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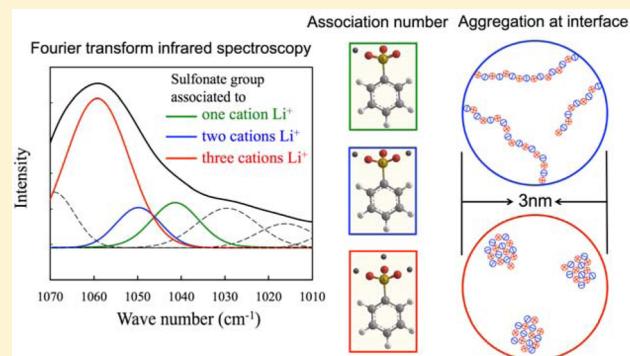
Linear Viscoelasticity and Fourier Transform Infrared Spectroscopy of Polyether-Ester-Sulfonate Copolymer Ionomers

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Supporting Information

ABSTRACT: Fourier transform infrared spectroscopy (FTIR) and linear viscoelasticity (LVE) were used to characterize amorphous copolyester ionomers synthesized via condensation of sulfonated phthalates with mixtures of poly(ethylene glycol) with $M = 600$ g/mol and poly(tetramethylene glycol) with $M = 650$ g/mol. The copolymer ionomers exhibited microdomain separation, as confirmed in previous X-ray scattering measurements. Since PEO has superior ion solvating ability compared with PTMO, the ions near the interface reside preferentially in the PEO microdomain. FTIR measurements were used to quantify fractions of ions in different association states, in turn quantifying the fractions in the PEO-rich domains, in the PTMO-rich domains, and at the interface between these domains. FTIR shows that the structure of the interfacial ion aggregates is quite different for the copolymers with different counterions; at the interface Na^+ aggregates into open string structures while Li^+ aggregates into denser sheets of ions, as depicted schematically at the far right. Ionic conductivity is dominated by ions in the PEO domain, due to superior cation solvation by PEO; in the PTMO-rich microdomain both Na^+ and Li^+ form dense aggregates with of order 15 ion pairs. The temperature dependence of viscoelastic properties depends primarily on the PEO segmental dynamics, due to much higher T_g for the PEO-rich microdomains that are continuous at all copolymer compositions studied. Increasing the PTMO fraction increases the ionic association lifetime and delays the LVE terminal relaxation, creating an extended rubbery plateau, despite the fact that the chains are quite short.



1. INTRODUCTION

Polymer electrolytes are inherently safer than traditional liquid electrolytes because of the superior mechanical performance and low volatility of polymers, which results in the suppression of Li dendritic growth and the prevention of liquid leaks, combustion, and explosion.^{1–5} Consequently, there has been extensive research on polymer electrolytes, especially bi-ion conductors obtained by dissolving salt in ion-solvating polymers.^{1–4} For bi-ion conductors, conduction of the cation (often Li^+ or Na^+) is of interest. Nevertheless, the anions interacting weakly with the polymer medium usually exhibit faster motion and carry most of the ionic conductivity. These conducting anions rapidly build up at the electrode/electrolyte interface, lowering the electric field that drives translational motion of the cations across the electrolyte. To solve this problem, one approach has been to covalently bond the anion to the polymer, so that the cations become the only conducting ion. This type of polymer-based single-ion conductor has been intensively studied recently, but the conductivity of these materials at room temperature is still too low for practical applications.^{6–11}

The design of highly conductive single-ion conductors requires understanding the mechanism of ion conduction. In general, ionic conduction experiences two stages: dissociation to create a charged species and transport of that species. The former relies on the energy of cation/anion interaction, which in turn is related to ion size, charge delocalization, the polarity of the surrounding medium, and its ability to solvate ions. The latter relies on the mobility of polymer segments and the motional coupling/decoupling between the ions and segments.^{1–4,9}

Cation single-ion conductors often contain poly(ethylene oxide) (PEO)^{1,4,6–10,12,13} due to its superior solvation of cations. Nevertheless, it is well recognized that pure PEO is insufficient to increase either the conductivity or the mechanical performance to a satisfactory level. Several improvements have therefore been attempted.^{5,14–16} The main idea is to independently improve the mechanical and conductive performance to avoid the well-known conflict

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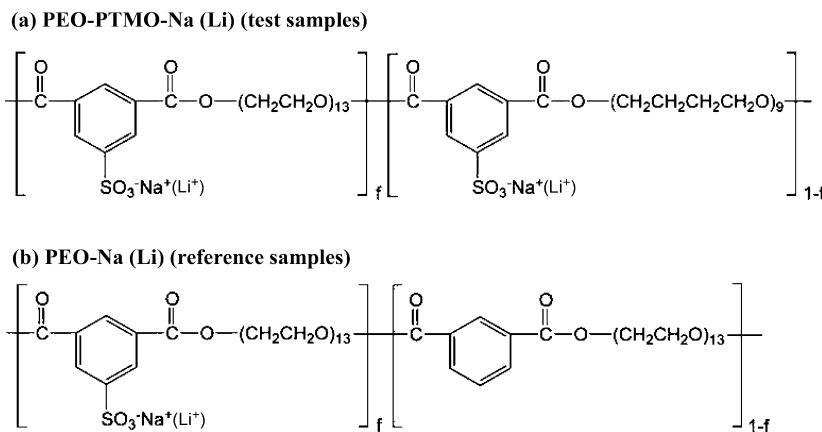


Figure 1. Chemical structure of (a) PEO-PTMO-Na co-ionomers⁹ with the fraction f of PEO spacer varied from 0 (PTMO-Na ionomer) to 1 (PEO-Na ionomer). (b) Reference PEO600-Na ionomers, where f is the fraction of the ionic units.^{6,13} PEO400-100%Na (and PEO1100-100%Na) have very similar structures¹³ with $f = 1$ but with 9 (and 25) ethylene oxide repeats between phthalates instead of 13.

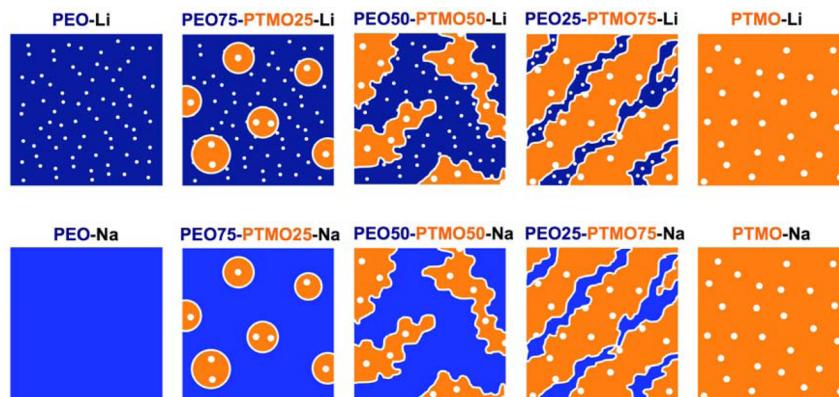


Figure 2. An approximate morphology schematic for PEO ionomers, PEO-PTMO co-ionomers, and PTMO ionomers at 20 °C. Blue indicates PEO, orange indicates PTMO, and white indicates ions.

between them: the improvement of mechanical performance usually leads to slower segmental motion and accordingly lower conductivity.^{9,16} In a previous study, PEO content was systematically varied in a series of single-ion conductors synthesized via condensation polymerization of sulfonated phthalates and mixtures of diols of PEO having a molecular weight of 600 g/mol (PEG600) and poly(tetramethylene oxide) having a molecular weight of 650 g/mol (PTMO650). The similarity of the two molecular weights keeps the overall ion content comparable in their copolymers. For convenience, a new term *co-ionomer* is introduced to specify these copolymerized ionomer samples, while the term *ionomer* is used to specify samples synthesized from a single oligomeric diol (either PEO or PTMO). The structures of the co-ionomers and ionomers are shown in Figure 1a (with $f = 1$ for the PEO ionomer and $f = 0$ for the PTMO ionomer). The co-ionomers are named as PEO#-PTMO#-Li/Na, with # representing the molar percentage of each diol. For example, PEO75-PTMO25-Na means 75% of the diols are PEO, 25% are PTMO, and the counterion is Na.

