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Ion Conduction in Poly(ethylene oxide) Ionically Assembled Complexes

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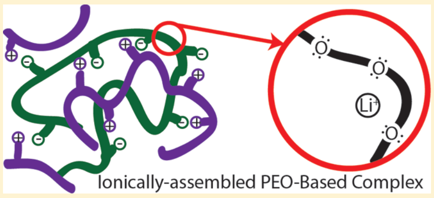
S *Supporting Information*

ABSTRACT: We report on relationships between conductivity and materials properties in novel complexes comprised of positively and negatively charged PEO-containing ionomers, where oppositely charged poly(ethylene oxide) (PEO) ionomers were blended with lithium salt to form a new class of PEO-based ionically associated complexes. The complexes were evaluated as potential solid polymer electrolytes using differential scanning calorimetry, impedance spectroscopy, tensile testing, and infrared spectroscopy. Under all salt concentrations investigated, the PEO complexes were amorphous and their glass transition temperatures increased with salt concentration. The glass transition temperature of the complex was elevated relative to the homopolymers, indicating a strong electrostatic interaction between the oppositely charged PEO ionomers. The maximum conductivity was 3.7 × 10^{-6} S cm^{-1} at 105 °C for an EO:Li^+ ratio of 40:1. As salt concentration further increased, ionic conductivity decreased due to an increase in glass transition temperature of the salt-doped complex and a decrease in free salt ions. These complexes present a new concept to control glass transition temperature, conductivity, and segmental relaxation in solid-state polymer electrolytes while maintaining robust mechanical properties compared to homopolymer PEO.



INTRODUCTION

Solid polymer electrolytes are potentially safer alternatives to liquid electrolytes for Li-ion batteries. For example, overheating can lead to exothermic decomposition of liquid electrolyte, ending in thermal runaway, pressure buildup, and explosion.[1−3] On the other hand, solid polymer electrolytes are less flammable than liquid electrolytes and can resist Li dendrite formation. Despite their advantages in safety, solid polymer electrolytes are challenged by their low conductivity. Here, we report new poly(ethylene oxide) (PEO)-based ionomer complexes and determine how the added salt concentration, ion-pairing, and matrix mobility influence their ionic conductivity.

Poly(ethylene oxide) (PEO) is a widely explored solid polymer electrolyte,[4−11] having advantages of chemical stability, electrochemical stability, and ability to solvate a variety of alkali metal salts. Generally, when a lithium salt is dissolved in a PEO matrix, Li^+ ions coordinate with ether oxygen (EO) groups. Ion conduction occurs through a segmental motion, where ions solvated by EO groups are transported through the segmental motion of polymer chains.[8,9] In this case, ion mobility (μ) is coupled with polymer segmental mobility, and ionic conductivity (σ) and mobility are related via

$$\sigma = \sum_{i=1}^{n} c_i \mu_i |q_i| \qquad (1)$$

where c_i and $|q_i|$ are the effective concentration and magnitude of the charge of carrier i. Polymer segmental mobility, and thus ionic conductivity, increases as the glass transition temperature (T_g) of the polymer decreases. The effective ion concentration is related to the fraction of ions that are mobile and contribute to the material's ionic conductivity. Ions may exist freely or as contact ion pairs, triple ions, and other combinations, of which free ions are considered the most mobile. Ideally, a solid polymer electrolyte would possess a low T_g and have a large number of freely moving ions. The fraction of "spectroscopically free" ions, which includes both free ions and separated ion pairs, can be characterized using Fourier transform spectroscopy, for example.[12]

Crystallization in PEO is generally viewed as detrimental to ionic conductivity because crystals impede segmental relaxation. However, it should be noted that under certain conditions conductivity of crystalline PEO exceeds that of amorphous PEO.[11] In most other cases, however, PEO-based electrolytes often have high degrees of crystallization and offer very low ionic conductivity at room temperature ($\sigma = 10^{-8}-10^{-7}$ S cm^{-1} for $LiClO_4-PEO$),[13] limiting their potential for practical applications. Many research efforts have targeted minimizing crystallization and increasing the ionic conductivity at ambient temperature. Adding a low-molecular-weight oligomer is one common approach to combating crystallinity and raising conductivity in PEO-based systems. For example, low-molecular-weight

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poly(ethylene glycol) (PEG) was added to PEO−$LiCF_3SO_3$ complexes, and the added plasticizer reduced crystallinity and increased free volume, both of which contributed to a higher conductivity.[14,15] Another common strategy to improve ionic conductivity is to incorporate liquid plasticizers/solvents into the polymer matrix, creating a polymer gel electrolyte.[8,9,11,15] However, the addition of plasticizers tends to sacrifice the mechanical properties of the polymer electrolyte and can lead to flammability and safety issues.

