α-Relaxation in PEO−LiTFSI Polymer Electrolytes

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ABSTRACT: Relaxation processes in the ns time regime in deuterated pure PEO and two different concentrations of PEO−LiTFSI electrolytes show a stretched exponential behavior identifiable with translational motions of the chain segments. The time scale of the dynamics is slowed by factors of 3 and 10 as a result of adding lithium salt at EO:Li concentrations of 7.5 and 3, respectively, presumably due to the increased rigidity of the lattice caused by inter- and intrachain cross-linking by the Li ions. At the same time the stretching parameter is reduced by 35% and 50%, respectively. Measurements of the Q dependence show that both the relaxation time and the stretching parameter have a positive correlation with $S(Q)$.

1. Introduction

Polymer electrolytes present a versatile medium for studying network dynamics: the introduction of even small quantities of salt produces dramatic effects on the rate and nature of the local relaxation in the polymer host. These effects are believed to result from the transient cross-linking of neighboring polymer segments by the conducting ions.[1] The strong coupling between the segmental relaxation and the ion transport—the essential feature for practical application of these materials—provides an additional incentive to comprehend the polymer dynamics.

Neutron scattering is an effective probe of network dynamics on the nanosecond time scale. In a recent quasielastic neutron scattering (QENS) study of segmental relaxation in PEO-based polymer electrolytes, we found that at least two distinct processes were involved: a slow relaxation with translational character and one or more fast processes with rotational character.[2] We ascribed the latter to conformal fluctuations of the chain segments between the cross-links formed by the Li^+ cations. We identified the slow relaxation with translational diffusion of the chain segments and suggested that it was similar to the stretched exponential relaxation observed in pure PEO but slowed to time scales beyond the QENS resolution ($\sim$0.1 ns) due to the cross linking by the Li^+ ions. In the present work, we employed the longer time scales (up to 1.7 ns) of neutron spin−echo spectrometry (NSES) to determine the nature of this relaxation through its time and wave vector dependence. In addition, we investigated the effects of composition and temperature on the polymer electrolyte dynamics.

2. Experimental Section

We selected the system $P(EO)_nLiTFSI$ ($TFSI = N(CF_3SO_2)_2$) for this investigation since we had previously determined the structure and dynamics of the $n = 7.5$ composition.[2,3] Furthermore, this electrolyte is considered a leading candidate for battery applications on account of its chemical stability, relatively high conductivity and low melting point.[4] The samples were prepared with deuterated PEO to ensure almost entirely coherent scattering. To investigate the role of salt concentration, samples were prepared with $n = \infty$ (i.e., pure PEO), 7.5, and 3.0. Films 38 mm in diameter, 0.9 mm thick, were prepared by stepwise drying solutions of the PEO (Polymer Source, Inc., $M_w = 52K$, ^2H enrichment = 99.8%, polydispersity = 1.06), together with the salt for the polymer electrolytes, in acetonitrile in a high-vacuum oven to 10^{-6} Torr. Each film was loaded inside a He-filled glovebox into a flat cell with thin Al windows sealed by Viton O-rings.

The NSES measurements were carried out at the IN11C spectrometer[5] at the Institut Laue-Langevin high-flux reactor. In this configuration the intermediate scattering function $I(Q,t)$ can be measured over a range in time t from 0.009 to 1.7 ns with an incident wavelength of 6 Å. Using two positions of the final flight path, centered at angles of 60 and 88°, we could cover a scattering angle range from 45 to 103°, corresponding to a range in wave vector Q of 0.82−1.62 $Å^{-1}$. The sample cell was placed in the spectrometer in a symmetrical transmission configuration for 60 and 88°, respectively. Measurements were made at 348 K for the pure PEO, at 323, 348, and 373 K for the two electrolytes, and at 348 K for an empty cell. The instrument resolution was measured with a silica glass standard run in a cell without windows. Each time scan was normalized with respect to the $I(Q,t=0)$ structure factor, determined from a standard flipper-on/flipper-off measurement, and then divided by the normalized spectrometer resolution function. All the runs except for $P(EO)_3LiTFSI$ at 323 K, which appeared static on the time scale of the spectrometer, exhibited relaxation behavior.

