Synthesis and Characterization of Poly(Ethylene Glycol)-Based Single-Ion Conductors

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A series of ionomers was synthesized by melt polycondensation of poly(ethylene glycol) (PEG) oligomers and dimethyl 5-sulfoisophthalate sodium salt. The molar mass of the PEG spacer was either 400, 600, or 900, and the cation was exchanged from sodium to lithium or cesium by dialysis. Since the anions are covalently attached to the ionomer chains and are essentially immobile relative to the cations, these ionomers are excellent models for polymeric single-ion electrolytes. The experimental evidence to date suggests that the cations do not aggregate to form the usual ion clusters seen in other ionomers. No relaxation time associated with ion clusters was observed in rheological measurements, nor was an "ionomer peak" observed in small-angle X-ray scattering measurements. The ionic conductivity increases significantly with increasing PEG spacer molecular weight, although the total cation content decreases at the same time. At room temperature, the highest conductivity (10^{-6} S/cm) was achieved for the sodium ionomer with PEG spacer $M_n = 900$, similar to other single-ion polymer electrolytes. The various ionomers, although with significantly different cation type and concentration, have almost the same ionic conductivity at the same temperature interval from the corresponding glass transition temperature. This strongly supports that ion migration in these ionomers is closely correlated with the segmental mobility of the polymer matrix.

1. Introduction

Poly(ethylene oxide) (PEO) has been extensively investigated as a candidate electrolyte for lithium rechargeable batteries due to its high solvating power for a variety of alkali and alkaline earth cations.[1,2] The cations diffuse through PEO (and other polymers) cooperatively with the matrix segmental relaxation, and this results in macroscopic ionic conductivity. Compared with traditional ceramic electrolytes, polymer electrolytes are relatively flexible and can be readily fabricated to different shapes for a variety of electrochemical applications. Flexible polymer electrolytes can also readily accommodate the volume change of the cell during charge–recharge cycling, avoiding physically disassembling the electrolyte–electrode interfacial contact. In addition, polymers can be easily cross-linked to make a solid with any desired modulus in the range 1–30 MPa, which effectively resolves the leakage problem encountered with solvent containing electrolytes[1,3] but is likely too small to prevent dendritic growth from the lithium electrode.

While most prior studies have been performed on solvent-free PEO/salt complexes, anions of the salt have very high mobility and aggregate over time at the cathode surface. This internal polarization arising from the ion concentration gradient significantly deteriorates cell performance. Hence, electrolytes in which the anions are covalently bound to the polymer chains (i.e., ionomers or single-ion conductors) are highly desirable.[1] Due to the size and relatively immobile nature of the polymer chains, only cations are able to migrate over long distances in the solid state on reasonable time scales, and a transference number of unity can be achieved.[1–4]

Single-ion polymer electrolytes have been prepared for the purpose of improving the conductivity and lifetime of lithium ion batteries.[5–11] For example, aluminosilicate/poly(ethylene glycol) (PEG) copolymers were synthesized by Rawsky et al. with sodium as the cations;[5] siloxyaluminate-Li+ polymers were reported by Fujinami et al.;[6] and polyanionic electrolytes with mono-oxalato-capped and mono-malonato-capped orthoborate structures were synthesized by Angell and co-workers.[7] More recently, Sun et al.[8] synthesized single-ion polymer conductors by grafting lithium bis(allylmalonato)-borate onto alkyl group-containing comb-branched polyacrylate or polymethacrylate ethers. Although these solvent-free electrolytes provide promising ionic conductivities (σ_0) ranging from 10^{-7} to 10^{-5} S/cm at ambient temperature, their

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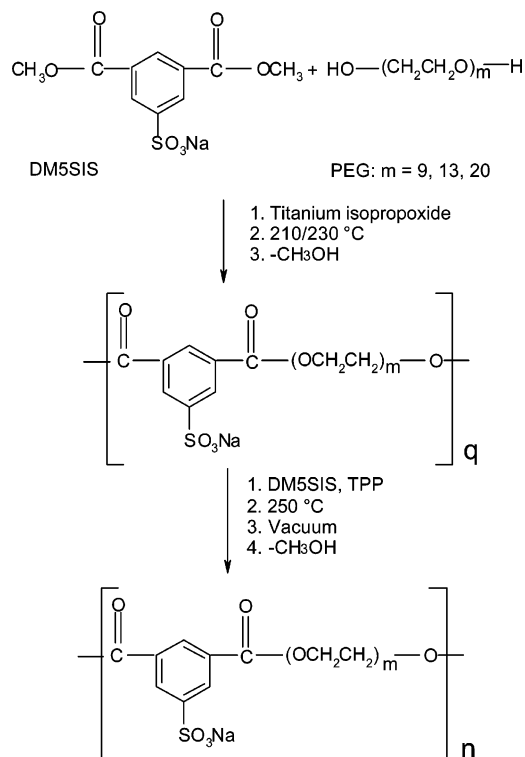
Figure 1. Schematic representation of the PEG ionomer synthesis.

synthesis usually involves multistep reactions and purifications. Moreover, the polymer chain structures and molecular weights have often not been clearly defined.