Other approaches to creating new polymer electrolytes have included fabricating nanocomposites and synthesizing block copolymers with the intent to boost conductivity and mechanical properties of PEO-based materials. A recent method to improve the ionic conductivity of PEO-based materials is to incorporate nano/microsized ceramic fillers, such as ZrO_2,[16] TiO_2,[17,18] Al_2O_3,[17] SiO_2,[19] and clays into composite polymer electrolytes.[20] The rationale behind this approach is that ceramic nano/microparticles increase mechanical stability and electrode/electrolyte compatibility.[21] A different approach targets block copolymers containing soft and hard phases.[22−25] These tailored macromolecules have soft and hard phases that are optimized to promote both ionic conductivity and mechanical stability, respectively.

One particularly promising route to obtaining completely amorphous, solvent-free solid polymer electrolytes is to use noncovalent interactions to prevent PEO crystallization. For example, PEO and poly(acrylic acid) (PAA) have been studied as hydrogen-bonded complexes[26] and multilayers;[27,28] the proton donated from PAA is accepted by the EO unit, and an amorphous ion-conducting material is obtained. Unfortunately this approach has numerous challenges: (i) PAA dilutes ion-conducting PEO, (ii) hydrogen bonding elevates matrix T_g value above room temperature and competes with Li^+ ions for EO occupancy, and (iii) the resulting segmental motion of the matrix complex is low.

Prior work elsewhere focused on homopolymer PEO ionomers, mainly as single-ion conductors.[12,29−32] Li^+ ions were the mobile species, and the anion was tethered to the polymer chain to achieve near-unity Li^+ transference numbers. Ionic conductivity of the PEO ionomer increased as the PEO spacer molecular weight increased; however, PEO ionomers with PEO spacers of 900 g mol^{-1} or greater were semicrystalline at room temperature.[29,32] In these types of materials, only a small fraction of ions were mobile (measured using electrode polarization), whereas the majority of ions were occupied in immobile ion aggregates or ion pairs.[12,30]

Our current approach focuses on electrostatic interactions instead of hydrogen bonding to form low-T_g PEO-based amorphous complexes with mechanical properties superior to homopolymer PEO. Specifically, we report on relationships between conductivity and materials properties in novel complexes comprised of positively and negatively charged PEO-containing ionomers (PEO^+ and PEO^-, respectively) (see Figure 1). Each PEO ionomer consists of EO blocks interspersed with pendant functional groups bearing positive or negative charge. The complex forms a cohesive network without occupying EO units (as a hydrogen bond with PAA might). Furthermore, crystallinity is suppressed by using relatively short (400 g mol^{-1}) EO blocks while maintaining ∼50 wt % EO in the structure. The advantage of using these types of PEO ionomers is that the charge density and EO block length can be synthetically tuned to control properties. As a proof-of-concept, one particular set of PEO ionomers is reported here. The molar EO:Li^+ ratio was adjusted by varying Li salt concentration. The results demonstrate that PEO-containing ionomer complexes behave similarly to PEO in terms of salt effects but that the complexes are completely amorphous and have superior mechanical properties to homopolymer PEO. There appears to be an optimum salt concentration (EO:Li^+ of 40:1) for maximum conductivity. Larger salt concentrations resulted in (1) decreasing polymer chain mobility as evidenced by an increasing glass transition temperature and (2) ion pairing/clustering of $LiClO_4$ as supported by FT-IR spectroscopy.

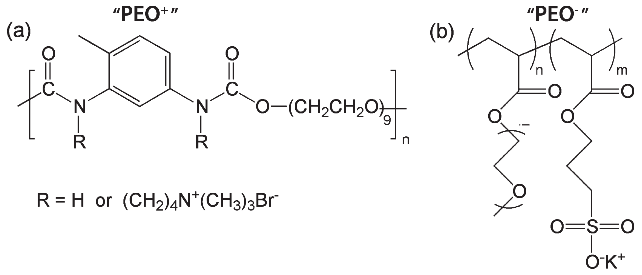

Figure 1. Chemical structure of (a) PEO^+, an aminated polyurethane where R is substituted with either 50 or 100 mol % quaternary ammonium groups, and (b) PEO^-, a copolymer of PEO acrylate and sulfopropyl acrylate, where the ratio of m:n is 1:2 or 1:1 and i = 8−9.