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3. Results

In the past decade there has been a considerable body of literature on the dynamics of polymer melts. Because of the interest in the glass transition and a connection with mode coupling theory, these have principally involved noncrystallizing polymers such as PB and PVC. The salient results may be summarized as follows:[6] at times longer than a certain crossover time t_c, generally around 1 ps, the normalized intermediate scattering function can be described by the stretched exponential function

$$\frac{I(Q,t)}{I(Q,0)} = A(Q)\exp\left[-\left(\frac{t}{\tau(Q)}\right)^{\beta(Q)}\right] \qquad (1)$$

where the amplitude factor $A(Q)$ accounts for vibrational and relaxation processes taking place prior to t_c. Both the scaling law implied by eq 1 and the temperature dependence of the $\tau(Q)$ are consistent with the predictions of mode coupling theory.[7] For incoherent scattering (hydrogenated polymers), the stretching parameter β depends weakly on Q and τ and is described by a power-law dependence on Q:

$$\tau(Q) = \tau_0\left(\frac{Q_0}{Q}\right)^{\nu} \qquad (2)$$

Both β and ν vary for different polymers, with typical values being $\beta \sim 0.5$, $\nu \sim 4$ so that the product $\beta\nu \sim 2$, corresponding to Gaussian behavior in $I(Q,t)$. For times $t < t_c$, a Debye behavior is found with a power-law dependence on Q with a different exponent, typically around 2. Measurements of Mos et al.[8] on hydrogenated $P(EO)_nLiI$ and $P(EO)_nNaI$ ($n = 15$ and 25) show a behavior of this kind, with β approximately independent of Q and $\beta\nu$ taking values between 1.4 and 1.9.

The temperature dependence of τ_0 has been found to behave in a manner similar to that of the viscosity, as predicted by mode coupling theory[9]

$$\tau_0 = a(T - T_c)^{-3.2} \qquad (3)$$

where T_c is a critical temperature typically 18% above T_g.[7,10]

Less work has been carried out on coherent (heavily deuterated) samples but studies by Zorn et al.[6,10] on deuterated PB find that β varies with Q (smaller at the first minimum in the structure factor $S(Q)$ than at the first maximum) while $\tau(Q)$ follows the Q-dependence of $S(Q)$, exhibiting the usual de Gennes frequency narrowing.[11] A recent molecular dynamics simulation of deuterated PB[12] exhibits generally the same features without, however, showing any significant Q dependence of τ.

The spectra obtained in the present measurements could be fitted satisfactorily by the stretched exponential function given above in eq 1. Typical results are shown for the three samples at 348 K and $Q = 1.25$ Å^{-1} in Figure 1, which shows the dramatic slowing down caused by the addition of the salt to the polymer. The log−linear plot of the short-time region shown in the inset of Figure 1 makes it clear that the polymer electrolyte results cannot be described by a pure exponential. The pure PEO spectrum is the closest to a simple exponential (dashed line), but clearly deviates at longer times. Initial fits were performed for each spectrum with all three parameters, A, β, and τ being allowed to vary independently. The Q dependence of the values obtained for β and τ showed a systematic behavior. The relaxation time τ exhibited a relatively flat, or slowly changing, region at lower Q followed by a pronounced peak at 1.3 to 1.4 Å^{-1}; this is somewhat below the peak in the structure factor $S(Q)$, which occurs at 1.5 Å^{-1} in PEO[13] and $P(EO)_{7.5}LiTFSI$;[3] the structure of $P(EO)_3LiTFSI$ has not been measured. We note that general arguments based on moment relations of $S(Q,\omega)$ imply that eq 2 could be replaced by

$$\tau(Q) = \tau_0\sqrt{S(Q)}\left(\frac{Q_0}{Q}\right)^{\nu} \qquad (4)$$

in the case of coherent scattering. The stretching parameter β had a somewhat similar, but less marked, Q dependence, with a flat region followed by a peak at 1.4−1.5 Å^{-1}, at least for the two electrolytes, whereas the values obtained for A showed no systematic Q dependence. Over the Q range covered, the values of τ varied by factors of 2−4, β by 15−75%, and A by ∼ 20%.

