

Solid-State NMR Investigation of Block Copolymer Electrolyte Dynamics

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Introduction

Recent trends in energy technology have driven considerable interest in solid polymer electrolytes. The electrolytic properties of lithium salt-doped poly(ethylene oxide), PEO, make this polymer and its derivatives, including noncrystallizable comb-shaped polymers, favored candidates for polymer electrolytes.^{1,2} Some of the primary applications for polymer electrolyte technology include high energy density lithium batteries and electrochromic devices.³ To improve mechanical properties while retaining high ionic conductivity, block copolymer electrolytes have been investigated.^{2,4–7} The microphase separation in those block copolymer electrolytes confers solidlike mechanical properties to the material at macroscopic scales even when both polymer blocks reside above their respective glass-transition temperature (T_g) values. A study of electrolytes composed of a comb-shaped poly(oligo-oxethylene methacrylate) block, POEM, and a poly(*n*-alkyl methacrylate) block showed that a low- T_g nonconductive phase results in higher conductivity than copolymers with a high- T_g nonconductive phase.⁷

To confirm and better understand this effect of T_g of the nonconductive phase on electrolyte conductivity in this family of block copolymers, we have studied these systems by solid-state nuclear magnetic resonance (NMR) line width and relaxation measurements. The ¹H rotating-frame relaxation times $T_{1\rho}$ and ¹H line widths of the POEM block, as well as ⁷Li line widths, were determined for several nonconductive blocks from the *n*-alkyl methacrylate family, with T_g values spanning the range –35 to 100 °C. Also, differences in dynamics along the side chain in the comb-shaped conductive POEM block were investigated by wide-line separation (WISE) NMR experiments with a spin-diffusion mixing time.^{8,9} The results of these NMR experiments are compared to the previously reported ac impedance spectroscopy and DSC measurements.

Experimental Section

Materials. Polymers and block copolymers from poly(ethylene glycol) methyl ether methacrylate macromonomer

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Scheme 1. Chemical Structure of Polymers Used To Prepare Ionically Conductive Copolymers

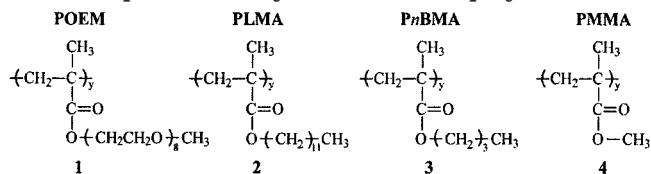


Table 1. Composition (Volume:Volume) and Molecular Weight (g/mol) of Polymers Studied by Solid-State NMR; the Approximate Glass Transition Temperature of the Poly(*n*-alkyl methacrylate) Component Is Also Listed for Reference

polymer	comp (v:v)	MW (K)	PDI	T_g (K)
POEM		100	1.3	
POEM- <i>b</i> -PLMA	53:47	65	1.1	238
POEM- <i>b</i> -PBMA	50:50	77	1.2	313
POEM- <i>b</i> -PMMA	51:49	52	1.1	373

($M \sim 475$ g/mol) (Polysciences) (referred to herein as oligo-oxethylene methacrylate, OEM), lauryl methacrylate (Aldrich), LMA, butyl methacrylate (Aldrich), BMA, or methyl methacrylate (Aldrich), MMA, were prepared by anionic synthesis in tetrahydrofuran (THF) using diphenylmethylpotassium as initiator. The structures of these polymers are shown in Scheme 1. The syntheses and characterization of the resulting copolymers have been described previously.⁷ The molecular weight characteristics and compositions of the polymer electrolyte materials are listed in Table 1. The table also lists the approximate glass transition temperature of pure poly(*n*-alkyl methacrylate) polymers.

To obtain doped samples, the block copolymer and LiCF₃SO₃ (lithium triflate) were first dried in a vacuum oven at 70 °C for several days. The materials were then transferred into an inert atmosphere, dissolved in anhydrous THF, and solution cast into a glass dish. The relative amounts of polymer and salt were determined by the desired stoichiometric ratio of ethylene oxide units [EO] to Li⁺, in this case 8:1. The samples were dried under vacuum prior to experiments.