In the present study, we synthesize a series of single-ion conducting ionomers by a two-step melt condensation between PEG and dimethyl 5-sulfoisophthalate sodium salt. The sodium was easily converted to lithium or cesium by dialysis after exposure to an excess of LiCl or CsCl. Initial experiments demonstrate that these ionomers provide reasonable ionic conductivities at room temperature. A second publication describes the quantification of the free ion mobility and concentration in these ionomers, using the phenomenon of electrode polarization.[12]

2. Experimental Section

2.1. Materials. The reagents used for ionomer synthesis in this study are commercially available. Poly(ethylene glycol) 400 (PEG400, M_n = 400 g/mol), poly(ethylene glycol) 600 (PEG600, M_n = 600 g/mol), triphenyl phosphate (TPP, 97%), titanium (IV) isopropoxide (99.999%), lithium chloride (99+ %), and dimethyl isophthalate (DMI, 99%) were supplied by Aldrich. Poly(ethylene glycol) 900 (PEG900, M_n = 900 g/mol) was purchased from Fluka Chemie GmbH. Dimethyl 5-sulfoisophthalate sodium salt (DM5SIS, 98%) and cesium chloride (optical grade, 99.99%) were supplied by Alfa Aesar and ICN Biomedicals, Inc., respectively. All reagents were used without further purification.

2.2. Synthesis. The preparation of the polyester ionomers was carried out by a two-step catalyzed melt transesterification (see Figure 1). A glass reactor was charged with the appropriate amounts of the oligomeric diol, DM5SIS (PEG/DM5SIS = 1:0.9 molar ratio), and the catalyst, titanium (IV) isopropoxide (0.05 wt %), and were maintained under an argon atmosphere. The mixture was

stirred mechanically, and the temperature of the reaction was maintained at 210 °C for 4 h and then at 230 °C for 2 h. The byproduct methanol was removed using a cold trap. Second, DM5SIS (10 mol % of PEG400) and triphenyl phosphate (0.05 wt % of total reagents) were added and the reaction temperature was raised to 250 °C and maintained for 2−3 h. The total molar ratio of diol/DM5SIS was controlled at 1:1. Vacuum (100 mtorr) was applied for the final 0.5−1 h at 250 °C to remove low molecular weight species. The completion of the reaction was signaled by a rapid increase in the viscosity, at which point the reactor was refilled with argon gas and cooled to room temperature. Neutral polymers were prepared in the same manner, replacing DM5SIS with DMI.

2.3. Diafiltration and Ion Exchange. The sodium polyester ionomer was dissolved in water and then diafiltered with deionized water using a 1000/3000 molecular weight cutoff membrane (Amicon). This ionomer was then dissolved in 0.5 M LiCl/H$_2$O (or 0.5 M CsCl/H$_2$O) and diafiltered to prepare lithium or cesium ionomers. Diafiltration was considered complete when the dialyzate exhibited a constant conductivity. The concentrated ionomer solution was freeze-dried and then vacuum-dried at 120 °C to constant mass. The ionomers in this paper are identified as PEy-M, where y is the molecular weight of the PEG oligomer used in the synthesis and M represents the type of cation (Li, Na, or Cs). The neutral polymers are denoted PEy-0.

2.4. ^{1}H NMR. ^{1}H NMR spectra were acquired on a DPX-300 spectrometer with perdeuterated dimethyl sulfoxide as the solvent. The spectra were used to verify the polyester ionomer structure and to determine the number-average molar mass (M_n) as all samples have M_n < 10 000, most likely due to hydrolysis during the diafiltration stage of sample preparation.

2.5. Rheology. Dynamic modulus and viscosity were measured using a Rheometric Scientific ARES rheometer with 7.9 mm diameter parallel plates for $T > T_g + 20$ K and with 4.0 mm diameter plates for temperatures near T_g. The ionomers were loaded directly into the instrument and then pressed between two parallel plates to the required geometry, at a temperature $T - T_g = 60$ K. Temperature stability was better than ±0.1 °C. Strain sweeps were used to ensure that the reported data represented a linear response.

2.6. X-ray Scattering. Small-angle X-ray scattering (SAXS) measurements were performed using a Molecular Metrology instrument equipped with a Cu target ($\lambda = 1.542$ Å) and a two-dimensional area proportional counter. Typical specimen count times were on the order of 3 h. Wide-angle X-ray diffraction (WAXD) data were collected using a Scintag diffractometer with a wavelength of 1.542 Å.

2.7. Thermal Characterization. Glass transition temperatures (T_g) were determined using a TA Q100 differential scanning calorimeter (DSC). Sample sizes were ∼15 mg. All samples were held at 120 °C for 3 min, and then cooled to −90 °C at 20 °C/min. After soaking at the lowest temperature for 5 min, samples were heated to 200 °C at 10 °C/min. T_g was defined as the midpoint of the heat capacity transition. A TA Q600 thermogravimetric analyzer (TGA) was used to examine the thermal stability.

2.8. Conductivity Measurement. Void-free ionomers were sandwiched between two round gold-sputtered stainless steel electrodes, and the thickness was controlled by 0.2 mm Teflon spacers. A Novocontrol GmbH Concept 40 broadband dielectric (impedance) spectrometer was used to measure the ionic conductivity (σ_0, in siemens per centimeter). An AC voltage amplitude of 0.5 V was used for all experiments. Frequency sweeps were performed isothermally from 10 MHz to 0.01 Hz in the temperature range from 120 °C to the corresponding T_g. Temperature stability during data acquisition was better than ±0.1 °C.