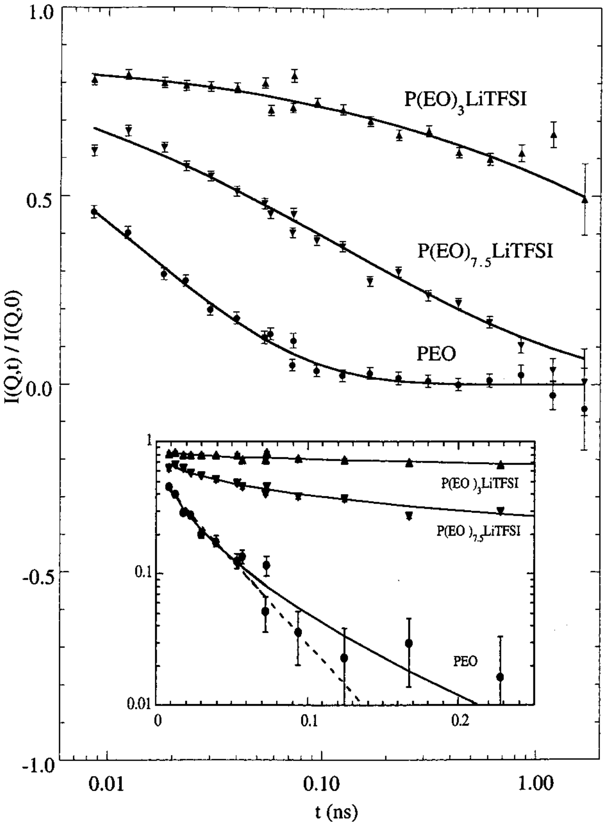

Figure 1. Intermediate scattering functions at $Q = 1.25$ Å^{-1} for PEO and $P(EO)_nLiTFSI$, $n = 7.5$ and 3, at 348 K, linear-log plot. Points: measurements. Solid lines: stretched exponential fit (eq 1). Inset: log−linear plot for the short-time region. Solid lines: stretched exponential fit. Dashed line: pure exponential fit.

Since the covariance matrixes in the initial fits showed significant correlations between the three parameters, we investigated the effect of reducing the number of free parameters to two by fixing β and A in turn. Typical results of the three- and two-parameter fits are illustrated in Figure 2 for the case of $P(EO)_{7.5}LiTFSI$ at 348 K, representing the middle composition and middle temperature. It is seen that τ is quite robust and retains the general Q dependence given by eq 4 with $\nu \sim 1$, β exhibits a rather similar Q dependence for the three-parameter fit and the fit with A held constant,