EXPERIMENTAL SECTION

Materials. The quaternary ammonium-containing PEO-based poly(urethane) (PEO^+) was synthesized from the condensation polymerization of a 1:1 molar ratio of toluene diisocyanate and 400 g mol^{-1} PEG diol to form linear PEO−poly(urethane)s with M_w = 42 300 g/mol and M_w/M_n = 3.02 by GPC with a 0.05 M LiBr in dimethylformamide mobile phase. The PEO−poly(urethane) was then reacted with 1.0 or 0.5 equiv of LiH per repeat unit to deprotonate the urethane nitrogens, followed by an excess of dibromobutane to attach bromobutyl groups to the polymer backbone. The bromobutyl groups were subsequently quaternized with trimethylamine, which resulted in trimethylbutyl quaternary ammonium bromide groups attached to 100% or 50% of the urethane nitrogens as confirmed by ^1H NMR spectroscopy.[33,34] The sulfonated PEO acrylate sample (PEO^-) was synthesized by the random free radical copolymerization of poly(ethylene glycol) methyl ether acrylate (PEG acrylate, Aldrich, M_n ∼ 480 g mol^{-1}) with 3-sulfopropyl acrylate potassium salt (SPA, Aldrich). Briefly, PEG acrylate and SPA (1:1 or 1:2 molar ratio) were first dissolved at 10 wt % in 1:2 by volume methanol:water with 2,2′-azobis(2-methylpropionamidine) dihydrochloride (0.5 wt % to total amount of monomer), a free radical initiator, in a round-bottomed flask equipped with a magnetic stirrer. Argon was purged through the solution for ∼30 min, and the flask was placed into an oil bath at 308 K. The reaction was allowed to proceed for 24 h. The resulting polymer was then isolated by solvent evaporation, washed with diethyl ether, and dried in a reduced pressure at 323 K. The composition of the random copolymer was determined using ^1H NMR, and the molar ratio of PEG acrylate and the SPA followed the monomer feed ratio. GPC was not performed on the PEG acrylate−SPA copolymers due to the presence of the sulfonate groups on the polymer backbone. However, PEG acrylate homopolymers synthesized under identical conditions yielded polymers with M_w = 67 600 g/mol and M_w/M_n = 2.32 by gel permeation chromatography in a THF mobile phase which serves as an estimate for the molecular weight of the PEO^-.

Preparation of PEO^+/PEO^- Complexes. Cationic and anionic polymers were dissolved separately into Milli-Q water to prepare aqueous solutions of 20 mM concentration based on the average repeat

Table 1. Properties of PEO^+/PEO^- Complexes of Varying $LiClO_4$ Content

EO:Li^+ ratio	Li^+ concn (mol/kg)	T_g (K)	σ at 298 K (S cm^{-1})	σ at 378 K (S cm^{-1})	fraction of free ClO_4^- ions
40:1	0.375	295	5.1×10^{-9}	3.7×10^{-6}	0.36
20:1	0.750	307	3.6×10^{-9}	9.1×10^{-7}	0.47
8:1	1.875	323	$<1 \times 10^{-10}$[a]	7.1×10^{-8}	0.18
6:1	2.50	339	$<1 \times 10^{-10}$[a]	8.2×10^{-9}	0.090

[a] Impedance reached the instrument's limit.

unit molar mass. Equal amounts by volume of cationic and anionic solutions were mixed and then stirred for 3 h. The solution became cloudy upon mixing and remained cloudy after standing 24 h at room temperature, indicating successful formation and good stability of the complex. To prepare Li salt-containing samples, lithium perchlorate ($LiClO_4$) (Aldrich, reagent grade, 99.99%) was added to the aqueous solution of polymer complex to obtain the desired EO:Li^+ molar ratio. KBr was present in each of the samples because K^+ and Br^- were the original counterions for the PEO ionomers. Each sample possessed the same amount of KBr, while the $LiClO_4$ concentraiton was varied. Water was removed from the complex by dehydrating the sample in a convection oven (323 K) for 24 h. Then, the complex was further dried under dynamic vacuum (298 K) for 12 h.

Herein, the concentration of salt relative to the polymers will be expressed as the ratio of ether oxygen units (EO) to lithium cations. The total number of EO units includes the sum of contributions from the anionic and cationic PEOs. Table 1 lists EO:Li^+ ratios and corresponding molar concentrations of Li^+ cations used in this investigation. Of note, these ionic polymers rapidly absorb water from surrounding air and become hydrated at ambient conditions. For example, upon exposure to air for 15 min, the dried complex became tacky and was difficult to handle. To minimize water exposure, complexes were investigated immediately after vacuum drying or the characterization was performed under dynamic vacuum.

Modulated Differential Scanning Calorimetry (MDSC) Experiments. MDSC experiments were conducted using a Q200 calorimeter (TA Instruments). Approximately 10 mg of dried complex or homopolymer was loaded into a Tzero aluminum pan and covered with a Tzero hermetic lid with pinhole (TA Instruments). The purpose of the pinhole is to allow any residual water to escape during the measurement. Each MDSC sample was equilibrated isothermally at 313 K under nitrogen for 20 min prior to the initiation of the experiment. The experimental procedure includes three steps: (1) cooling to 193 at 3 K min^{-1}; (2) heating from 193 to 403 K at 3 K min^{-1}; (3) cooling from 403 to 193 K at 3 K min^{-1}. The temperature-modulated amplitude was 0.636 K, and the period was 40 s. An empty Tzero pan and Tzero hermetic lid with pinhole was used as a reference. All MDSC thermograms were plotted with exotherm down. Data reported herein were taken from the second cooling cycle and were analyzed using TA Universal Analysis software. The glass transition temperature was taken as the inflection point of the reversing curve from the second cooling cycle.