Sample Characterization. Solid-state NMR experiments were performed at ¹H, ⁷Li, and ¹³C frequencies of 300.13, 116, and 75.5 MHz, respectively. ¹H line width and rotating-frame relaxation time, $T_{1\rho}$, and ⁷Li line width were measured using a Bruker DSX-300 spectrometer. The ¹H line width and $T_{1\rho}$ values were measured on undoped copolymers except POEM-*b*-PMMA, which does not separate into two domains without addition of LiCF₃SO₃. The ¹H experiments were performed in a 7 mm variable-temperature magic-angle-spinning (MAS) probe at spinning rates of 1 kHz. The ⁷Li line widths were determined in a 5 mm diameter coil of a static variable-temperature probe. Typical 90° pulse lengths were 4.0 μs for the ¹H experiments and 3.0 μs for the ⁷Li experiments. The spin lock field for the $T_{1\rho}$ experiment corresponded to 62 kHz.

Reproducible temperature determination is paramount for measuring the small differences in dynamics between the copolymers. The experiments were conducted with a constant flow of N₂ gas through the liquid nitrogen cooled heat exchanger and a Bruker temperature controller. The liquid nitrogen dewar was maintained fully filled. The temperature was calibrated with methanol twice, and the deviation between the two calibrations was less than 1 K at all temperatures.

To assess whether the different relaxation rates observed for the poly(ethylene oxide), PEO, side chain is a result of the comb architecture, WISE experiments⁹ with a spin-diffusion mixing time were performed at 263 K using a Bruker MSL-300 spectrometer. In the t_1 dimension, 48 slices with increments of 10 μs were acquired. The carbon and proton 90° pulse lengths were 2.8 μs and 3.6 μs, respectively. A cross-polariza-

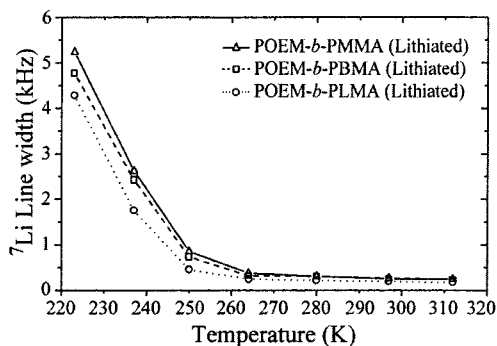


Figure 1. Temperature dependence of the ^7Li line width in LiCF_3SO_3 -doped POEM-*b*-PLMA, POEM-*b*-PBMA, and POEM-*b*-PMMA copolymers. The T_g 's of PLMA, PBMA, and PMMA are 238, 313, and 373 K, respectively. The uncertainty in temperature is ± 1 K.

tion time of 0.1 ms and a mixing time of 0.1 ms were used in one experiment, and a longer cross-polarization of 0.5 ms was used for the second WISE experiment with a mixing time of 100 ms. The signal acquisition time was 8 ms.

Results and Discussion

The ^7Li line width measurements show a small, but measurable, difference between LiCF_3SO_3 -doped block copolymer electrolytes with different nonconductive phases, as shown in Figure 1. The segmental motion of the polymer chains averages orientation-dependent interactions of the observed nucleus with its environment. A steep change in the ^7Li line width occurs when the motional rate exceeds the frequency width of the rigid limit spectrum (~ 6 kHz). The ^7Li line width measurements display a shift toward higher temperatures as the T_g of the poly(alkyl methacrylate) block increases; the PLMA, PBMA, and PMMA blocks exhibit glass transitions at 238, 313, and 373 K, respectively. The ^7Li results are in agreement with the ac impedance spectroscopy measurements, which also show a higher ionic conductivity and lower activation energy for POEM-*b*-PLMA.⁷ The specific conductivities for doped POEM, POEM-*b*-PLMA, POEM-*b*-PBMA, and POEM-*b*-PMMA ([EO]:[Li⁺] = 20:1) at 30 °C were reported to be 14, 3.5, 2.0, and 1.6×10^{-6} S/cm, respectively.⁷ (Effects including tortuosity and lower volume fraction of conducting phase must be considered when comparing the homopolymer to the copolymer.) The conductivity curves of POEM-*b*-PBMA and POEM-*b*-PMMA are shifted toward higher temperatures relative to the POEM-*b*-PLMA conductivity curve by approximately 4 and 6 K, respectively. These differences are similar to the shifts of 3 and 5 K observed in the ^7Li line width experiments. This difference is greater than the uncertainty in temperature, ± 1 K.