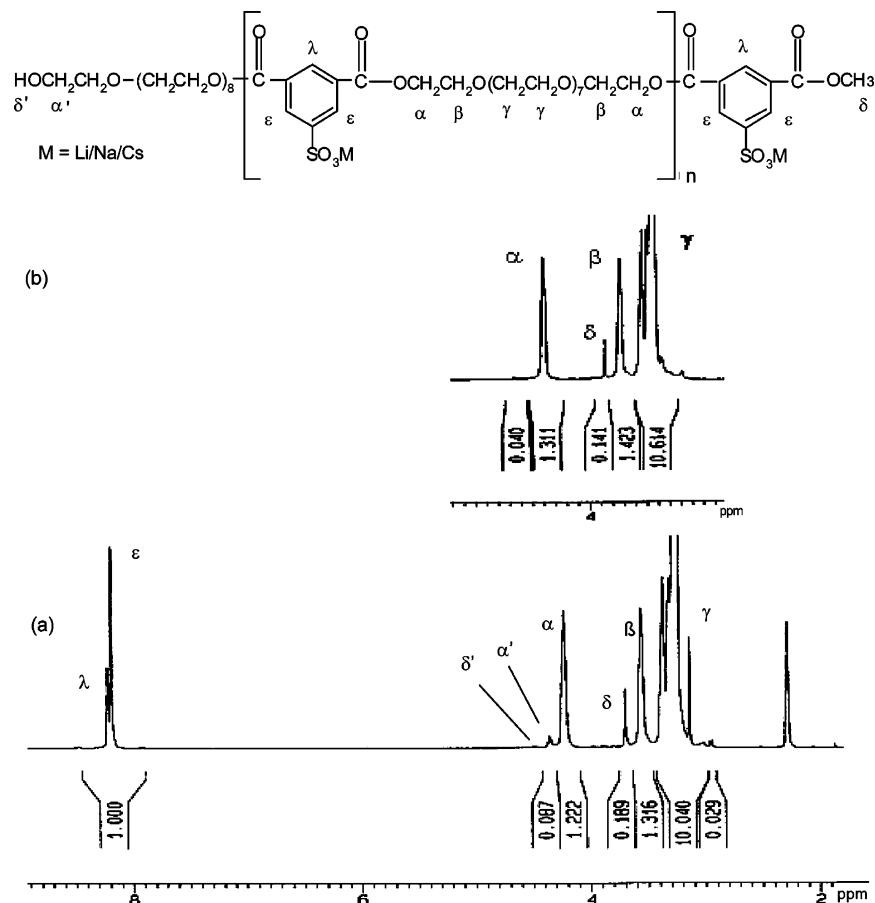(12) Klein, R. J.; Zhang, S.; Dou, S.; Jones, B. H.; Colby, R. H.; Runt, J. *J. Chem. Phys.* **2006**, *124*, 144903.

Figure 2. Representative ^1H NMR spectra of two PE400-Na ionomers: (a) PE400-Na [M_n = 4200] and (b) PE400-Na-hmw [M_n = 6700].

3. Results and Discussion

3.1. Ionomer Chain Characterization. Figure 2 shows the ^1H NMR peak assignments for two PE400-M ionomers with different molecular weights. The two peaks at ~8.2 ppm are assigned to the adsorption of aromatic protons λ and ϵ. The peaks of the α protons at 4.2 ppm and those of the β protons at 3.5 ppm are separated from those of other protons, reflecting the interactions between the carbonyl group and the OCH$_2$CH$_2$ repeat unit at the ends of the of the PEG400 segments. The chemical shifts at 4.5 and 3.7 ppm correspond to OH (δ') and OCH$_3$ (δ) groups at the chain ends, respectively. The peak at 4.35 ppm corresponds to the CH$_2$ (α') connected to the hydroxyl group at the chain ends. The more complicated chemical shifts around 3.3 ppm are assigned to the adsorption of the other protons (γ) in the PEG400 segments.

There are three aromatic protons (λ and ϵ) in the phenyl ring, and four protons in two OCH$_2$ (α) groups connected to two carbonyl groups in one repeat unit. Provided that the end groups are CH$_2$OH (α') and OCH$_3$ (δ), degrees of polymerization (n) can be calculated from the ratio of monomers and end groups

$$n = \frac{(I_{(\lambda+\epsilon)}/3) + (I_\alpha/4)}{(I_{\alpha'}/2) + (I_\delta/3)}$$

where I_i is the integrated intensity of the i protons, with $i = \lambda + \epsilon$ denoting the sum of the λ and ϵ peaks. The degree of polymerization of the PE400-Na-hmw (hmw indicates a

higher molecular weight than the samples in Table 1) in Figure 2b (n = 10; M_n = 6700) is significantly higher than that of PE400-Na in Figure 2a (n = 6; M_n = 4200).