The randomly copolymerized PEO600 and PTMO650 units exhibit microdomain separation, as confirmed by X-ray scattering.⁹ The PTMO-rich microdomain exhibits a $T_g \sim -60$ °C, the same as that of the PTMO650 ionomers and the nonionic PTMO650-0,⁹ made from PTMO650 condensation with neutral dimethyl isophthalate, while the PEO-rich microdomain exhibits $T_g > -20$ °C, higher than that of the

PEO600 ionomers with similar overall ion content. This result indicates that PEO and PTMO are microphase separated and ions bias toward residing in the stronger ion-solvating PEO microdomain. For all co-ionomers, the temperature dependence of ion conductivity is similar to that of the PEO ionomer (distinct from the PTMO ionomer⁹), suggesting that the PEO forms a continuous microdomain and dominates ionic conduction. All these features lead to the schematic morphology of the co-ionomers and the two ionomers shown in Figure 2. Note that (1) the ions aggregate strongly in PTMO microdomains, less strongly in the PEO domain when the counterion is Li, and hardly at all in the PEO microdomain when the counterion is Na, and (2) the PEO microdomain is always continuous with domain size decreasing as PTMO content increases.

Figure 2 is a modified version of the previous scheme (Figure 4 in ref 9) to incorporate ions near the interface (white boundary between the microdomains). This is because the statics and dynamics of the current co-ionomer samples can be well understood by classifying the ionic groups into three classes: Since each ionic group connects two spacers and the fractions of PEO and PTMO spacers are f and $1 - f$, respectively, the possibility for ions to connect (1) two PEO spacers is f^2 , (2) two PTMO spacers is $(1 - f)^2$, and (3) one PEO and one PTMO spacers is $2f(1 - f)$. It is natural to regard that ionic groups of type 1 and type 2 reside in the PEO and PTMO microdomains, respectively, while that of type 3 resides

near the interface. The composition dependence of these populations are shown in Figure 3, where $2f(1-f)$ has the

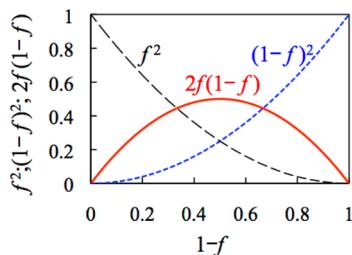


Figure 3. Number fraction of ions residing in the PEO domain, f black long-dashed curve; residing in PTMO domains $(1-f)^2$, blue short-dashed curve; and near the PEO–PTMO interface $2f(1-f)$, red solid curve.

largest value at $f = 0.5$ (solid curve), simply meaning that the largest amount of ions reside near the interface when the compositions of PEO and PTMO become comparable. The analysis of Figure 3 relies only on the copolymer being random, since each sulfonate is between two polyether segments (either PEO or PTMO).

2. EXPERIMENTAL SECTION

All samples in this study were synthesized through a two-step melt condensation between dimethyl-5-sulfoisophthalate sodium salt and various proportions of oligomeric diols PEO600 and PTMO650,⁹ with structures shown in Figure 1a. For comparison, some PEO-based reference ionomers previously made via the same condensation reaction, for which the diesters are mixtures of dimethyl isophthalate and dimethyl-5-sulfoisophthalate sodium salt (see Figure 1b) condensed with diols PEO400, PEO600, or PEO1100.^{6,13} The variations of (1) the fraction of the phthalates that are sulfonated and (2) the PEO spacer length allow the ion content to be tuned over a wide range. The reference ionomers are named PEO#-FNa/Li with # denoting the molecular weight of the PEO diol and F the number fraction of phthalates that are sulfonated.

The structures of the ionomers and co-ionomers were verified via ¹H NMR using a DPX-300 spectrometer and perdeuterated dimethyl sulfoxide as solvent.^{9,13} The number-average molecular weight (M_n) of these samples was estimated via the ratio of chain end protons to midchain protons. Possible ring structures with no end protons may lead to an overestimation of M_n , and thus the NMR M_n can be regarded as an upper bound. Na samples were directly synthesized and exhaustively dialyzed against ultrapure water; Li samples were obtained via ion exchange during dialysis.^{9,13} The M_n , ion content, and T_g of the PEO ionomers are listed in Table 1, while those data for the PEO-PTMO co-ionomers are listed in Table 2.

Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier transform infrared (FTIR) spectrometer. A wavenumber resolution of 1 cm^{-1} was used, and 100 scans were signal-averaged.

Ionomer and co-ionomer samples were prepared by casting 4 wt % solutions in methanol onto KBr windows. The solvent is first removed slowly under ambient conditions for 1 h, and the sample was then dried in a vacuum oven at 80 °C overnight to remove residual solvent. Film thickness was controlled to ensure the absorbance of the bands of interest is within the range of the Beer–Lambert law. During the infrared spectra collection, all FTIR samples were maintained under a dry purge.

Linear viscoelastic (LVE) measurements of the samples were conducted using an Advanced Rheometric expansion system (ARES)-LS1 rheometer (Rheometric Scientific) using 7.9 and 3.0 mm diameter parallel plates and a nitrogen atmosphere. The linear strain amplitudes were verified by strain amplitude sweeps and instrument compliance was not a problem, as verified by consistent results from multiple geometries. Samples were dried in vacuum at 90–120 °C for 3–5 days prior to rapid loading into ARES followed by heating under nitrogen for >1 h at 120 °C. This step enables removal of water and voids and facilitates proper contact between the samples and the plates. Time–temperature superposition (tTs) was found to work well for both glassy and rubbery moduli but fails moderately in the glassy–rubbery transition region. All master curves are shown at a reference temperature of $T_r = 20\text{ }^\circ\text{C}$.