Measurements of the ^1H line width can provide information on segmental mobility of the polymer. As the motional rate exceeds $10^5/\text{s}$, the line width drops from its rigid-limit value of ~ 50 kHz to hundreds of hertz in the melt. ^1H line width measurements, shown in Figure 2, were performed on the undoped copolymers and on pure POEM. A shift in the line width transition is observed in this comparison as well. The differences between the POEM curve and the POEM-*b*-PLMA and POEM-*b*-PBMA curves are 2 and 5 K, respectively.

To complement the ^1H line width data, ^1H $T_{1\rho}$ measurements were also conducted on the undoped samples. Since the rotating-frame relaxation data for the protons of the PEO side chain could not be fit by a

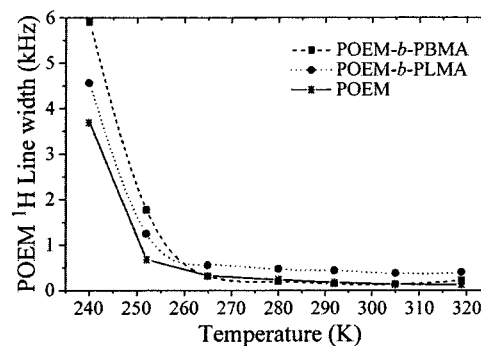


Figure 2. Temperature dependence of the ^1H line width of the peak at 3.8 ppm (PEO side chain) in POEM, POEM-*b*-PLMA, and POEM-*b*-PBMA copolymers. The samples were measured with a spinning rate of 1 kHz. The line width increases with decreasing temperature as the rates of the segmental motions approach rates below $10^5/\text{s}$. The uncertainty in temperature is ± 1 K.

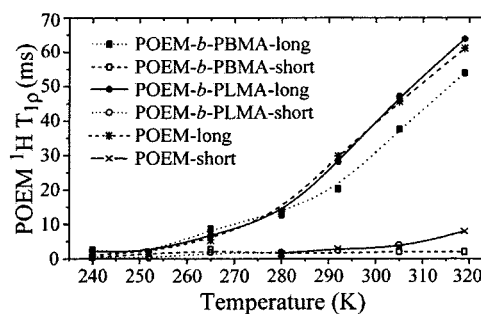


Figure 3. Temperature dependence of the ^1H $T_{1\rho}$ relaxation constants of the peak at 3.8 ppm (PEO side chain) in POEM, POEM-*b*-PLMA, and POEM-*b*-PBMA copolymers. Two $T_{1\rho}$ values are reported for each sample, obtained by fitting the observed decay of the magnetization with the sum of two exponential functions. $T_{1\rho}$ increases as the motional rate exceeds $\gamma B_1 = 4 \times 10^5/\text{s}$. The uncertainty in temperature is ± 1 K.

simple exponential decay, a biexponential function with both long and short $T_{1\rho}$ values was used to fit the relaxation data. The resulting pairs of values are shown in Figure 3. The short $T_{1\rho}$ values are nearly independent of temperature for all samples.

According to fundamental relaxation theory, $T_{1\rho}$ reaches a minimum for motional rates near $2\pi \times 62$ kHz.¹⁰ In the polymers studied here, the long $T_{1\rho}$ relaxation component is from segments that move with rates exceeding the minimum. Thus, a longer $T_{1\rho}$ corresponds to faster mobility. Comparison of the behavior of the long $T_{1\rho}$ component for the various samples shows a trend consistent with the ^1H and ^7Li line width measurements: the PBMA phase decreases the mobility in the POEM phase. The $T_{1\rho}$ behaviors of the POEM-*b*-PLMA copolymer and the POEM homopolymer at temperatures greater than the T_g of PLMA are similar. This shows that the previously observed difference in ionic conductivity is at least partially due to slower dynamics of segments and ions in the POEM phase. Note that these differences in POEM mobility between all samples as shown by the three types of NMR experiments, although significant, are very small.