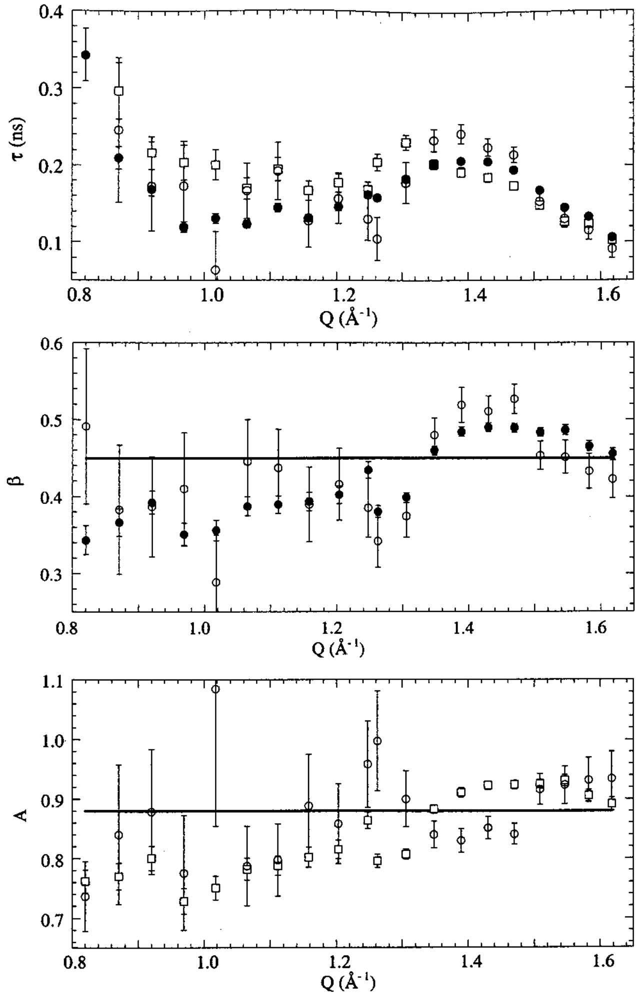

Figure 2. Q dependence of the relaxation time τ, stretching parameter β and amplitude factor A for P(EO)$_{7.5}$LiTFSI at 348 K: fits with three free parameters (○), A fixed (●), and β fixed (□). The solid lines represent the values chosen for the fits in which the parameter was fixed.

whereas fixing β introduces a systematic Q dependence into the values for A which is not present in the free fit. In light of these results, we proceeded with the two-parameter fits in which A was held constant at a value of 0.9 (0.88 in the case of P(EO)$_{7.5}$LiTFSI at 348 K). This procedure is consistent with QENS results obtained on deuterated P(EO)$_{7.5}$LiClO$_4$ at 348 and 373 K where the amplitudes of the fast and slow relaxation follow the Q dependence of $S(Q)$ but with the ratio of the slow process to the total remaining relatively constant.[14]

Values of $\tau(Q)$ and $\beta(Q)$ obtained with the above procedure are shown in Figures 3 and 4, respectively, for the three samples. In Figure 3 results are shown for the two electrolytes at 348 and 373 K. In Figure 4 they are shown only for 373 K for clarity of presentation.

4. Discussion

The Q dependence described above now shows quite clearly in Figures 3 and 4; for pure PEO $\tau(Q)$ rises gradually to a broad peak around 1.4 Å^{-1}, and $\beta(Q)$ rises monotonically over the entire Q range. For the two electrolytes $\tau(Q)$ initially falls gradually and then rises a peak at 1.4 (for P(EO)$_{7.5}$LiTFSI) or 1.3 (for P(EO)$_3$LiTFSI) Å^{-1}, and $\beta(Q)$ rises gradually to a peak at 1.5 (for P(EO)$_{7.5}$LiTFSI) or 1.4 (for P(EO)$_3$LiTFSI) Å^{-1}.