Ab initio calculations were carried out for benzenesulfonate with one, two, or three Li^+ (or Na^+) cations using the Gaussian03 package, the Hartree–Fock Theory (HF functional), and the 6-31+G(d,p) basis set. The ions were studied in the recently developed cluster-continuum model:¹⁷ Dimethyl ether molecules fill the first shell around each cation to mimic the specific solvation of ether oxygens, and that entire cluster is embedded in a cavity surrounded by a polarizable continuum of dielectric constant 4.3. After structural optimization, vibrational frequency calculations were performed to investigate the IR symmetric stretching of the three S–O bonds for the benzenesulfonate anion with 0, 1, 2, or 3 cations nearby. Limitations of the electron correlation and basis set mean that vibrational frequencies can often be improved by rescaling, depending on the level of electronic structure theory and basis set. This has been studied in detail in the literature, and to accurately reproduce experimental IR frequencies, a scale factor of 0.928 is used to correct deficiencies in HF/6-31+G(d,p) based on a database that provides reliable scale factors in conjunction with tabulated electronic model chemistries.^{18,19}

3. RESULTS AND DISCUSSION

3.1. Statics I: Quantification of the Bias of Ions toward the PEO Domain. DSC glass transition temperature $T_{g,\text{PEO}}$ of the PEO microdomain of the co-ionomers⁹ (see Table 2) is higher than $T_{g,\text{PEO}}$ of the PEO600-Li/Na ionomers (see Table 1). This result reflects the migration of ions from the PTMO microdomain to the PEO microdomain. To quantify this migration of ions, Figure 4 plots $T_{g,\text{PEO}}$ against the number density of ions, p_0 , for the PEO400-100%Li/Na, PEO600-100%Li/Na, and PEO1100-100%Li/Na ionomer samples (see open symbols—all three samples can be regarded as a mixture of PEO and sulfoisophthalate Li/Na salts). It is noted that T_g

Table 1. PEO Ionomer Number-Average Molecular Weight M_n , Number-Average Molecular Weight between Ionic Groups M_s , Number Density of Ionic Groups p_0 , and Glass Transition Temperature $T_{g,\text{PEO}}$ for Reference PEO Ionomers^{6,7,10,13}

sample	M_n (g/mol)	M_s (g/mol)	Li		Na	
			p_0 (nm^{-3})	$T_{g,\text{PEO}}$ (K)	p_0 (nm^{-3})	$T_{g,\text{PEO}}$ (K)
PEO600-0%	14000		0	228	0	228
PEO600-11%	5800	6800	0.079	228	0.079	232
PEO600-17%	8700	4400	0.12	230	0.12	233
PEO600-49%	4700	1600	0.35	239	0.35	245
PEO600-100%	4600	830	0.72	255	0.72	271
PEO400-100%	3300	630	0.95	285	0.95	295
PEO1100-100%	4500	1300	0.45	236	0.45	242

Table 2. Molecular Weight M_n , Number Density of Ionic Groups p_0 , and Glass Transition Temperature of PEO-Rich and PTMO-Rich Microdomains, $T_{g,PEO}$ and $T_{g,PTMO}$, for Ionomer and Co-ionomer Based on $T_{g,PEO}$ Samples⁹

sample	M_n (NMR)	Li			Na		
		p_0 (nm^{-3})	$T_{g,PEO}$ (K)	$T_{g,PTMO}$ (K)	p_0 (nm^{-3})	$T_{g,PEO}$ (K)	$T_{g,PTMO}$ (K)
PEO	4600	0.72	255		0.72	271	
PEO75-PTMO25	6400	0.70	258	212	0.70	272	213
PEO50-PTMO50	7300	0.69	261	213	0.69	277	213
PEO25-PTMO75	6500	0.67	269 ^a	213	0.67	286	212
PTMO	6700	0.66		210	0.66		209

^aUpdated value from that in ref 9; all other data are identical to ref 9.

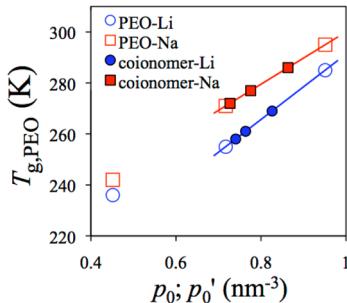


Figure 4. Plots of effective $T_{g,PEO}$ against number density of ions p_0 of the PEO-100%Li/Na reference ionomers (open symbols). $T_{g,PEO}$ determined for the PEO microdomain of the co-ionomers allows an evaluation of p_0' in the PEO microdomain of the co-ionomers via linear interpolation of plots of $T_{g,PEO}$ against p_0 of the PEO ionomers (filled symbols).

increases with p_0 . Fortunately, $T_{g,PEO}$ obtained for all the co-ionomer samples falls between those of the PEO600-100%Li/Na and PEO400-100%Li/Na polymers, enabling us to evaluate the number density of ions in the PEO600 microdomain, p_0' , via interpolation between the data for PEO600-100%Na/Li and PEO400-100%Na/Li. The interpolating points are shown by filled symbols in Figure 4. For either Na or Li co-ionomers, $T_{g,\text{eff}}$ increases with PTMO content, meaning the ratio $1 < p_0'/p_0 \leq 1.2$ (where p_0 is the ionic content of PEO600-100%Li/Na) increases with PTMO content.

It is natural that the fraction of ions near the interface, $2f(1-f)$, has the freedom to migrate toward either the PEO or PTMO microdomain but prefers the PEO microdomain because of its stronger ion solvating ability. The ions near the interface can then be divided into two subtypes: (a) a fraction $2\phi f(1-f)$ that prefers the PEO microdomain and (b) a fraction $2(1-\phi)f(1-f)$ that prefers the PTMO microdomain. Note that $\phi = 0.5$ if there is no preference of ions for one microdomain over the other, leading to a fraction of ions in PEO and PTMO microdomains of $f^2 + 2\phi f(1-f) = f$ and $(1-f)^2 + 2(1-\phi)f(1-f) = 1-f$, respectively. However, the preference toward PEO microdomains leads to $p_0'/p_0 > 1$ and the relationship $[f^2 + 2\phi(1-f)f]/f = p_0'/p_0$, giving $\phi = (p_0'/p_0 - f)/[2(1-f)] = 0.58 \pm 0.05$ for both Li and Na.⁹ All p_0' and ϕ values obtained from the T_g of the PEO-rich microdomain in Figure 4 are listed in Table 3.

3.2. Statics II: Ionic Status via FTIR. Information on ion association status can be obtained by analyzing FTIR spectra in the region from 1070 to 1010 cm^{-1} , which includes bands assigned to the SO_3^- symmetric stretching modes near 1045 cm^{-1} , which are sensitive to ion coordination. However, in this region, strong bands from the PEO backbone overlap significantly with the SO_3^- absorbance. In order to clearly

Table 3. Number Density of Ionic Groups in the PEO-Rich Microdomain, p_0' , and Fraction of Ions Biased toward the PEO Microdomain, ϕ , for Co-ionomers

sample	Li			Na		
	p_0 (nm^{-3})	p_0' (nm^{-3})	ϕ	p_0 (nm^{-3})	p_0' (nm^{-3})	ϕ
PEO75-PTMO25	0.70	0.74	0.60	0.70	0.73	0.53
PEO50-PTMO50	0.69	0.76	0.57	0.69	0.78	0.58
PEO25-PTMO75	0.67	0.83	0.57	0.67	0.86	0.64

observe the SO_3^- symmetric stretching mode near 1050 cm^{-1} , the spectrum of the PEO-PTMO nonionic counterpart is subtracted from the spectrum of PEO-PTMO Li/Na, as described in the Supporting Information.