Ionic Conductivity Measurements. The ionic conductivities of PEO^+/PEO^- complexes with varied Li^+ concentrations were measured using ac impedance spectroscopy (Solartron 1260 impedance analyzer coupled to a Solartron SI 1287 electrochemical interface). The amplitude voltage was 100 mV with 0 V bias, and the frequency range was 10 MHz to 0.1 Hz. A controlled volume of complex was lightly pressed between two aluminum plates separated by a 100 μm thick PTFE spacer with a 1/4 in. diameter reservoir. The assemblage was annealed at 353 K for 3 h in a vacuum oven. The electrodes and sample was then mounted into a spring-loaded cell (Supporting Information, Figure S1) in a vacuum oven. First, samples were allowed to equilibrate at 378 K under vacuum for at least 24 h or until successive impedance measurements over 1 h remained stable. Then, impedance spectra were taken during cooling from 378 to 298 K under vacuum at 10 K intervals. Samples were allowed to equilibrate at each temperature interval for more than 12 h. ZView software was used to analyze all complex impedance measurements to obtain a through-plane resistance (R_p). An equivalent circuit model of a resistor in series with a resistor in parallel with a constant phase element (CPE) was fit to the data (see Figure S2). A CPE was necessary because the spectra often produced slightly depressed semicircles, which suggested a distribution of dielectric constants within the material.[35] The ionic conductivity (σ) of the polyelectrolyte complex was then calculated according to the following equation:

$$\sigma = \frac{l}{R_p A} \tag{2}$$

where l is the thickness of the sample and is set by the spacer, R_p is the measured through-plane resistance of the polyelectrolyte complex sample, and A is the cross-sectional area available for ion transport.

Fourier Transform Infrared (FTIR) Spectroscopy. Infrared absorption spectra were recorded using an ALPHA FTIR spectrometer (Bruker) with 4 cm^{-1} wavenumber resolution in transmission geometry. Polymer complexes with varied salt concentrations were drop-cast onto a ZnSe crystal (International Crystal Laboratories), and 1024 scans were signal-averaged for each sample. Origin software was used to model the summation of two Gaussian–Lorentzian peaks at 610 and 624 cm^{-1}. Desiccant packs within the spectrometer maintained a dry atmosphere.

Tensile Testing. Thin films of PEO^+/PEO^- complexes were obtained by drying the aqueous solutions under vacuum (323 K) for 24 h, and films were subsequently sectioned into 16 mm × 10 mm × 0.2 mm samples for tensile testing. Samples were mounted onto the tensile grips of an Instron 3342 fitted with a 10 N load cell. The samples were then subjected to 0.83 mm/s elongation until failure. The tensile test was performed under ambient conditions, where the film was allowed to absorb water from the environment.

RESULTS AND DISCUSSION

Four types of complexes were made from combinations of aminated polyurethane-based PEOs (PEO^+, where R is either 50% or 100% quaternary ammonium groups) and sulfonated polyacrylate-based PEOs (PEO^-, where the PEO:SPA ratio was either 1:1 or 1:2). The T_g values of the homopolymers ranged from 236 to 250 K (Table S1). Each mixture (equimolar by repeat unit PEO^+:PEO^-) initially formed a turbid solution, indicating the formation of a polyelectrolyte complex. However after 3 days, only the mixture containing PEO^+, where R was 50% quaternary ammonium groups, and PEO^-, where the PEO:SPA ratio was 1:2, remained turbid. For this reason, this stable combination for PEO ionomers was selected for further analysis. The ionic stoichiometry of this PEO^+/PEO^- complex was one quaternary ammonium group for every two sulfonate groups. We speculate that this combination of PEO^+/PEO^- samples may have a sufficient number of charged groups for ionic complexation, while not having too high of an ion content that promotes reversible solubility of the electrostatically bonded macromolecules.

Influence of Salt on Glass Transition Temperature. Because crystallization is undesirable in PEO-based ion conductors, MDSC was performed on homopolymers PEO^+ and PEO^-, as well as PEO^+/PEO^- complexes, to detect glass transitions and evidence of crystallization. MDSC uses a modulated temperature profile to separate reversing from nonreversing thermal events. Reversing events (i.e., glass transitions) occur on time scales less

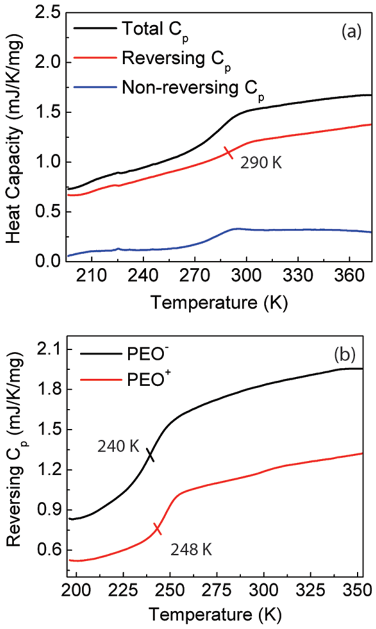

Figure 2. (a) MDSC thermogram of PEO$^+$/PEO$^-$ complex without added salt. (b) MDSC reversing heat capacities of homopolymers PEO$^+$ and PEO$^+$. Samples were cooled at a rate of 3 K/min, amplitude of 0.636 K, and period of 40 s. All data shown were taken from the second scan. Some curves have been shifted along the *y*-axis to improve clarity.

than the modulation period; nonreversing events occur on time scales longer than the modulation period (i.e., physical aging, crystallization). In this manner, overlapping thermal phenomena can be isolated from one another. The total heat capacity, C_p, is the sum of the reversing and nonreversing C_p curves. Figure 2a shows a sample MDSC thermogram of a PEO$^+$/PEO$^-$ complex sample without added salt during cooling, where a glass transition (290 K in the reversing curve) with slight physical aging (in the nonreversing curve) was observed. No crystallization was observed in the nonreversing curve; therefore, the complex was considered completely amorphous. Because only slight physical aging was observed in all other nonreversing curves for samples investigated, we will confine our discussion to events in the reversing curve from here on.