The results of the TGA experiments demonstrate that there is essentially no weight loss below 160 °C in air for any of the ionomers under investigation here. When N$_2$ was used as the purge gas, PE600-Li did not exhibit any detectable weight loss until 270 °C, suggesting that thermal oxidation is the most important degradation mechanism. The weight fraction of residual mass after heating to 800 °C is provided in Table 1. It is evident that more mass remains for ionomers with shorter PEG spacers and with heavier cations, suggesting that the final residue is likely the SO$_4^{2-}$ or SO$_3^{2-}$ salt of the corresponding cation. The estimated cation concentrations, assuming that the final product is M$_2$SO$_4$, are provided in Table 1. These values are very close to those calculated based on the theoretical stoichiometry.

3.2. X-ray Scattering. Figure 3 presents the combined small- and wide-angle scattering of the PE400-Na, PE600-Na, and PE900-Na ionomers and the neutral polymer PE400-0. All four polymers exhibit a single peak in the WAXD region, associated with the amorphous halo of PEO. There are no peaks originating from the small-angle scattering from ion clusters, in contrast with many previous studies of conventional ionomers.[13-16] On the basis of our charge

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Table 1. Characterization of PEG-Based Ionomers

	$M_n{}^a$	$T_g{}^b$ (K)	σ_0 at 25 °C (S/cm)	TGA residual[c] (wt %)	cation conc[d] (wt %)	theoretical conc (wt %)
PE400-0	4400	N/A[e]	2.90×10^{-13}	0	0	0
PE400-Li	4100	285	1.65×10^{-10}	8.3	1.1	1.1
PE400-Na	4200	295	1.14×10^{-11}	10.4	3.4	3.6
PE400-Cs	4900	294	1.68×10^{-10}	22.6	16.6	17.9
PE600-Li	4700	258	2.69×10^{-8}	6.7	0.88	0.85
PE600-Na	4700	267	9.10×10^{-9}	9.6	3.1	2.8
PE600-Cs	5300	270	1.24×10^{-8}	15.2	11.2	14.1
PE600-Na($^1/_2$)	6800	242	3.58×10^{-7}			
PE900-Li	5400	236	6.27×10^{-7}	4.0	0.51	0.6
PE900-Na	5400	236	1.07×10^{-6}	5.4	1.8	2.0
PE900-Cs	5900	238	1.56×10^{-6}	11.1	8.2	10.7

[a] The number-average molecular weight (M_n) was determined by ^{1}H NMR. [b] T_g was measured by DSC. [c] Residual mass after heating to 800 °C. [d] The derived cation concentration, assuming the final residual is M_2SO_4. [e] This polymer is highly crystalline, and a T_g could not be detected by DSC, even after quenching into liquid N_2.
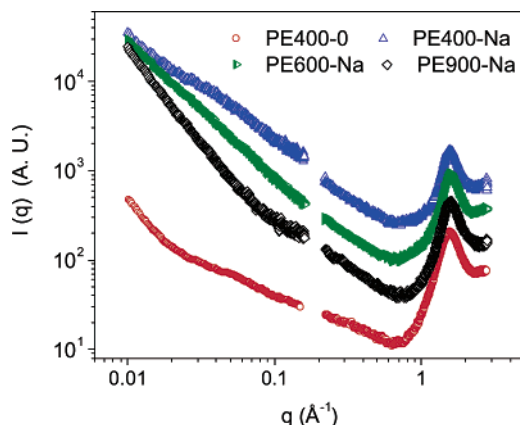

Figure 3. Combined SAXS and WAXD intensities (arbitrary units and offset for clarity) as a function of the scattering vector for PE400-Na, PE600-Na, and PE900-Na ionomers and the PE400-0 neutral polymer. Note that both the intensity and wavevector are plotted on logarithmic scales.

densities, we would expect to see a strong peak[16] near wavevector $q = 0.1$ Å^{-1}, but no peak is seen. There is considerable extra scattering at low wavevectors in the ionomers, compared with PE400-0, which may indicate some interesting new structure for the ions in our ionomers, but that structure remains unidentified at present.

3.3. Rheological Properties. Figure 4 shows a master curve of the storage and loss moduli of a particularly high molar mass PE600-Na-hmw ($M_n = 8900$). The ionomer chains are weakly entangled (the entanglement molar mass of poly(ethylene oxide)[17] is $M_e = 2000$, but the ionomers with their bulky isophthalate group may have considerably larger M_e values). A clear relaxation of ionic aggregates is observed in conventional ionomers,[18,19] but this relaxation is not evident in Figure 4. PE600-Na shows interesting viscoelastic response between the glassy modulus (at the highest frequencies in Figure 4) and the terminal response at the lowest frequencies, but no strong relaxation at intermediate frequencies is observed. Recently, Han et al.[20]

reported a clear ion-aggregate relaxation in their oscillatory shear data for a sulfonated polyester ionomer made from DM5SIS. Consequently, we expect that the very different aggregate structure of our ionomers, seen in both SAXS and rheology, is caused by the ether oxygens of the PEO segments stabilizing the ions. The dielectric constant of the polymers is still low (roughly 12), so the ions are expected to be mostly paired (our dielectric analysis[12] suggests that the ions are more than 99.99% paired); however, those pairs are stabilized by the ether oxygens and consequently do not microphase separate to form the large ionic aggregates that characterize most ionomers.