The result after spectral subtraction for a representative co-ionomer, PEO50-PTMO50-Li, is shown in Figure 5, where three bands related to the symmetric stretching of the SO_3^- group are resolved near 1042, 1050, and 1059 cm^{-1} . These correspond to association of the sulfonate groups with one, two, and three cations, respectively. There is no detectable band corresponding to free sulfonate groups (i.e., associated with no cations), expected near 1035 cm^{-1} . The geometries of

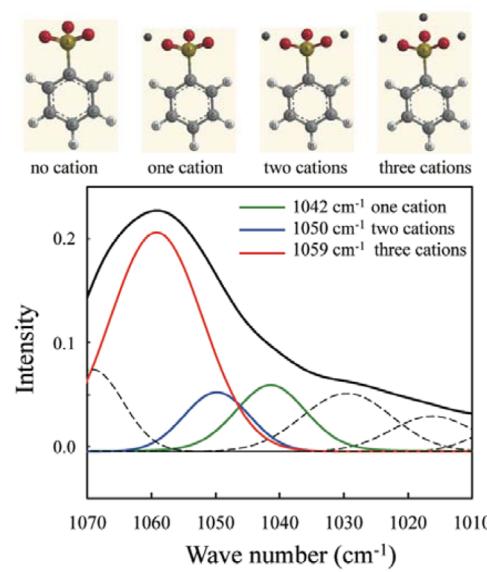


Figure 5. Curve resolving results of the difference spectrum of PEO50-PTMO50-Li and its neutral counterpart in the region from 1010 to 1070 cm^{-1} . Above the plot, geometries of benzenesulfonate groups associated with 0, 1, 2, and 3 cations are schematically shown. The strong solvation of the cation (Li or Na) by ether oxygens makes monodentate cation coordination; in all cases each cation is coordinated to one and only one sulfonate oxygen.

the sulfonate group associated with 0, 1, 2, and 3 cations are shown at the top of Figure 5. The three-cation association band was reported previously^{20–22} to be close to 1059 cm⁻¹ in PEO/salt complexes at relatively high salt concentrations, and it is attributed to a higher degree of coordination/aggregation between cations and SO₃⁻.

These band assignments are verified using *ab initio* calculations. Increasing the number of associated cations leads to a red-shift, if the solvating effect of ether oxygens is not considered (in the gas phase). However, proper incorporation of solvation using the cluster-continuum model¹⁷ predicts a blue-shift in accordance with experiments. The wavenumbers from *ab initio* calculations in the cluster-continuum model are very close to the experimental values, as shown in Table 4.

Table 4. Comparison of FTIR Wavenumbers Obtained in Experiments and *ab Initio* Calculation for Sulfonates with Different Association Number of Counterions (Li⁺ or Na⁺)

no. of association	Li		Na	
	exp (cm ⁻¹)	<i>ab initio</i> (cm ⁻¹)	exp (cm ⁻¹)	<i>ab initio</i> (cm ⁻¹)
0	1035	1022	1035	1022
1	1042	1030	1042	1027
2	1050	1048	1050	1053
3	1059	1059	1059	1062

The number fraction of sulfonates, Φ_1 , Φ_2 , and Φ_3 (the subscript denotes the number of associated cations, with $\Phi_1 + \Phi_2 + \Phi_3 = 1$, with $\Phi_0 = 0$ as noted above), can be calculated from the area of the corresponding band in the difference spectrum, assuming the absorption coefficients of these bands are the same.²³ Figures 6a, 6b, and 6c show Φ_1 , Φ_2 , and Φ_3 as a function of PTMO fraction $1 - f$. Figure 3 shows the ions belonging to three groups: fraction f^2 are in the PEO domain, fraction $(1 - f)^2$ are in the PTMO domain, and fraction

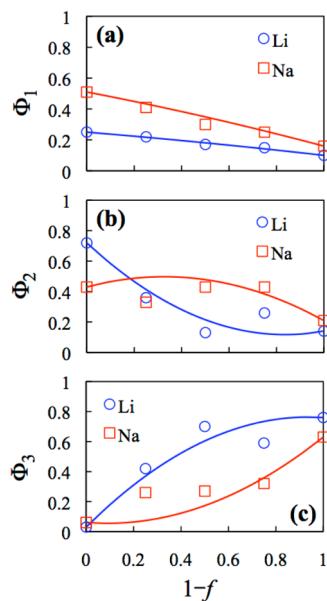


Figure 6. Number fractions of sulfonate groups associated with (a) one, (b) two, and (c) three cations as a function of the fraction of PTMO in PEO-PTMO Li/Na co-ionomers. The solid lines show the predictions of eq 1 for Li (blue) and Na (red) counterions.

$2f(1 - f)$ are near the interface. The last group can be further divided into two subgroups: $2\phi f(1 - f)$ biased toward the PEO microdomain and $2(1 - \phi)f(1 - f)$ biased toward the PTMO microdomain, with $\phi \approx 0.58$, as determined earlier. In Figure 6a, the fraction of ion pairs changes almost linearly with $1 - f$, allowing simple weighting of the contribution from each microdomain by the number of ionic groups as in eq 1a.

$$\Phi_1^{\text{co-ionomer}} = [f^2 + 2\phi f(1 - f)]\Phi_1^{\text{PEO}} + [(1 - f)^2 + 2(1 - \phi)f(1 - f)]\Phi_1^{\text{PTMO}} \quad (1a)$$

$$\Phi_2^{\text{co-ionomer}} = f^2\Phi_2^{\text{PEO}} + (1 - f)^2\Phi_2^{\text{PTMO}} + \delta_2$$

with $\delta_2 = 0$ for Li

$$\delta_2 = \text{all remaining ions at the interface for Na} \quad (1b)$$

$$\Phi_3^{\text{co-ionomer}} = f^2\Phi_3^{\text{PEO}} + (1 - f)^2\Phi_3^{\text{PTMO}} + \delta_3$$

with $\delta_3 = \text{all the remaining ions at the interface for Li}$

$$\delta_3 = 0 \text{ for Na} \quad (1c)$$

Here Φ_X^Y is the fraction of sulfonate groups associated with X cations of the Y sample ($Y = \text{PEO}$ (ionomer), PTMO (ionomer), or co-ionomer). From Figures 6b and 6c (for $X = 2$ and 3), it is clear that a simple linear weighting rule like eq 1a should not work because convex curves are observed for $X = 2$ with Na as the counterion and for $X = 3$ with Li as the counterion. This feature suggests that the sulfonate groups near the interface, which also shows a convex curve when plotted against $1 - f$ (see Figure 3), contribute more to Φ_2 if the counterions are Na and contribute more to Φ_3 if the counterions are Li.

The FTIR ionic status reported in Figure 6 can be understood using the molecular picture that Li forms sheetlike aggregates near the interface ($X = 3$ may also correspond to dense three-dimensional aggregates; however, the sheetlike aggregates is a reasonable picture considering the two-dimensional interface and that cations are strongly solvated by PEO), while Na forms stringlike aggregates near the interface. First, it is natural to assume the ions in PEO and PTMO microdomains have the same distribution of ionic states as those in the PEO-Na/Li and PTMO-Na/Li ionomers, respectively. If so, there should be $f^2\Phi_X^{\text{PEO}} + (1 - f)^2\Phi_X^{\text{PTMO}}$ in the weighting rules for the co-ionomers with $X = 2$ and 3. The remaining sulfonate groups near the interface are further assumed to all be associated with two cations when the counterion is Na and three cations when the counterion is Li. Then, the weighting rules for the co-ionomers with $X = 2$ and 3 can be written as eqs 1b and 1c.