PEO$^+$ and PEO$^-$ had glass transition temperatures of 248 and 240 K, respectively (Figure 2b). The polymers were considered single-phase materials as no second glass transition was observed. For comparison, Dou et al. observed a T_g of 285 K for PEO—poly(ester) ionomers with isopthalate linker groups and EO spacer lengths of 400 g/mol.[29] In contrast, the T_g of the PEO$^+$/PEO$^-$ complex (T_g = 290 K) was about 40—50 K higher than that of either component. This dramatic increase in the T_g of the complex is most likely a result of strong electrostatic interactions between PEO$^+$ and PEO$^-$. For an equal volume fraction homogeneous mixture of two noninteracting components, one might predict a T_g value midway between that of the homopolymer's T_g value. However, the failure of this prediction supports that the two polymers are strongly interacting, where electrostatic interactions between oppositely charged polymers reduce chain mobility and elevate T_g.

Figure 3 shows the effect of salt concentration on the observed T_g value for PEO$^+$/PEO$^-$ complexes. The T_g value increased from 295 to 339 K when salt concentration was increased from EO:Li$^+$ ratios of 40:1 to 6:1. Results suggest a linear relationship between T_g value and salt concentration. Linear regression of the data gave $T_g = m[\mathrm{Li}^+] + T_{g0}$, where m is the slope of the line in units of (K kg mol^{-1}), [Li$^+$] is the concentration of Li$^+$ in units of (mol/kg), and T_{g0} is the T_g value for a PEO$^+$/PEO$^-$ without added salt (290 K). The equation for the fitted line was $T_g = 19.3[\mathrm{Li}^+] + 290$.

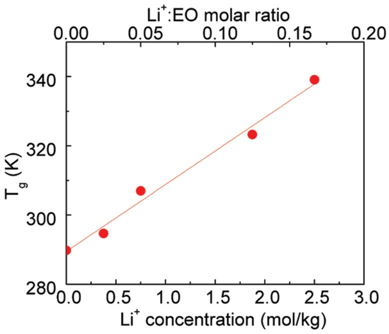

Figure 3. T_g values vs Li$^+$ ion concentration. The solid circles are experimental data, and the solid line is a linear fit of the experimental data.

A similar linear relationship has been reported previously for blends of homopolymer PEO and LiClO$_4$, and the linear increase in T_g was attributed to a linear increase in the *B* parameter of the Vogel—Tammann—Fulcher (VTF) equation.[36,37] *B* corresponds to the apparent activation energy for polymer relaxation; as salt concentration increases, the activation energy for relaxation increases, and the polymer relaxes more slowly. Accordingly, a longer relaxation time leads to a lower mobility (μ), which decreases conductivity. The reduced mobility is attributed to interactions between Li$^+$ and EO, where Li$^+$ ions act as transient cross-links.[36,38] For comparison, we calculated the slope of the T_g vs [Li$^+$] line for PEO/LiClO$_4$ blends from ref 35 to be about 12 K kg mol^{-1}, whereas the slope for the PEO$^+$/PEO$^-$ complexes with LiClO$_4$ was 19.3 K kg mol^{-1}. The larger slope indicated that the T_g values of the PEO$^+$/PEO$^-$ complexes are more strongly affected by the presence of LiClO$_4$; in other words, segmental mobility decreased more for the PEO$^+$/PEO$^-$ complex than for homopolymer PEO at a given salt concentration. This effect could possibly be due to interactions of ionic linker groups with the Li salt or stronger EO—salt interactions in the presence of the ionic linker groups.

Salt Effects on Ionic Conductivity. Because conductivity scales with both segmental mobility and concentration of mobile ions and the T_g value of the PEO$^+$/PEO$^-$ complex was strongly dependent on salt concentration, it is reasonable that conductivity will be strongly influenced by the amount of salt added to the complex. PEO$^+$/PEO$^-$ complex conductivity was measured using ac impedance spectroscopy for varying salt concentrations and temperatures (Figure 4a). Ionic conductivity for the case of no added LiClO$_4$ salt was generally between that of EO:Li$^+$ ratios of 20:1 and 8:1. The conuctivity of LiClO$_4$-free materials is explained by the presence of KBr in the sample, which contributes to the conductivity. As LiClO$_4$ is added to the complex, the conductivity increases (EO:Li$^+$ 40:1) and then decreases (EO:Li$^+$ 20:1, 8:1, and 6:1). For example, ionic conductivity at 378 K was 3.7 × 10^{-7} S cm^{-1} for the LiClO$_4$-free sample and decreased from 3.7 × 10^{-6} S cm^{-1} at an EO:Li$^+$ ratio of 40:1 to 8.2 × 10^{-9} S cm^{-1} at an EO:Li$^+$ ratio of 6:1. Results are summarized Table 1. The results also show that ionic conductivity increases with increasing temperature for all complexes