3.4. Thermal Properties. All of our ionomers exhibit a single T_g in DSC. For those with the same cation, T_g decreases rapidly with increasing PEG spacer length (Table 1). T_g values of the PE400 ionomers generally reside around 285−295 K, resulting in high viscosity liquids ($\eta \sim 10^7$ Pa s) at room temperature. Those with PE600 spacers exhibit 258 K $\leq T_g \leq$ 270 K and have lower viscosities at room temperature ($\eta \sim 10^5$ Pa s). The PE900 ionomers have 236 K $\leq T_g \leq$ 238 K and are pourable liquids at ambient temperature ($\eta \sim 10^2$ Pa s). No clear dependence on cation type can be discerned.

It is worth pointing out that although similar single T_g behavior has also been observed for other single-ion ionomers, two glass transitions have been reported for the complex of LiClO$_4$ with poly(propylene oxide), arising from the coexistence of ion-rich and ion-poor domains.[21−23] Clearly, similar ion clusters do not exist in the present ionomers, based on the results of the rheological, thermal, and X-ray scattering measurements.

Figure 5 displays a comparison of T_g for the Na$^+$ single-ion conductors prepared in the present study with values reported previously for PEO with NaClO$_4$ and NaCF$_3$SO$_3$.[23] Although similar at low Na$^+$ content, the concentration dependences of T_g are markedly different, with a much larger T_g for our PEG ionomers at a given Na$^+$ content. The stronger concentration dependence of T_g for the ionomers is

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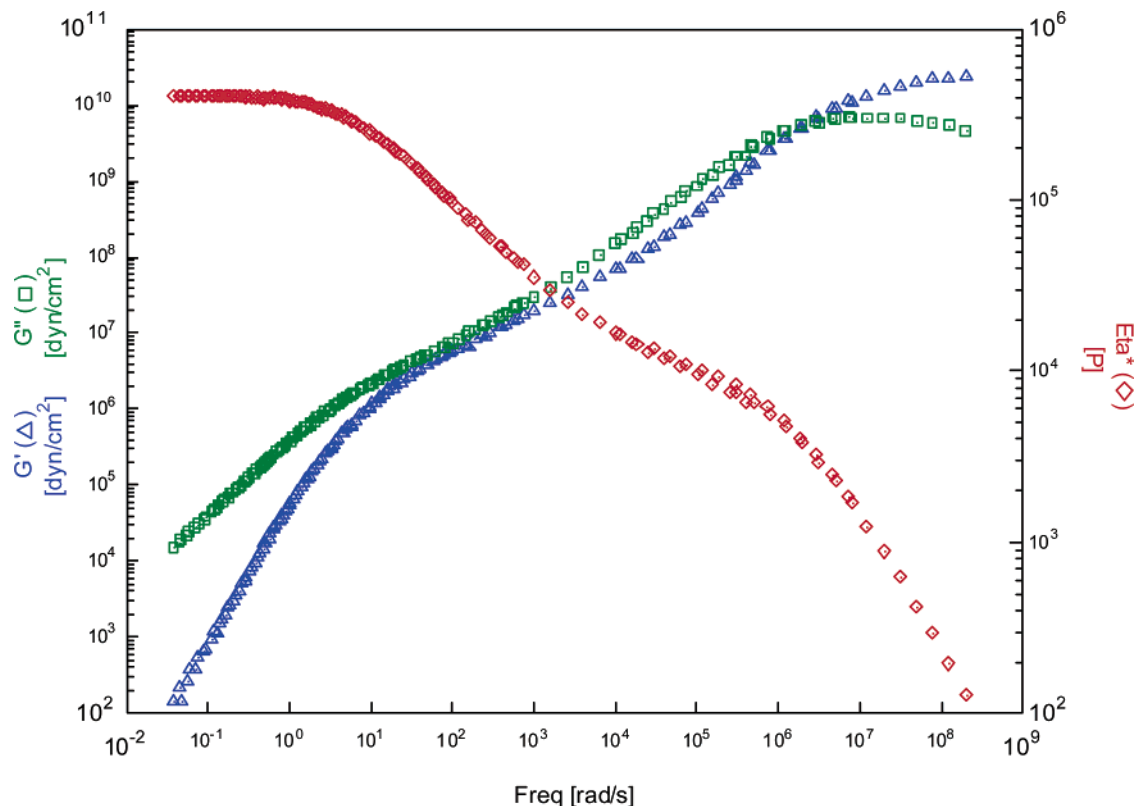
Figure 4. Master curves of the storage modulus (triangles), loss modulus (squares), and complex viscosity (diamonds) at $T_{ref} = 30.0$ °C for PE600-Na-hmw ($M_n = 8900$ g/mol) based on data at temperatures 0, 5, 10, 20, 30, 40, 50 and 60 °C.
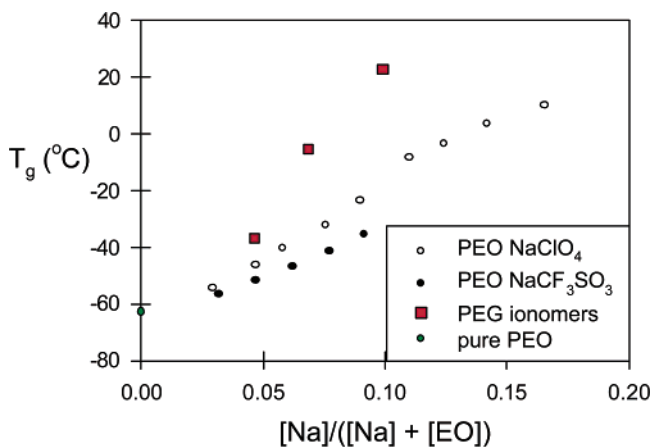