The predictions of eqs 1 are shown as the curves in Figure 6 and agree well with the experimental ionic status from FTIR (symbols), strongly supporting this molecular picture. $X = 3$ is visualized as a two-dimensional dense sheetlike aggregation and $X = 2$ as a sparse stringlike aggregation at the interface. Then, Figure 6 suggests that near the interface sulfoisophthalate Li forms a dense sheetlike aggregation while sulfoisophthalate Na forms a sparse stringlike aggregation.

Do the ions confined to be near the two-dimensional interface have the requisite freedom to aggregate in these different forms? Since the number density of ions near the interface is $2p_0f(1 - f)$, the interfacial area occupied by one ion would be $S_{\text{ion}} = \langle S/V \rangle / [2p_0f(1 - f)]$, where $\langle S/V \rangle$ is the mean interfacial area per unit volume that can be estimated from the

domain spacing provided by X-ray scattering:⁹ (1) For PEO50-PTMO50-Li/Na, this domain spacing $D \approx 10$ nm, and assuming lamellar structure, $\langle S/V \rangle = 2/D = 0.2 \text{ nm}^{-1}$ and then $S_{\text{ion}} = \langle S/V \rangle / [2p_0f(1-f)] \approx 0.5 \text{ nm}^2$. (2) For PEO75-PTMO25-Li/Na, the domain spacing $D \approx 18$ nm, and assuming spherical PTMO domains of radius r , $1-f = 4\pi r^3 / 3D^3$ yields $r = 7$ nm, making $\langle S/V \rangle = 4\pi r^2 / D^3 = 0.1 \text{ nm}^{-1}$ and $S_{\text{ion}} = \langle S/V \rangle / [2p_0f(1-f)] \approx 0.4 \text{ nm}^2$. In each case, one ion near the interface occupies an average area of $S_{\text{ion}} \sim 0.4\text{--}0.5 \text{ nm}^2$, between the $\sim 0.1 \text{ nm}^2$ for one bond and $\sim 1 \text{ nm}^2$ for one Kuhn segment. Consequently, ions with average separation of $\sim 0.7 \text{ nm}$ are neither too sparse nor too crowded, so the observed variations in aggregation state are reasonable.

3.3. Dynamics I: DC Conductivity and the Nernst–Einstein Equation. The temperature dependences of conductivity for the PEO ionomer and all co-ionomers are similar and of the Vogel–Fulcher–Tammann (VFT) type.⁹ However, conductivity of PTMO ionomers exhibits a much weaker temperature dependence of the Arrhenius type. This observation was interpreted to indicate that the PEO microdomains must be continuous and contain most of the conducting ions.⁹

This point can be tested quantitatively utilizing the Nernst–Einstein equation:

$$D_\sigma = \frac{kT\sigma_{\text{DC}}}{pe^2} \quad (2)$$

Here, D_σ is the diffusion coefficient of conducting ions, k is the Boltzmann constant, σ_{DC} is the DC conductivity, and e is the elementary charge. If the ion motion in the PEO microdomains governs the conductivity, D_σ in eq 2 can be normalized by $T_{g,\text{PEO}}/T$, by using the number density of conducting ions p equal to p_0f^2 , corresponding to counterions in the PEO-rich microdomains.

To test this idea, $\sigma_{\text{DC}}/f^2p_0$ is plotted against $T_{g,\text{PEO}}/T$ for the PEO ionomer and co-ionomers in Figure 7, which reduces to common curves for either Li or Na. Other normalization number densities were tried, such as p_0 , corresponding to all ions in the system or $[f^2 + 2\phi f(1-f)]p_0$, corresponding to a sum of ions in the PEO microdomain and at the interface but biased toward the PEO domain. Nevertheless, good data collapse with these alternative scenarios cannot be achieved, suggesting that the ions between two PEO segments, well inside the PEO microdomains, dominate the conductivity. This is in accordance with the results shown in Figure 6 that most of the ionic groups aggregate near the interface for either Li or Na co-ionomers. In other words, although a fraction of $2\phi f(1-f)$ ions from the interface raises the T_g of the PEO microdomains, they hardly participate in ion conduction because they form aggregates at the interface.

3.4. Dynamics II: Linear Viscoelasticity. **3.4.1. Overview.** Figure 8 compares master curves of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, reduced to a reference $T_r = 20^\circ\text{C}$, as functions of angular frequency ω for the ionomer and co-ionomer samples having Li (blue) and Na (red) counterions. From top to bottom, the ratio between the number fractions of PEO and PTMO units changes systematically, from 100% PEO (PEO-Li/Na) to 100% PTMO (PTMO-Li/Na).

Since the application of time–temperature superposition (tTs) to microphase-separated systems is usually questionable, this is discussed immediately: In the case when PEO is the majority and the sole continuous domain, i.e. PEO75-

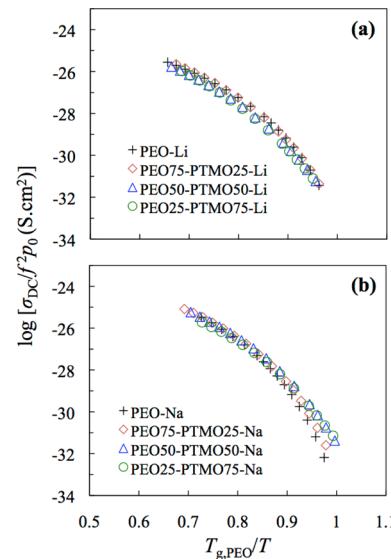


Figure 7. DC conductivity normalized by number density of ions residing in the PEO domain, p_0f^2 , plotted against $T_{g,\text{PEO}}/T$ for the PEO ionomer and the three co-ionomer samples having (a) Li and (b) Na counterions, where $T_{g,\text{PEO}}$ is the glass transition temperature of the PEO microdomains, listed in Table 2. The data collapse well, strongly suggesting that ion conduction is primarily in the continuous PEO domains. Reproducibility had been checked, and σ_{DC} of PEO-Li has been updated from ref 9.

PTMO25-Li/Na samples, it is not surprising that tTs works because the modulus is governed by the PEO domain. However, for the cocontinuous case, both PEO and PTMO should contribute to the modulus. The tTs should fail when two (or more) sources of stress have comparable contributions with different T dependences. In the LVE measurements, tTs does fail moderately in the transition from rubbery to glassy modulus where quenched PEO segments manifest in LVE, while tTs holds approximately at either lower or higher T , possibly indicating that one component governs the modulus within the limited ω window.

The PEO75-PTMO25-Li/Na samples (Figure 8b) exhibit a glassy relaxation (ω from 10^2 to 10^8 rad/s) very similar to that of PEO-Li/Na (Figure 8a), suggesting that the PEO microdomain governs the glassy relaxation. This is in accordance with the proposed morphology (see ref 9 and Figure 2), i.e., isolated PTMO domains in a continuous PEO microdomain for PEO75-PTMO25-Li/Na. In contrast, for PEO50-PTMO50-Li/Na (Figure 8c) and PEO25-PTMO75-Li/Na (Figure 8d), both the PTMO and PEO microdomains contribute to the glassy modulus. The former appears at ω values between 10^8 and 10^{16} rad/s , while with increasing PTMO content the latter are more delayed, with ω ranging from 10^0 to 10^8 rad/s . The two glass transitions in LVE are in accordance with the bicontinuous morphology (see ref 9 and Figure 2). The delay of the PEO glassy relaxation with increasing PTMO content is due to the bias of ions toward the PEO microdomain, as discussed earlier in Figure 4.