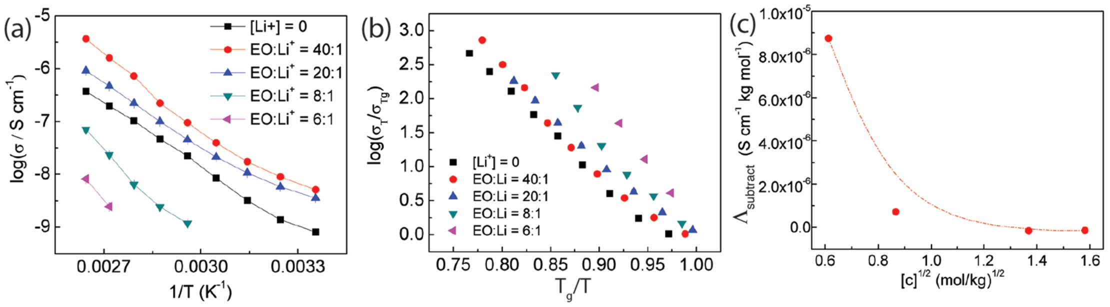

Figure 4. (a) Temperature dependence of ionic conductivity for PEO^+/PEO^- complexes of varied $EO:Li^+$ ratios. (b) WLF plots of ionic conductivity for PEO^+/PEO^- complexes of 40:1 and 20:1 $EO:Li^+$ ratio using a reference temperature $T_0 = T_g + 50$ K. (c) Li^+ concentration dependence of corrected molar conductivity ($\Lambda_{subtract}$) at $T = 378$ K.

investigated. For example, ionic conductivity for an $EO:Li^+$ ratio of 40:1 increased from 5.1×10^{-9} S cm^{-1} at 298 K to 3.7×10^{-6} S cm^{-1} at 378 K.

Conductivity for PEO^+/PEO^- complexes was normalized to their conductivity at the glass transition temperature to produce a master plot (Figure 4b). A linear dependence of the logarithm of reduced conductivity vs T_g/T is observed, indicative of Arrhenius-type behavior. PEO^+/PEO^- complexes with no added $LiClO_4$ or with an $EO:Li^+$ ratio of 40:1 or 20:1 fall near one each other, whereas large $EO:Li^+$ ratios (8:1 and 6:1) are shifted upward and the slope slightly increases. The increase in slope suggests that the activation energy for ion transport increases in PEO^+/PEO^- complexes of higher $LiClO_4^-$ concentration. For comparison, blends of homopolymer PEO with $LiClO_4$ have demonstrated both VTF and Arrhenius behavior, depending on salt concentration; for high salt concentration, Arrhenius behavior was observed, and VTF behavior was observed for low salt concentration.[13,39,40] For example, Weston and Steele observed Arrhenius behavior for blends of homopolymer PEO and $LiClO_4$ ($EO:Li^+$ 8:1) with an activation energy of 127 kJ/mol.[41] In the present study, an $EO:Li^+$ ratio of 8:1 PEO^+/PEO^- complex had an activation energy of 42 kJ/mol, which is considerably lower. Because of the KBr in the PEO^+/PEO^- complexes, the high total salt concentration (KBr + $LiClO_4$) likely leads to the observed Arrhenius behavior rather than VTF behavior.

To determine the relative mobility of ions in the complexes, the molar conductivity was examined. Recall that $\sigma = nq\mu$ and that n is the number of mobile carriers. Assuming that the $n \sim [c]$, one may take the molar conductivity as $\Lambda = \sigma/[c] = q\mu$ for a qualitative measurement of ion mobility. To remove the contribution of KBr on the molar conductivity, a corrected molar conductivity ($\Lambda_{subtract}$) was calculated from a corrected conductivity, where the conductivity at $[LiClO_4] = 0$ was subtracted from the measured conductivity. The result gives a qualitative understanding of how mobility within the matrix is affected by $LiClO_4$. Figure 4c shows the Li^+ concentration dependence of the corrected molar conductivity, which decreases with increasing salt concentration. In other words, ion mobility decreases with increasing salt concentration. These results are not surprising considering that the T_g value is strongly influenced by salt concentration for our complexes.