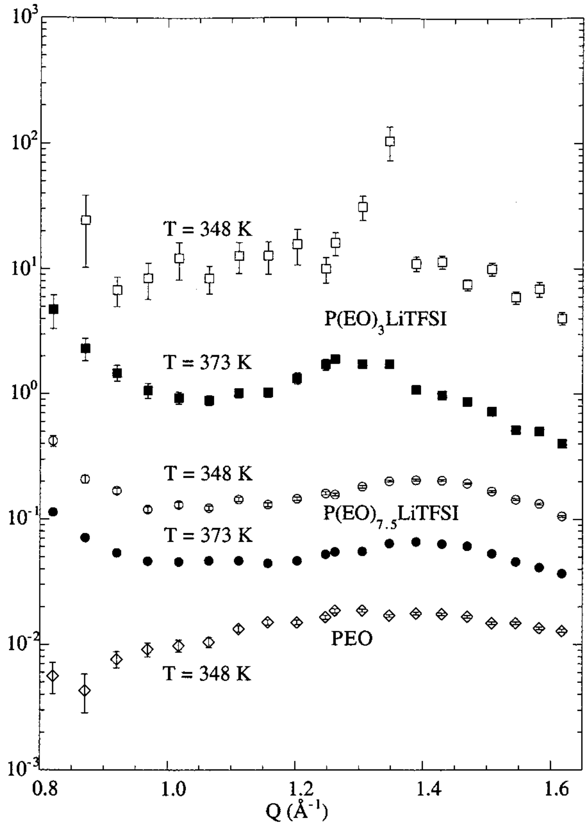

Figure 3. Q dependence of the relaxation time τ for PEO (◊) at 348 K, P(EO)$_{7.5}$LiTFSI at 348 (○) and 373 K (●), and P(EO)$_3$LiTFSI at 348 (□) and 373 K (■). For clarity, P(EO)$_{7.5}$LiTFSI at 323 K is not shown, but parameters are included in Table 1.

The addition of salt to the polymer increases the relaxation times by 2−3 orders of magnitude and decreases the stretching parameter by factors of 2−3.

For each sample and temperature, characteristic values of the relaxation time, τ_0, and the stretching parameters, β_0, corresponding to Q = 1.5 Å^{-1} were obtained by fitting a cubic function over the last seven points in the spectrum. These are listed in Table 1. Temperature has the effect of decreasing relaxation times by a factor of 3−10 per 25 K. The errors quoted are those obtained for individual points from the fits to the scattering data. These are close to the average deviations of each point from the fits of the cubic functions. In the table we also list the values of the parameter a in eq 3, to separate the effect of T_g from the intrinsic slowing down. T_c was taken as 18% above the reported values of T_g = 207, 241, and 265 K, for PEO and the n = 7.5 and n = 3 electrolytes, respectively.[14] The values obtained for a are essentially independent of temperature for P(EO)$_{7.5}$LiTFSI, and the two values for P(EO)$_3$LiTFSI are within a factor of 2. Addition of the salt increases the time scale of the relaxation process by factors of 3 and 10, respectively.

The values of β and τ for PEO at 348 K are in agreement with those obtained for -d-PEO by QENS.[2,14] As remarked above, for P(EO)$_{7.5}$LiTFSI the values of A are also approximately consistent with the fraction of the intensity going into the slow relaxation in the QENS results, about 0.8 over the same Q range. Since this mode appears static on the time scale of the spectrometer used (~0.1 ns), the values of β and τ could not be extracted in those experiments.

Table 1. Characteristic Values of Relaxation Times and Stretching Parameters

	sample					
	PEO	$P(EO)_{7.5}LiTFSI$			$P(EO)_3LiTFSI$	
temp (K)	348	323	348	373	348	373
τ_0 (ns)[a]	0.0157 ± .0003	0.90 ± 0.02	0.176 ± 0.002	0.0550 ± 0.0007	8.6 ± 1.2	0.74 ± 0.03
β_0[a]	0.73 ± 0.02	0.426 ± 0.005	0.488 ± 0.005	0.520 ± 0.008	0.324 ± 0.009	0.390 ± 0.007
$T_c = 1.18T_g$ (K)	244		284			313
a (eq 3)	4×10^4	1.1×10^5	1.1×10^5	1.0×10^5	7×10^5	4×10^5

[a] Referred to $Q = 1.5$ Å^{-1}.