For the co-ionomers, the glassy modulus of the PEO microdomain with Na counterions is always more delayed than that with Li counterions. This result confirms our previous argument that Na pairs interact more strongly with the PEO medium than Li pairs which aggregate more.⁹ The evidence for this is (1) the ionomer scattering peak, corresponding to the interaggregate spacing, is only observed for the Li ionomers but

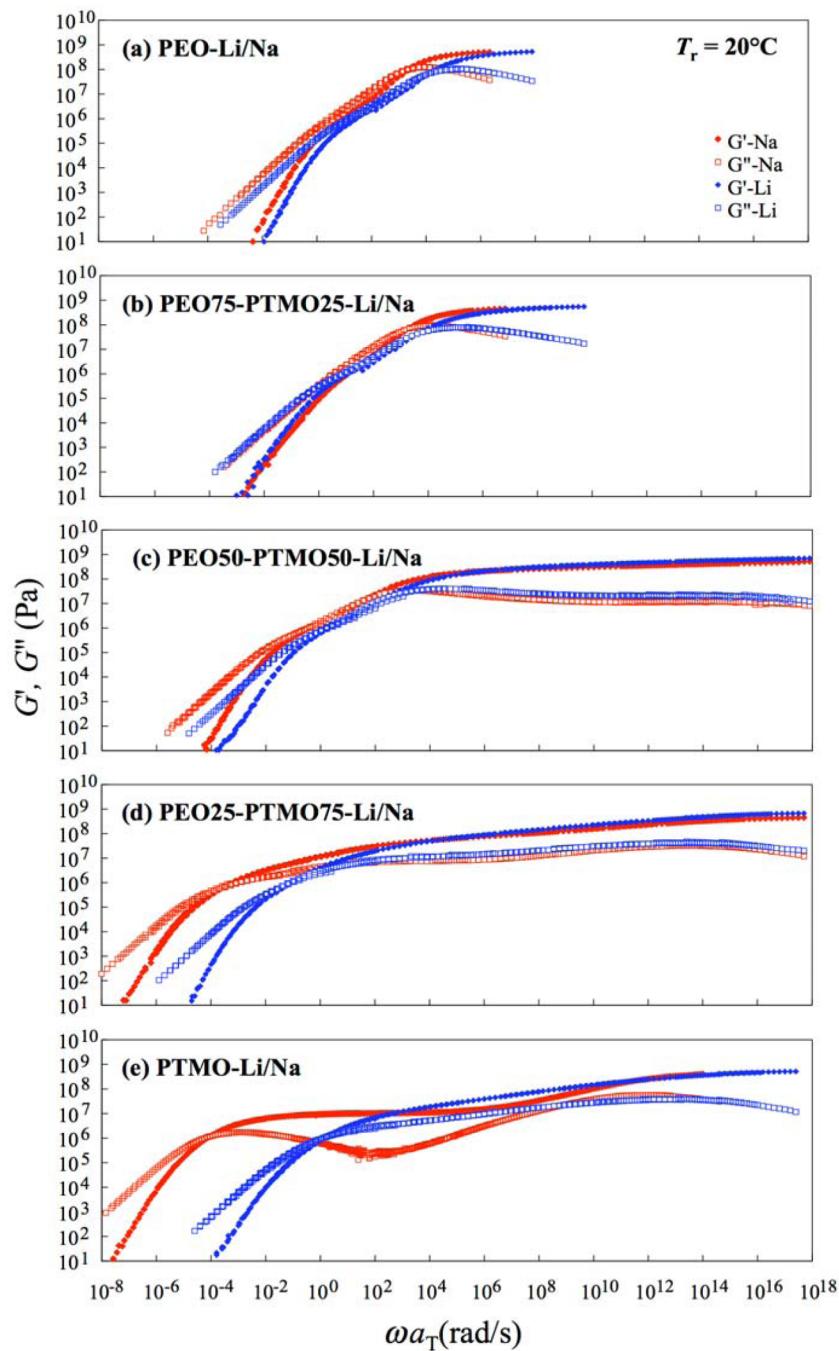


Figure 8. Master curves of storage modulus $G'(\omega)$ (filled symbols) and loss modulus $G''(\omega)$ (open symbols), obtained as functions of angular frequency ω for (a) PEO-Na/Li, (b) PEO75-PTMO25-Li/Na, (c) PEO50-PTMO50-Li/Na, (d) PEO25-PTMO75-Li/Na, and (e) PTMO-Na/Li. These master curves are reduced at $T_r = 20^\circ\text{C}$, from LVE measurements in the T range of -80 to 120°C .

not for the Na ionomers near room temperature,⁹ and (2) the T_g of the PEO microdomain is higher for each ionomer and co-ionomer with Na counterions compared with Li counterions (see Figure 4). The recently developed cluster-continuum density functional theory model also supports this argument:¹⁷ The energy difference between a Li–benzenesulfonate quadrupole solvated by dimethyl ether and two solvated contact pairs is -9 kJ mol^{-1} , meaning that the quadrupole (and more generally ion aggregation) is significantly favored when Li is the counterion. In contrast this energy difference is $+20\text{ kJ mol}^{-1}$ for Na–benzenesulfonate,¹⁹ suggesting that Na counterions prefer the pair state and are not as prone to aggregate.

Figure 9 compares the master curves shown in Figure 8 in a different way; all samples with Na counterions are compared in Figure 9a, and all samples with Li counterions are compared in Figure 9b. For all the samples, the glassy modulus amplitudes are roughly the same, as expected, since the glassy moduli of the PTMO-Li/Na and PEO-Li/Na ionomers are nearly the same. For the samples with Na counterions, it is noted that the terminal relaxation becomes more delayed with increasing PTMO content, reflecting a higher activation energy for ionic hopping. In contrast, the delay for Li samples is much weaker, reflecting the smaller ion hopping energy barrier for the Li samples compared to the Na samples. Interestingly, for the Li

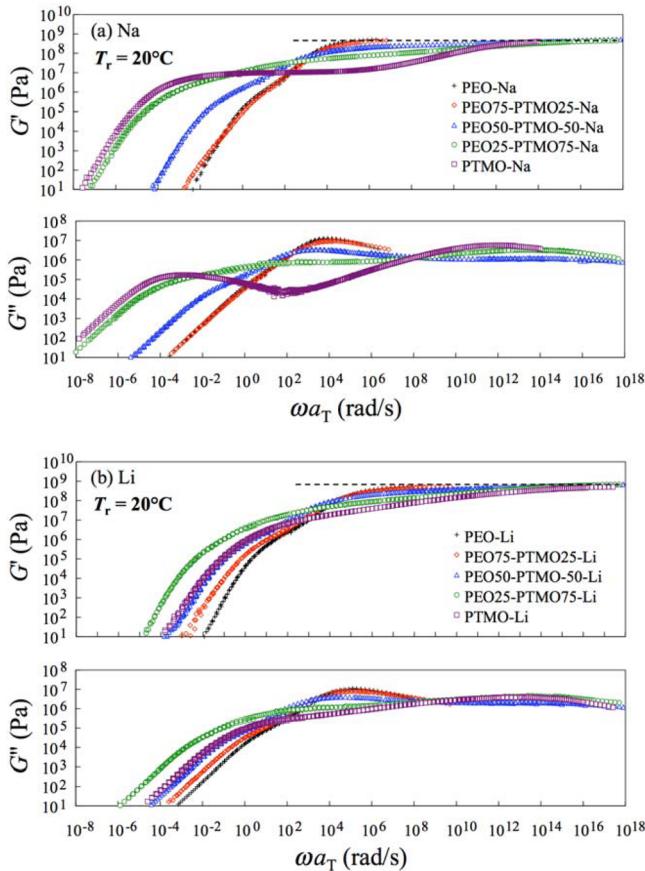


Figure 9. Master curves of storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$, obtained as functions of angular frequency ω for all ionomers and co-ionomers with (a) Na and (b) Li counterions. These master curves are reduced at $T_r = 20^\circ\text{C}$.

