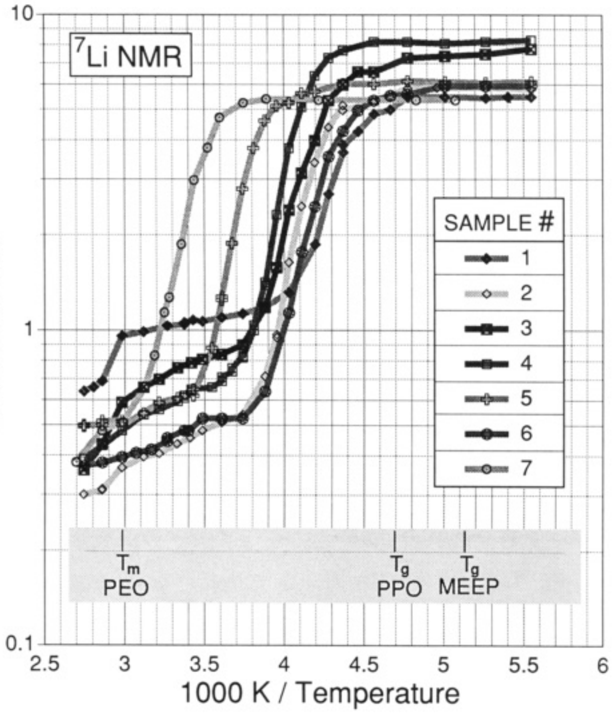

Figure 4. Arrhenius plots of ^{7}Li NMR line widths.

sponds to the glass transition.

A second feature that is clearly observable in the samples containing the highest proportions of PEO (samples 1 and 3) is the relatively abrupt decrease in line width occurring just above 60 °C, again corresponding to melting of the crystalline phase. Although predictable from the spectroscopic results with regard to the kinetics of recrystallization cited earlier, it is interesting to note that the line-width temperature dependences of the multiphase samples (in particular samples 1 and 3) are not the same upon cooling as upon heating. That is, the slope of the cooling curve (not shown in the figure) is close to that of the heating curve above 60 °C and does not exhibit the discontinuity associated with melting (or recrystallization) of the PEO crystallites. The activation energies for all samples in the motional narrowing regime (characterized by linear approximations to the steepest part of the curves) vary between roughly 0.06 and 0.09 eV. Since these values are considerably lower than those that correspond to Arrhenius fits to the ac conductivity over the same temperature region,[9] the tens to hundreds kilohertz motions responsible for line-narrowing are apparently somewhat more localized than the lower frequency motions that characterize the ac conductivity. The observation of different activation energies for processes occuring at different frequencies is quite common in solid electrolytes.[10]

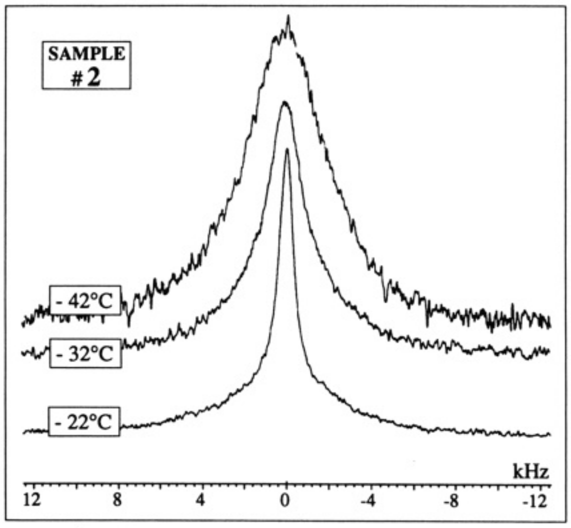

Figure 5. ^{7}Li NMR spectra of MEEP/PEO:$LiClO_4$ (sample 2) at −42, −32, and −22 °C. The broad component of the signal, clearly discernible from the motionally narrowed central peak at −22 °C, reflects Li in the crystalline phase.

Due to the inhomogeneous nature of the samples and their NMR line shapes, it is necessary to point out a major limitation of the data in Figure 4 in faithfully conveying information about all of the Li ions present in the material. Because the fwhm line width was chosen for presentation, the contribution of the crystalline component appears, in some cases, as only a broad baseline above the low-temperature glass transition. Hence, the motionally narrowed line widths shown in Figure 4 reflect primarily Li present in the amorphous phase above its glass transition. Figure 5 displays spectra for sample 2, taken at three relatively low temperatures (−42, −32, and −22 °C) but beginning above the low-temperature glass transition, in which the inhomogeneity of the motional narrowing and hence the total line shape are clearly illustrated. Nevertheless, the previously mentioned discontinuity in the heating curve of some of the samples at 60 °C does reflect the influence (albeit somewhat deemphasized) of the crystalline phase.