Figure 5. Comparison of measured T_g of PE-Na ionomers with reported values for PEO complexes with NaClO$_4$ and NaCF$_3$SO$_3$ (from ref 23), as a function of Na content.

a telltale mark of what Eisenberg calls the "ionomer effect" and is usually associated with the presence of ionic domains in the ionomers.[16] Indeed, the slope in Figure 5 of 8 K/mol % is considerably larger than the 1 K/mol % reported for other polyester ionomers made from sulfonated isophthalate.[24] There is no evidence of ion-cluster formation in either our PEG-based ionomers or the PEO/salt mixtures in ref 23. However, the nature of the salts in the three systems is quite different and we do not have enough information at this juncture to explain the relative changes in segmental motion in these systems.

While most of the ionomers under investigation here are amorphous at room temperature, PE900-Li is in fact semi-

crystalline. DSC reveals a weak melting process at 27 °C with an enthalpy (ΔH_m) of 2.4 J/g. On the basis of a perfect crystal heat of fusion of PEO of 203 J/g,[25] this represents a degree of crystallinity of only ~1%. After holding at 10 °C for 30 min, a significant amount of the PE900-Li crystallizes and the crystal phase melts at 28 °C with $\Delta H_m = 35$ J/g (~17% PEO crystallinity). At the same time, T_g increases from −37 to −27 °C after crystallization. No crystallization is observed for PE900-Na and PE900-Cs under the same annealing conditions.

3.5. Ionic Conductivity. The dielectric loss spectrum in the frequency domain shows a rapid increase in ϵ'' at low frequencies, as a consequence of direct current (dc) conduction (Figure 6). The ionic conductivity σ_0 (S/cm) can be obtained by fitting $\epsilon'' = \sigma_0/\epsilon_{Vac}\omega$, in which ϵ_{Vac} is the vacuum permittivity and ω is the angular frequency. A slope of −1 should be observed in the logarithmic plot of ϵ'' vs ω if the conduction is dominated by contributions from ion drift. However, dipolar polarization from the ionomer dominates at higher frequencies and electrode polarization (i.e., the accumulation of cations at the electrode/electrolyte interface) inhibits ion migration at lower frequencies. Reliable conductivities can be obtained by limiting the fitting to the frequency range where a slope of −1 is observed (10−10^4 Hz in Figure 6).

The complex conductivity $\sigma^* = \sigma' + i\sigma''$ is related to the complex permittivity ϵ^* by $\epsilon'' = \sigma'/\omega$ and $\epsilon' = \sigma''/\omega$. Therefore, the conductivity σ_0 can also be assessed from the plateau value of the real part of conduction spectra (Figure

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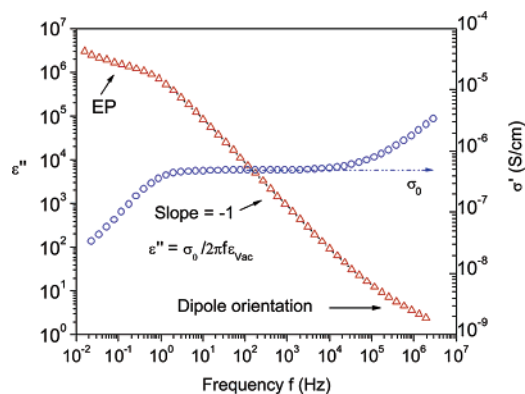
Figure 6. Dielectric loss and conductivity of PE600-Li at 50 °C. Circles represent σ', and triangles are ϵ''. The dc conductivity σ_0 is determined from the plateau in σ'.

6). The dielectric loss ϵ'' is preferable, since the dynamics of the ionomer chain can be simultaneously obtained to explore the fundamental correlation between ion migration and segmental relaxation.[26,27] Conductivities at 25.0 °C are reported in Table 1.

PE900-Li is semicrystalline, having a melting temperature slightly above ambient. Continued crystallization with time leads to a dramatic reduction in σ_0. Immediately after cooling from the melt, PE900-Li has a conductivity of 6.3×10^{-7} S/cm at 25 °C. However, after aging under ambient conditions overnight inside the dielectric sample holder, σ_0 decreases to 1.2×10^{-8} S/cm at 23 °C, a reduction by a factor of 50X.

Although the isothermal conductivity only weakly depends on cation type for ionomers synthesized from the same PEG, it increases significantly with increasing PEG spacer length. For the lithium ionomers, σ_0 at room temperature is raised from 1.7×10^{-10} to 7.7×10^{-8} and, then, to 6.3×10^{-7} S/cm when the PEG400 spacer is changed to PEG600 and PEG900, respectively. The dramatic increase in σ_0 is also observed at other temperatures (Figure 7), although the differences diminish as the temperature is raised. Similar behavior is also observed for the sodium and cesium ionomers. A room temperature conductivity of $\sim10^{-6}$ S/cm can be achieved for the ionomers with PEG900 spacers, close to the performance reported for other solvent-free single-ion conductors. The conductivity increases to $10^{-5}-10^{-4}$ S/cm at 80 °C.