samples, the terminal relaxation time does not always increase with PTMO content—the terminal relaxation is faster for PTMO-Li compared with PEO25-PTMO75-Li. This seemingly contradictory result reflects the fact that the terminal relaxation is related not only to ionic hopping but also to chain friction that is governed by the PEO microdomain having a higher T_g than the PTMO microdomain, as explained later in the discussion of Figure 12.

3.4.2. Apparent LVE Frequency-Scale Shift Factors. The temperature dependence of the apparent LVE shift factors reflects changes in the frictional environment with T and the extra activation energy required for ionic dissociation. To analyze the apparent shift factors, the reference PEO ionomers with different ionic fractions and PEO spacer lengths are first analyzed.

In ref 10, the apparent shift factors a_T with respect to the same reference temperature $T_r = 20^\circ\text{C}$ were reported to be quite different for PEO#-FNa ionomers of different ionic contents (see Figure 4a of ref 10). The sources of this difference could be (1) frictional differences arising from the T_g difference and (2) a different activation energy for ionic dissociation for these samples. Figure 10a plots $\log a_T$ against a new reference temperature $T'_r = T_r + (T_{g,\text{PEO}} - T_{g,0})$ to account for the difference of $T_{g,\text{PEO}}$, with $T_{g,0} = 228\text{ K}$ the glass transition temperature of the neutral sample PEO600-0%. In Figure 10a, all apparent shift factors collapse to a single WLF curve, $\log a_T = -4.5(T - T'_r)/(102 + T - T'_r)$, indicating a

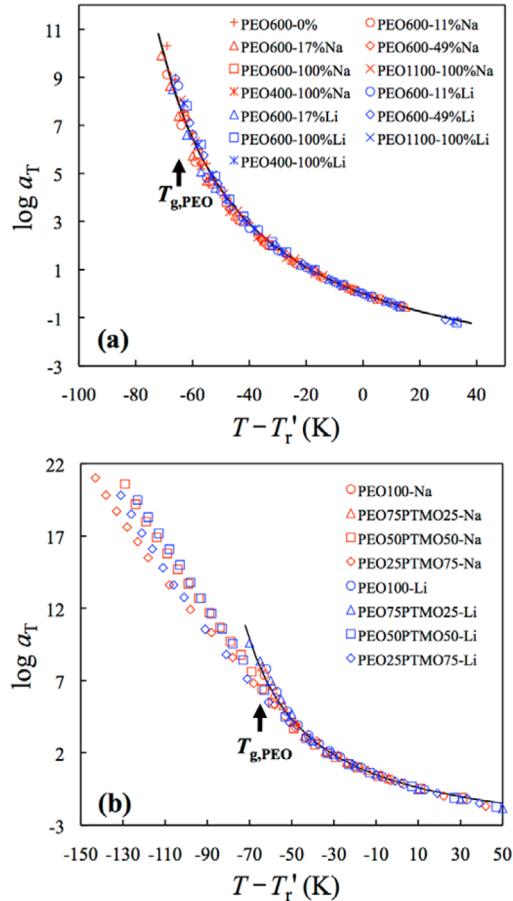


Figure 10. Temperature dependence of apparent frequency-scale shift factors $\log a_T$ against $T - T'_r$, with T'_r being a shifted reference temperature to account for the T_g of the PEO domain for (a) PEO ionomers and (b) co-ionomers and PEO ionomers.

uniform T dependence for all these PEO ionomers when the change in T_g is properly accounted for.

For the PEO-PTMO co-ionomers, the apparent LVE shift factors are separated into two regions by the glass transition of the PEO microdomain. The LVE reflects motion of both the PTMO and PEO segments at T higher than $T_{g,\text{PEO}}$, while the motion of PTMO segments coexists with immobile PEO segments below $T_{g,\text{PEO}}$. Here, the analysis on the reference samples is followed by defining $T'_r = T_r + (T_{g,\text{PEO}} - T_{g,0})$, where $T_{g,\text{PEO}}$ is the DSC glass transition temperature of PEO microdomains. In Figure 10b, the reduced apparent shift factors are compared as functions of $T - T'_r$ for the co-ionomers and the PEO reference ionomers. The temperature dependence for co-ionomers at $T > T_{g,\text{PEO}}$ agrees nicely with those of the PEO ionomers. This result strongly suggests that the LVE temperature dependence of the co-ionomers is governed by the PEO microdomain, which is reasonable since the PEO microdomain is always continuous and has $T_{g,\text{PEO}}$ more than 45 K larger than the $T_{g,\text{PTMO}}$ of the PTMO microdomains.

Nevertheless, the temperature dependence below $T_{g,\text{PEO}}$ becomes weaker than that expected from the Williams–Landel–Ferry (WLF) trend and appears to be nearly Arrhenius. This change may reflect motion of the PTMO segments confined by the coexisting glassy PEO microdomains. A similar T dependence has also been reported in several miscible polymer blends when one component is below its T_g .^{24,25}

3.4.3. Relaxation Time. The LVE master curves of the ionomers and co-ionomers shown in Figures 8 and 9 exhibit $G' \propto \omega^2$ and $G'' \propto \omega$ terminal tails at low ω , from which the terminal relaxation time can be evaluated as

$$\tau = \lim_{\omega \rightarrow 0} \left[\frac{G'}{\omega G''} \right] \quad (3)$$

The LVE study of PEO- and PTMO-based ionomers confirmed that the entanglements are not important for the LVE of the PEO and PTMO ionomers^{9,10} because their $M_n \leq 12\,000$. For nonentangled nonionic polymer chains, the Rouse relaxation time is $\tau_R = \tau_0 N^2$, where τ_0 is the segmental time and N is the number of segments.^{26,27} For ionomer chains, an additional activation energy E_a for ionic hopping leads to additional chain friction. The terminal relaxation time is expressed as

$$\tau = \tau_s N_s^2 = \tau_0 N_s^2 \exp\left(\frac{E_a}{kT}\right) = \tau_0 \left(\frac{M}{M_s}\right)^2 \exp\left(\frac{E_a}{kT}\right) \quad (4)$$

Here, τ_0 is the segmental time of a chain, E_a is an effective activation energy for ion hopping, and $N_s = M/M_s$ is the number of sticky Rouse segments per chain, with M_s the molecular weight of chain between two ionic groups. The power 2 on N_s is based on the sticky Rouse model with no entanglement effects.