The ionic conductivities measured from room temperature to 378 K for the complex containing EO:Li = 40:1 were comparable to that of blends of homopolymer PEO and $LiClO_4$ measured under similar temperatures and salt concentrations (10^{-8} at room temperature to 10^{-3} S cm^{-1} to 378 K).[13] The PEO/$LiClO_4$ blend outperforms the complex at elevated temperatures (>333 K) because the PEO/$LiClO_4$ blend melts whereas PEO^+/PEO^- complex with $LiClO_4$ remains solid. Also, for comparison, the ionic conductivities of PEO/$LiClO_4$ blends of $EO:Li^+$ ratio of 30:1 reported by Maranas et al. range from 10^{-9} to 10^{-3} S/cm for the same temperature range; the crystalline fraction was 0.55, and conductivity sharply increased at the melting point.[43] Vallée et al. observed a maximum in conductivity of 2×10^{-4} S/cm at 50 °C at about 1 mol/kg ($EO:Li^+$ 20:1) in blends of homopolymer PEO and $LiClO_4$.[37]

Given that complexation appears to increase the T_g value and decrease mobility, it would be advantageous to control the extent of ion pair cross-links between PEO^+ and PEO^- and to balance the EO content within the polymer. In the present study, the complex is 55 mass % PEO, and the remainder is linkages and functional groups that do not necessarily participate in conduction. The ionic conductivity of the PEO-based complexes can be expected to increase by reducing the charge density on the polymer chains, which leads to decreasing number of PEO^+/PEO^- ion pairs and consequently enhanced chain mobility. Also, increasing the EO content within the polymer backbone is another promising strategy to boost conductivity. However, if the EO spacer length is too long, then crystallization can occur within the PEO ionomer,[29,32] and if there are too few ion pairs to complex, then the mechanical properties of the material or its ability to form a stable complex may be compromised. Therefore, it will be important to balance charge density and EO spacer length with chain mobility and complex stability in future investigations.

Influence of Salt on Ion Pairing. FTIR spectroscopy was performed on PEO^+/PEO^- complexes with the aim of identifying morphology and ion pairing (Figure 5). As previously reported, the CH_2 wagging mode observed at 1350 cm^{-1} splits into two peaks (~1343 and 1360 cm^{-1}) and C−O−C stretching vibrations observed around 1096 cm^{-1} splits into three peaks (~1144, 1107, and 1062 cm^{-1}) when PEO crystallizes.[42,44,45] In contrast for all PEO^+/PEO^- complexes studied here, single peaks were observed around 1350 and 1096 cm^{-1}, indicating that the complexes are completely amorphous. In addition, the spectra demonstrate a redshift of the peak at ~1096 cm^{-1}; such a red shift has been previously attributed to the formation of $EO-Li^+$ transient cross-links in blends of homopolymer PEO and $LiClO_4$, which decrease the vibrational frequency of C−O−C stretching.[42] The extent of the red shift increases for complexes with increasing salt concentration.

FTIR spectra in the frequency range of 720 to 520 cm^{-1} show two separate peaks with maxima at ~610 and 624 cm^{-1}

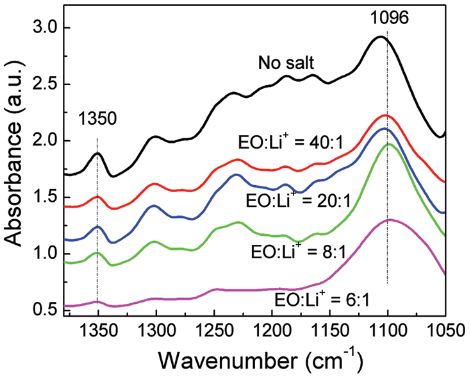

Figure 5. FTIR spectra for PEO complexes with varied salt concentration in the frequency range from 1380 to 1050 cm^{-1}. Spectra are shifted along the *y*-axis to improve clarity.

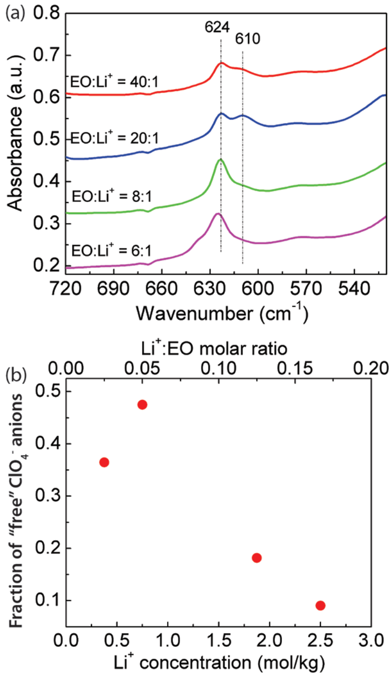

Figure 6. (a) FTIR spectra recorded for PEO^{+}/PEO^{-} complexes with varied salt concentration in the frequency range from 720 to 520 cm^{-1}; spectra are shifted along the *y*-axis to improve clarity. (b) Fraction of spectroscopically free anions as a function of salt concentration.

(Figure 6a) for the PEO^{+}/PEO^{-} complex. Previous work on blends of homopolymer PEO and LiClO$_4$ reported two peaks at ~624 and 632 cm^{-1}, corresponding to the vibrations of free ClO$_4^-$ anions and of Li$^+$ClO$_4^-$ contact ion pairs, respectively.[42] In this terminology, for every free ClO$_4^-$ anion there exists a Li$^+$ cation associated with EO units. Because the term "free" ion can have different meanings based on measurement technique, we note that these ions are spectroscopically free. Spectroscopic techniques capture only contact ion pairs, so that free ions include separated pairs and unpaired ions.[12] Separated pairs occur when the cation and anion are separated by one or two polymer chains.[46] In the present work, these two peaks are red-shifted to 610 and 624 cm^{-1} for the free and contact ion pair states, respectively.