The strong dependence of isothermal conductivity on PEG spacer length suggests that the matrix T_g plays a critical role in ion migration.[27] To examine this, Figure 8 compares the conductivities as a function of $T - T_g$. It is immediately evident that all three lithium ionomers (Figure 8a) have essentially the same σ_0 at the same $T - T_g$. As discussed above, the low σ_0 of PE900-Li at low temperatures is simply a result of partial crystallization. The Na and Cs ionomers with PEG600 and PEG900 segments have nearly the same ionic conductivity at a given $T - T_g$, although those prepared with PEG400 have slightly ($\sim$3X) higher conductivity, which likely results from their higher ion concentrations. The

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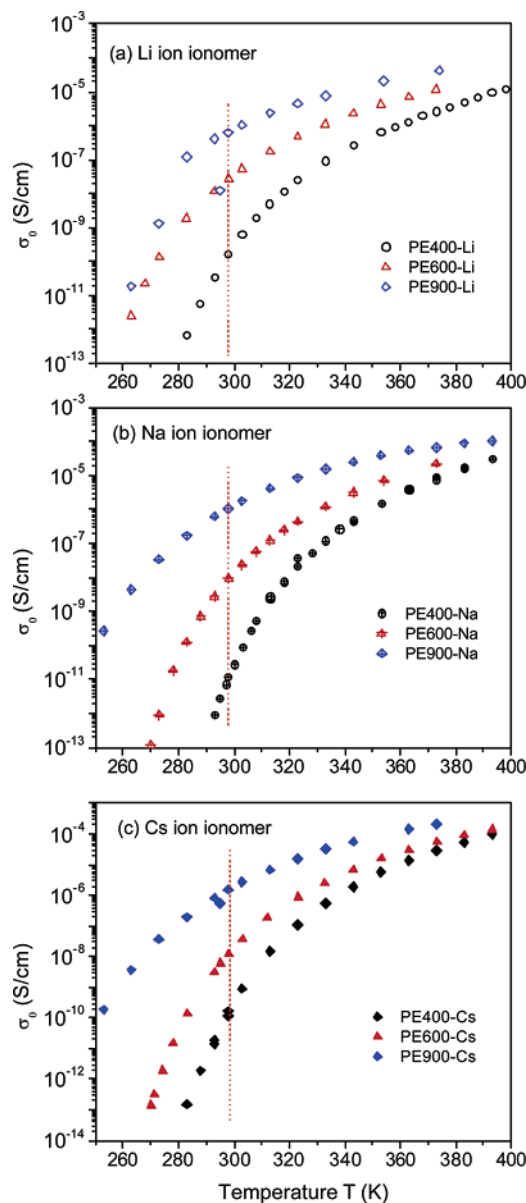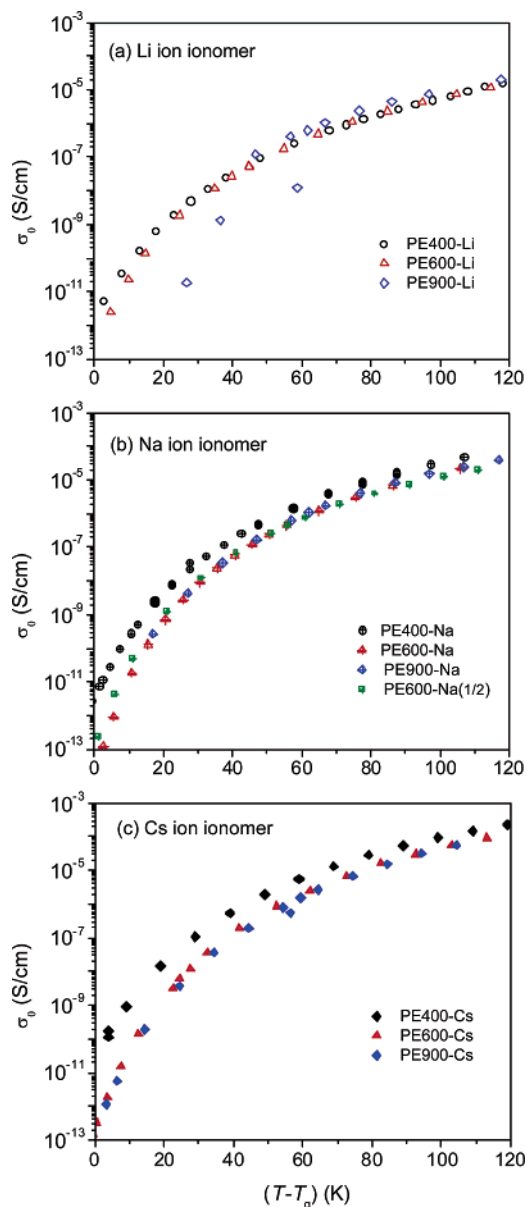(27) Zhang, S.; Dou, S.; Colby, R. H.; Runt, J. *J. Noncryst. Solids* **2005**, *351*, 2825.