The disparity between the short and long $T_{1\rho}$ components indicates that the chain dynamics is quite complex. To explain the persistence of a short $T_{1\rho}$ component over a wide temperature range, it is reasonable to assume that a gradient of mobility exists along the OEM side chains and that it slowly shifts toward the less

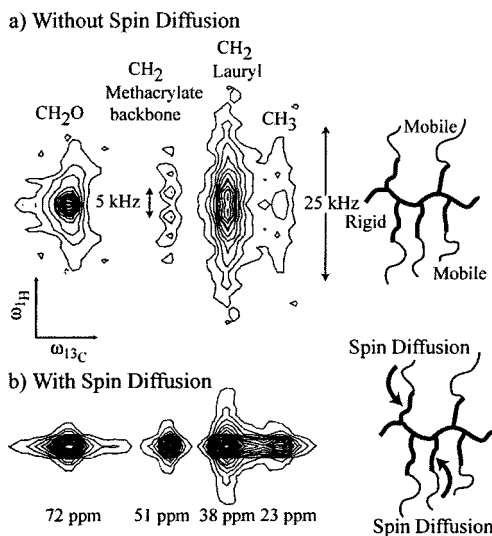


Figure 4. 2D WISE spectra of POEM-*b*-PLMA at 263 K with spin-diffusion mixing and cross-polarization times of (a) 100 μ s, 100 μ s and (b) 100 ms, 500 μ s, respectively. At short CP and spin diffusion times, the signal of the more rigid units is observed selectively. The more mobile (narrow peak) component of the PEO side chain transfers magnetization to the more rigid component during the 100 ms spin-diffusion mixing time.

mobile backbone as the temperature is increased. Thus, a fraction of OEM segments would always move with a rate near γB_1 , i.e., at the $T_{1\rho}$ minimum. While the ^1H line of this slow-moving component must be rather broad, through ^1H spin diffusion its magnetization can nevertheless become detectable in the narrow signal component of the more mobile segments. The similar biexponential behavior of the $T_{1\rho}$ relaxation curves for the POEM homopolymer shows that this gradient of motion is not due to the diblock structure.

To confirm the hypothesis that the dynamic heterogeneity is due to a gradient of mobility in the POEM side chain, 2D WISE experiments were conducted on the POEM-*b*-PLMA sample at 263 K. The WISE technique allows determination of ^1H line width of specific components in inhomogeneous systems. The pulse sequence is similar to the standard CP-MAS experiment with the addition of an incremented delay t_1 after the initial ^1H 90° pulse, thus correlating the ^1H wide-line spectrum and the ^{13}C isotropic shifts in the ω_1 and ω_2 dimensions, respectively.

The WISE spectrum^{8,9} obtained without ^1H spin-diffusion effects (at both short cross-polarization and mixing times) is shown in Figure 4a. The signal of the PEO side chain, at 72 ppm, shows a composite peak shape in the ^1H dimension, with both a narrow-line (highly mobile) and a 23 kHz line width (relatively rigid) component. The WISE spectrum with both long cross-polarization and mixing times (500 μ s and 100 ms, respectively) is shown in Figure 4b. The line shapes of all peaks are dominated by a narrow component, showing that ^1H magnetization has transferred through spin diffusion from the mobile to the rigid segments. Assuming Fickian spin diffusion with an effective diffusion coefficient of approximately 0.4 nm²/ms,¹¹ the distance between the highly mobile ethylene oxide units and the more rigid units must be less than 6 nm. The maximum limit on the size of the dynamic inhomogeneity is shorter

than the domains of the diblock copolymer. This finding is consistent with the hypothesis that the free ends of the side chains exhibit fast dynamics relative to the backbone.

Conclusions

^1H and ^7Li NMR have shown that the enhanced conductivity of diblock copolymer electrolytes with a low- T_g nonconductive phase is at least partially due to faster chain dynamics in the conductive phase. A higher T_g nonconductive block shifts the observed dynamics curves toward a higher temperature; this shift is small (approximately 5 K) but significant. For a secondary block whose T_g is comparable to that of POEM, mobility in the POEM domain is roughly equivalent to that in POEM homopolymer, despite the ordering of the block copolymer. This result suggests the intriguing possibility that the dynamics within the ion-conducting POEM domain might actually be enhanced above that of POEM homopolymer by choosing a secondary block whose glass transition resides substantially below that of POEM. Investigations to address this hypothesis are currently underway.

A second observation, suggested by the biexponential behavior of the ^1H $T_{1\rho}$ relaxation curves and confirmed by WISE experiments with and without ^1H spin-diffusion effects, is that the chain dynamics in the PEO side chain is inhomogeneous. The ends of the short chains have much faster motional rates than units near the backbone.

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