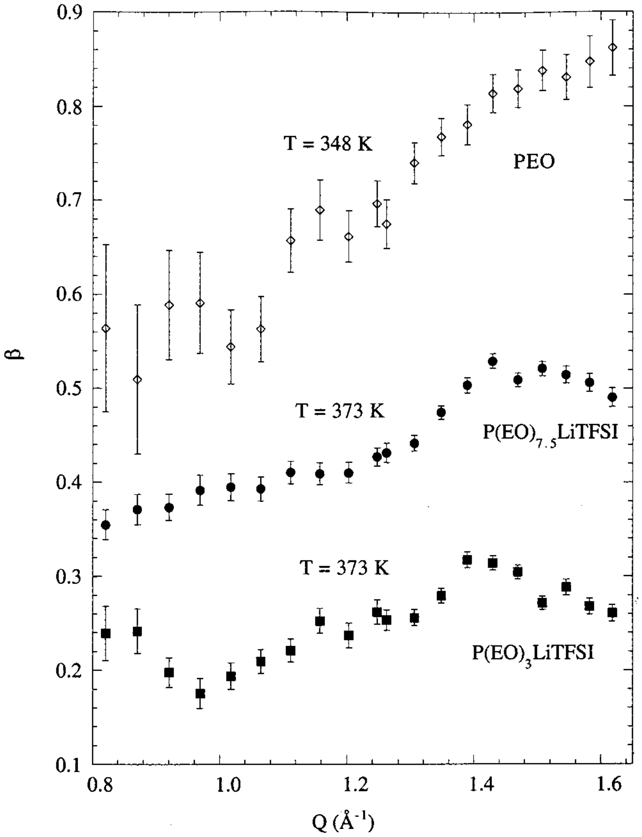

Figure 4. Q dependence of the stretching parameter β for PEO (◊) at 348 K and $P(EO)_{7.5}LiTFSI$ (●) and $P(EO)_3LiTFSI$ (■) at 373 K. For clarity, values for PEO have been shifted up by 0.1 and those for $P(EO)_3LiTFSI$ down by 0.1.

Similar trends were observed in the incoherent NSES measurements on $P(EO)_nLiI$ ($n = 15$ and 25) mentioned above,[8] with τ_0 (eq 2) increasing by an order of magnitude and β_0 decreasing by about 20% on going from pure PEO to the $n = 15$ electrolyte.

5. Conclusions

The behavior of $\tau(Q)$ observed in the present measurements, with a form that is generally consistent with eq 4 for $\nu \sim 1$, suggests that the slow relaxation processes observed in both the pure polymer and the two electrolytes are associated with translational motions of the chain segments. This is consistent with our interpretation of the QENS measurements on hydrogenated PEO and PEO-based electolytes,[2] although in those studies the slow processes in the electrolytes were outside the time window of the instrument. The slow processes are quite distinct from the fast processes observed in those measurements on the electrolytes,[2] which were ascribed to conformal fluctuations of the chain segments between the Li^+ cross-links. The characteristic dependence on time, wave vector and temperature of the slow motions place them firmly in the family of α-relaxation processes that have been extensively investigated both theoretically and experimentally in pure polymer melts.

The time scale of the dynamics, represented by the parameter a in eq 3, is slowed by factors of 3 and 10 as a result of adding lithium salt at EO:Li concentrations of 7.5 and 3, respectively, This could be due to the increased rigidity of the lattice caused by inter- and intrachain cross-linking by the Li ions, inferred from our structural studies of this system.[3] The dramatic reduction in the stretching parameter β resulting from the addition of the salt, and also to a lesser extent from lowering the temperature, is harder to understand on physical grounds. A reduction of β below unity is normally ascribed to an assembly of relaxation processes with a spread in relaxation rates. It is possible that the cross-linking by the Li ions introduces an additional degree of randomness into the dynamics of the polymer host.

A further significant finding of this work relates to the effects of coherence, which we were able to study in detail thanks to the new extended detector bank on IN11C. As noted above, a positive correlation of $\tau(Q)$ with $S(Q)$ was observed in NSES experiments on deuterated PB,[10] and the two values quoted for $\beta(Q)$ are also consistent with a similar correlation, as are values of $\tau_D(Q)$ measured for $t < t_c$ on a time-of-flight spectrometer.[6] A recent molecular dynamics study of the same material[12] finds the same two values of $\beta(Q)$ but no apparent Q dependence of τ. In the present work $\tau(Q)$ and $\beta(Q)$ are shown to have a positive correlation with $S(Q)$. Since the peak at 1,5 Å^{-1} is associated with structural correlations between chains, it is reasonable to expect that the effects of the rigidity caused by the cross linking of neighboring chains by the Li ions will be most pronounced on this length scale, and perhaps also on the length scale of the extended-range order[3] which is just below the Q range of the present measurements. Similarly, the randomness introduced by the interchain cross links might be expected to be minimized at this Q value, leading to a smaller reduction in β than at other scattering vectors.

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