Figure 7. Temperature dependence of conductivity for ionomers made from different PEG spacer lengths. A longer spacer length raises the conductivity by lowering T_g.

independence of σ_0 from the molar mass of the precursor PEG oligomer suggests that not all cations are dissociated from the sulfonate anions and that there is significant ion pairing, which reduces the effective mobile ion concentration. In fact, we demonstrate in a recent publication on these same ionomers that the fraction of mobile ions in these materials is remarkably low (e.g., <0.004% of the total Li content in PE600-Li at 20 °C).[12]

To further examine the T_g effect, PE600-Na($^1/_2$) was synthesized from PEG600 with a 50/50 mixture of dimethyl 5-sulfoisophthalate sodium salt and dimethyl isophthalate. This polymer is similar to the PE600-Na ionomer, but with significantly lower Na content, and thus less dense coordination between the alkali ions and oxygens. Consequently, its T_g is 25 K lower than that of PE600-Na. Despite its much lower Na concentration, PE600-Na($^1/_2$) has substantially higher conductivity than PE600-Na, and the difference becomes more significant as temperature decreases. The σ_0

Figure 8. Conductivity as a function of $T - T_g$. Ionomers with the same cation have similar σ_0 at constant values of $T - T_g$.

Figure 9. Correlation of ionomer T_g with their 25 °C conductivity. The value of σ_0 increases significantly with decreasing ionomer T_g.

value of PE600-Na($^1/_2$) at 25 °C is ∼30 times higher than that of PE600-Na.

Figure 9 displays the strong correlation between conductivity at 25 °C and the T_g of PEO-based ionomers. Here, σ_0 exhibits a clear increase with decreasing T_g. The T_g of ionomers bearing the same cation decreases by ∼45 K when the spacer is changed from PEG400 to PEG900, leading to a 10^4 increase in σ_0 at 25 °C. Extrapolation of the data in Figure 9 to the glass transition of PEO suggests an upper bound for the 25 °C conductivity of PEO-based ionomers of order 10^{-4} S/cm, if crystallization could be avoided at low ion content.

The strong correlation between ionic conductivity and the matrix T_g supports the mechanism that ion migration is realized through cooperative polymer segmental relaxation[26,27] and suggests that the ionic conductivity can be improved by decreasing the T_g of the ionomers. Although this can be achieved by increasing the PEG spacer molecular weight, unfortunately, ionomers with longer PEG oligomers
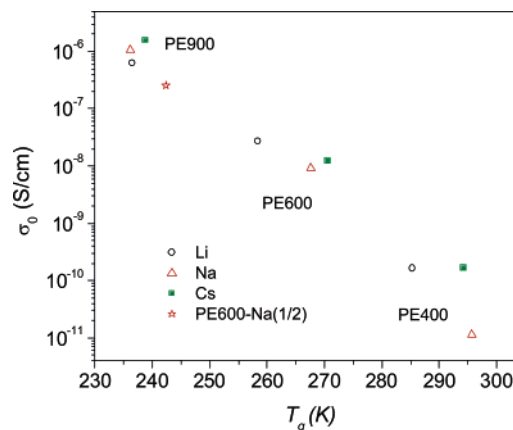
are semicrystalline materials. Plasticization of these ionomers with low volatility high dielectric constant liquids can more significantly decrease T_g, while also avoiding crystallization. In initial experiments, we observed a 1000X increase in σ_0 by adding 20% amorphous PEG400 oligomer to the PE400-Li ionomer.[27]

For the ionomers synthesized here, the molar ratios of EO to Li are 8.7, 13.2, and 20.0 for PE400-Li, PE600-Li, and PE900-Li, respectively. Their conductivities are comparable to other polymer single-ion conductors with similar PEG spacer lengths but are significantly lower than that of the P(EO)$_{10}$−LiN(SO$_2$CF$_3$)$_2$ electrolyte reported by Armand et al.[28,29] However, anions contribute most of the measured conduction in the latter and the lithium transference number is of order 0.3.

4. Summary

Inexpensive ionomers incorporating Na, Li, and Cs cations were synthesized by a two-step melt condensation of PEG oligomers and dimethyl 5-sulfoisophthalate sodium salt. Their chemical structures and molecular weights were characterized by ^{1}H NMR. Cation concentrations were estimated using a TGA procedure, and the results were consistent with the polymerization feed ratio. No scattering peaks associated with ion clusters were observed in SAXS and WAXD experiments. Time−temperature superposition can be successfully applied to the storage and loss moduli for all of our ionomers, but there is no obvious ion domain relaxation present. The glass transition temperature is strongly dependent on ion content, despite the fact that the conventional ion domains are not observed in either SAXS or rheology. This suggests that the ether oxygens may prevent microphase separation of the ion pairs from the polymer chains.

The ionic conductivity exhibits a strong dependence on ionomer T_g. At constant temperature, cations are more mobile in low-T_g systems and, therefore, higher conductivity results, even though the cation content is lower. Consistent with the

(28) Armand, M.; Gorecki, W.; Andreani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: London and New York, 1990; p 91.
(29) Mao, G.; Saboungi, M.-L.; Price, D. L.; Armand, M. B.; Howells, W. S. *Phys. Rev. Lett.* **2000**, *84*, 5536.

change in T_g, PE900 ionomers have conductivities significantly higher than the PE600 and PE400 ionomers. By normalizing temperature with the corresponding T_g, different ionomers have similar conductivity at the same $T - T_g$ without significant dependence on cation content. This supports the correlation between polymer segmental motion and ion mobility[27] in these ionomeric single-ion conductors.

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