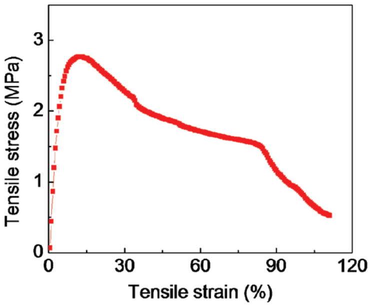

Figure 7. Tensile test of a representative PEO^{+}/PEO^{-} complex with no added LiClO$_4$ at 291 K and 50% relative humidity.

To quantify the distribution between these two states of ion association, we analyzed the area of the two peaks as two overlapping Gaussian–Lorentzian functions and calculated the ratio of the area under the 610 cm^{-1} peak to the total area under two peaks (610 and 624 cm^{-1}) to obtain the fraction of free ClO$_4^-$ anions (Figure 6b). The fraction of spectroscopically free ClO$_4^-$ anions first increases from 0.36 to 0.47 as the Li$^+$:EO ratio increases from 1:40 to 1:20 and then decreases dramatically with increasing Li$^+$ concentration, suggesting that the fraction of ion pairs in the PEO-based complex increases.

This phenomenon has been observed elsewhere for blends of homopolymer PEO and LiClO$_4$ and can significantly lower ionic conductivity because ion pairing reduces the concentration of mobile ions.[7] Wieczorek et al. also investigated the effect of salt concentration on the ionic conductivity of PEO-based polyelectrolytes and discovered a similar trend for PEO/LiClO$_4$ blends within the same Li$^+$ concentration range.[42] Comparably, adding salt to the PEO^{+}/PEO^{-} complex does not increase conductivity because much of that added salt exists as immobile ion pairs.

In the present work, it was assumed that all covalently bound charged groups on PEO ionomers participate in complexation and do not contribute to conductivity because they are occupied by intrinsic rather than extrinsic charge compensation.[47] This assumption is reasonable considering entropy as a driving force for complexation.[48] During complexation, PEO^{+} and PEO^{-} counterions are released and entropy increases. Therefore, the motion of small ions associated with EO units rather than covalently bound ionic groups likely dominates conductivity.

Mechanical Properties. The mechanical properties of a PEO^{+}/PEO^{-} complex with no added LiClO$_4$ were examined via tensile testing in ambient conditions (Figure 7). The yield stress and strain were 2.8 MPa and 11.7%, respectively. The Young's modulus was 50 MPa, and the strain at break was 110%. The low modulus and high extensibility are likely a result of plasticization caused by water absorbed from the ambient environment. It should be noted that the complexes are very hygroscopic. Therefore, the mechanical properties reported here represent those of the complex's hydrated state. It is expected that a dry complex would possess a higher modulus. The complex has a much higher strain at break and a lower modulus when compared with semicrystalline homopolymer PEO (strain at break = 1–5% and modulus = 0.08–3 GPa).[49–51] Also, low-molar-mass PEG, comparable to the molar mass of the ionomer's spacer's group, is liquid. These qualities, along with the shape of the stress–strain curve,[52] suggest that the complexes behave as ductile polymers.

CONCLUSIONS

Oppositely charged PEO ionomers were blended with lithium salt to form a new class of ion-conducting PEO-based complexes. Under all salt concentrations investigated, PEO^+/PEO^- complexes were amorphous. The T_g values for the complexes increased linearly with salt concentration, which corresponded to a linear increase in the B parameter in the VTF relation. The glass transition temperature of the complex was elevated relative to the homopolymers, indicating a strong electrostatic interaction between PEO^+ and PEO^-. Ionic conductivity and segmental mobility decreased as salt concentration increased. As salt concentration increased, the extent of ion pairing largely increased and the fraction of mobile ions decreased. The maximum conductivity observed was 3.7×10^{-6} S cm^{-1} at 105 °C and an EO:Li^+ ratio of 40:1. Compared to homopolymer PEO−$LiClO_4$ blends, the complexes had comparable or slightly lower conductivity when considering samples of similar salt composition at room temperature but had superior mechanical properties. In future work, ionic conductivity can be further enhanced by (1) the introduction of plasticizer to the complex system to enhance chain mobility at room temperature and (2) the synthesis of new PEO ionomers bearing a lower charge density (to reduce the number of ion pair linkages) and longer EO spacer groups (to enhance chain flexibility). Beyond single ion conductors, complexes of high PEO content are potentially useful in other applications such as nonfouling coatings and drug delivery.

ASSOCIATED CONTENT

Supporting Information. Glass transition temperatures of various PEO ionomers examined, device used for ionic conductivity measurements, and equivalent circuit modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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