The low-temperature (the region where the temperature dependence is flat, commonly referred to in NMR terminology as the "rigid" line-width region) NMR line-width data in Figure 4 suggest the presence of strong cation–anion interactions via the observation of heteronuclear dipole broadening of the ^{7}Li resonance attributable to ^{19}F nuclei associated with the BF_4^- anions. In particular, it is observed that the rigid line widths of both $LiBF_4$-containing complexes are 25–30% greater than those of all other samples, which contain $LiClO_4$ at the same concentration. Assuming that the heteronuclear dipole interaction between ^{7}Li and ^{35,37}Cl is negligible (it is zero for ^{16}O), the additional line width of the $LiBF_4$ complexes can be attributed to the relatively close proximity of cations to their counterions. Given the strong spatial dependence of the nuclear dipole–dipole interaction (proportional to $1/r^3$), the average cation–anion separation in the polymer complex can be estimated to be within a factor of 2 of its value in crystalline $LiBF_4$. The argument given above does

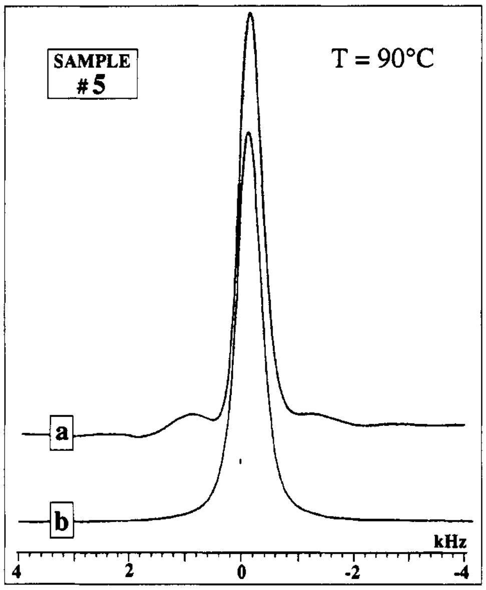

Figure 6. ^{7}Li NMR spectra in MEEP/PPO:$LiClO_4$ (sample 5) at 90 °C: (a) repeat delay of 20 s; (b) repeat delay of 0.1 s, in which the broad outer line-shape component is completely saturated. The broad component is attributed to salt crystallites that have precipitated out of the polymer complex.

not consider the possible contribution of nuclear quadrupole effects that may result from differences in the symmetry of the charge distribution in the vicinity of the Li caused by changing the anion. This effect is most likely too small to yield the line-width differences observed, although it cannot be ruled out with certainty. The existence of strong cation–anion association has been postulated on the basis of the high ion concentration and relatively low dielectric constant characteristic of these materials.[3] In addition, various manifestations of these strong ion–ion interactions have been observed by NMR[12] and vibrational[15,16] spectroscopies.

Finally, line shapes of sample 5 measured above about 80 °C reveal interesting behavior. As mentioned earlier this sample, which consists of a MEEP/PPO mixture complexed with $LiClO_4$, exhibits a glass transition and corresponding onset of ^{7}Li motional line-narrowing (Figure 4) at considerably higher temperature than all of the other materials containing MEEP but at lower temperature than pure PPO–salt complex (sample 7). This was attributed to the formation of an intermediate (between MEEP and PPO) amorphous network as opposed to the distinct phases observed in the MEEP/PEO complexes. Figure 6 displays ^{7}Li absorption spectra of sample 5 at 90 °C. The top and bottom spectra were obtained with repeat delays of 20 and 0.1 s, respectively. The easily saturable (long T_1) broad outer portion of the top spectrum can be attributed most likely to the presence of $LiClO_4$ crystallites that have precipitated out of the polymer complex. Salt precipitation in PPO–sodium salt complexes at elevated temperature has been reported previously.[12] The Na salt precipitation is characterized by a strong DSC endotherm which corresponds to most of the salt coming out of the polymer. However, from the DSC data in Figure 1a, only a weak (but reproducible) feature occurring at about 50 °C can be noted. This observation, coupled with the relatively small NMR intensity of the broad line-shape component (compared to the strong central resonance), suggests that only a small fraction of the salt precipitates out at 90 °C. The salt apparently redissolves in the polymer quite easily as demonstrated by the disappearance of the broad line-shape component after the sample is cooled to below about 70 °C and equilibrated for at least 1 h.

Conclusions

Polymer MEEP/PPO consisting of mixtures of MEEP and PEO complexed with Li salts exhibit mechanical properties superior to those of MEEP complexes while retaining high ionic conductivity at room temperature characteristic of the latter materials. DSC, X-ray diffraction, and ^{7}Li NMR measurements have shown that these materials are multiphase in that they exhibit distinct phases identifiable with their amorphous MEEP and partially crystalline PEO components. The MEEP/PEO composite that was investigated does, however, appear to possess a unique amorphous phase in addition to one associated with complexed PPO. Li^+ ions present in the amorphous and crystalline phases of the MEEP/PEO composites are clearly distinguishable by their ^{7}Li NMR characteristics such as line width and T_1. There is, in addition, a close correspondence between the glass transition and the onset of ^{7}Li motional line narrowing, which is consistent with previous NMR studies of polymer electrolytes.

Finally, strong cation–anion association effects have been observed spectroscopically in two ways: by increased line broadening of complexes containing $LiBF_4$, which was attributed to the heteronuclear dipole interaction between ^{7}Li and ^{19}F, and by the appearance of a broad, long T_1 resonance at elevated temperature, which was presumed to result from the precipitation of salt crystallites from the polymer.

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Registry No. MEEP (SRU), 98973-15-0; PEO (SRU), 25322-68-3; PPO (SRU), 25322-69-4; $LiClO_4$, 7791-03-9; $LiBF_4$, 14283-07-9.

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