For the samples used in this study, if only the T_g difference of the two microdomains is considered, the PEO microdomain would govern τ , since $T_{g,PEO}$ is much larger than $T_{g,PTMO}$. Nevertheless, the strong ionic aggregation in the PTMO microdomains must also be considered, which leads to a high activation energy for large-scale chain motion. To understand different contributions to the delay of the terminal relaxation, Figure 11 plots terminal relaxation time τ , multiplied by a factor $(M_r/M)^2$ to account for M difference ($M_r = 6000$ is a reference M), against $T - T_r'$ for reference PEO ionomers having (a) Na and (b) Li counterions. Since the T_g difference has been properly accounted for in T_r' , a difference $\tau(M_r/M)^2$ should reflect effects of N_s and E_a (see eq 4).

For either PEO-Li or PEO-Na, E_a should be similar. Then, the greater delay with increasing ion content is attributable to different numbers of sticky Rouse segments $N_s = M/M_s$ that increases with decreasing M_s (see Table 1 for M_s). The increase of $\tau(M_r/M)^2$ with decreasing M_s is stronger for Li than for Na, which is related to the detailed mechanism for ion hopping discussed in a future paper. (The effective time scale for ion pair hopping does depend not only on the time to escape from the cluster but also on the number of times the original cluster is revisited before the pair joins a new cluster and accordingly on the cluster-cluster separation distance which depends in a complex way on N_s .)

For comparison, the normalized terminal relaxation time $\tau(M_r/M)^2$ is plotted vs $T - T_r'$ for the co-ionomer samples in Figure 12. Since the PEO and PTMO diols have similar M and are joined by 100% sulfonated diester, M_s should be nearly the same for all the co-ionomers to give $N_s \sim M$. Thus, the different $\tau(M_r/M)^2$ for co-ionomers seems not attributable to a change of N_s . For the co-ionomers, there are three types of sticky points: ion aggregates in the PEO domain, in the PTMO domain, and near the interface. The ion aggregation is apparently strongest in the PTMO domain, making those ion pairs have the largest E_a and control the overall friction of the co-ionomer chain. In other words, the terminal relaxation time should be controlled by the number of ion pairs in the PTMO

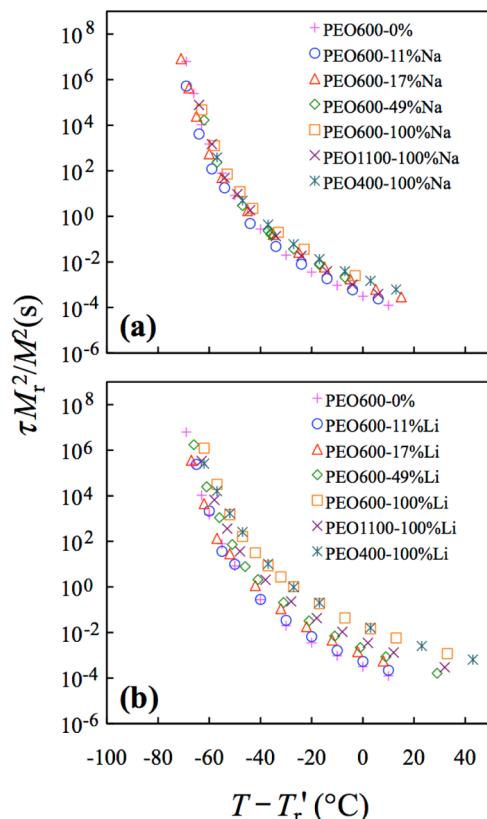


Figure 11. Terminal relaxation time τ multiplied by an M -correction factor M_r^2/M^2 based on the Rouse model and plotted against $T - T_r'$ for ionomers and co-ionomers with (a) Na and (b) Li counterions. T_r' is a shifted reference temperature that accounts for the T_g of the PEO domain.

domain, the strongest stickers (largest source of friction). In this sense, the delay with increasing PTMO content in Figure 12 is similar to the delay with increasing ion content.

In summary, although the introduction of low- T_g PTMO does not improve conductivity due to its relatively low ion solvating ability, it results in a remarkable improvement in mechanical performance due to the microdomain-separated structure as well as the strong cross-links formed by aggregation in the PTMO microdomains.

4. CONCLUSIONS

In this study, the LVE, FTIR, and conductivity of PEO-PTMO co-ionomers were analyzed. Relaxation of the co-ionomer chains is mainly governed by two dynamic aspects: (1) high segmental friction in the PEO microdomain and (2) extra activation energy arising from ionic dissociation in the PTMO microdomain.

A combination of LVE and FTIR measurements allows clarification of the residence and status of the ionic groups in the co-ionomers: (1) the ions near the interface bias toward the PEO microdomain, (2) the ions aggregate near the interface, with sheetlike structures for Li co-ionomers and stringlike structures for co-ionomers with Na counterions, (3) the conducting ions mainly reside in the PEO microdomain, and (4) the activation energy for terminal relaxation observed at high temperatures is determined by ions strongly aggregated in the PTMO microdomain.

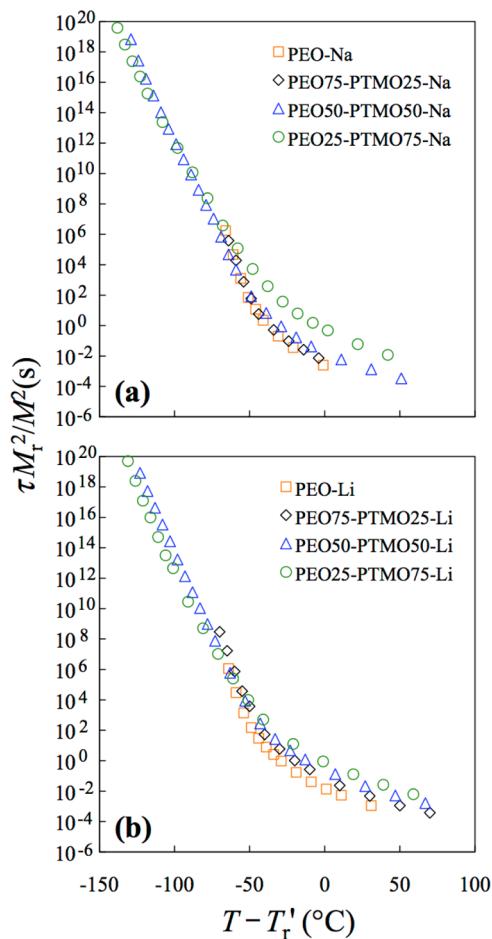


Figure 12. Terminal relaxation time multiplied by an M -correction factor of M_r^2/M^2 and plotted against $T - T_r'$ for ionomers and co-ionomers with (a) Na and (b) Li counterions. T_r' is a shifted reference temperature that accounts for the T_g of the PEO domain.

The introduction of low- T_g PTMO remarkably improves the mechanical performance due to the microdomain separated structure and the stronger ionic cross-links in the PTMO-rich domains. Particularly for Na counterions, the PTMO ionomer and the 75% PTMO co-ionomer have terminal relaxation greatly delayed, owing to strong ion associations in the PTMO domain, despite its lower T_g . The co-ionomer with 75% PTMO is rubbery near room temperature, with an extended plateau owing to the ionic cross-links in the PTMO-rich domains, yet maintains continuous PEO-rich domains for facile ion conduction. This study provides a new path for design of single-ion conducting polymer electrolytes with good mechanical performance.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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