Aggregated Ions

Solvated Ions

Plasticize with PEG

Ionic Aggregate Dissolution and Conduction in a Plasticized Single-ion Polymer Conductor

Michael V. O'Reilly^{2,†}, Hanqing Masser^{1,†,#}, Daniel R. King^{1,&}, Paul C. Painter¹, Ralph, H. Colby¹, Karen I. Winey^{2,*}, James Runt^{1,*}

¹ Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

² Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272

[†] Equal Contribution

* Correspondence to: James Runt (runt@matse.psu.edu) or Karen I. Winey (winey@seas.upenn.edu)

Current address: The Dow Chemical Company, Spring House, PA 19477

& Current address: Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003

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ABSTRACT

Poly(ethylene glycol) plasticizer is blended with a PEO-based single-ion conductor to lower the glass transition temperature of the ionomer and solvate the lithium counterions. With increasing plasticizer content at room temperature, FTIR spectra indicate that the fraction of ions in isolated ion pairs increases relative to those in ionic aggregates, and X-ray scattering data

indicate that the ionic aggregates are further apart than expected by dilution alone. Together these data show that the average size of ionic aggregates decreases as PEG plasticizer is added. The dissolution of aggregates into ion pairs promotes ion conduction. Coupled with faster segmental dynamics and ion mobility from the depressed T_g , the ionic conductivity of plasticized ionomers improved by two orders of magnitude at room temperature. Resolving the alpha relaxation of these ionomer blends reveals that the mechanism for ion transport is segmentally-assisted ion motion.

1. INTRODUCTION

Lithium ion rechargeable batteries have been intensively studied and widely used in portable electronic devices for many years. First commercialized in 1991, lithium ion batteries have the advantages of high energy density and a relatively green chemistry.¹ Current commercial lithium ion battery electrolytes consist of polar organic liquids with dissolved lithium salt, contained in a porous polymer separator. However, the flammability of liquid electrolytes is a safety concern.²

Since Wright's discovery of high ionic conductivity in complexes of alkali metal salt and poly(ethylene oxide) (PEO),³ polymer electrolytes have been recognized as having the potential to substitute for conventional liquid electrolytes.^{3, 4} Compared to traditional liquid systems, polymer electrolytes have good electrochemical stability, low toxicity, low flammability and ease of processing.⁴ However, ion conduction in polymer electrolytes is generally lower than in small molecule liquid electrolytes, due to the strong coupling between ion motion and polymer segmental motion.^{5, 6} Strong solvation exists in both systems, but ions move faster in liquid electrolytes than in polymers.

PEO is the most widely investigated polymer for solid polymer electrolytes arising from its low glass transition temperature ($\sim -60\text{ }^{\circ}\text{C}$) and from its ability to solvate cations via its ether oxygens. Ion conduction in PEO-based systems is facilitated by their low glass transition temperatures (T_g), above which polymer segmental relaxations allow ion transport.⁷ As T_g is depressed, ion dynamics at room temperature accelerate. Further, PEO chain segments associate with cations, with 4-6 coordination to cations in the case of Li^+ .⁸ In PEO/salt mixtures, anions that have low binding energies with lithium, such as bis(trifluoromethane)sulfonimide,⁹ typically demonstrate good ion dissolution, and consequently, high conductivities. But because the anion and cation are both mobile in these dissolved salt systems, anions polarize at the electrodes without being intercalated, causing concentration gradients that reduce the voltage across the cell. High Li^+ transference number, the fraction of the total current carried by Li^+ ions, is most desirable for performance consistency in high capacity batteries. Single-ion conductors take aim at achieving cation transference numbers close to unity by covalently attaching the anion to the polymer, greatly reducing its mobility.¹⁰

Previous experimental and simulation work has provided some additional insight into the ion transport mechanism in ionomers. Dielectric relaxation spectroscopy (DRS) studies on PEO-based sulfonated polyester ionomers show that the simultaneously conducting ion concentration is less than 1% of the total ion content, and the ionic conductivity shows a strong dependence on the glass transition temperature.¹¹⁻¹³ Ionic aggregation in these ionomers was observed by X-ray scattering and is suspected to be the cause of immobilized LiSO_3 .^{14, 15} Recent Fourier transform infrared spectroscopy (FTIR) studies on the same ionomer detected no free (unassociated SO_3^-) anions.^{16, 17} *Ab initio* calculations evaluated the interaction energy between ions and found the majority of Li^+ ions reside within 0.4 nm of sulfur due to the high ion pair binding energy.¹⁸

A simple approach for improving ionic conductivity in polymer electrolytes is to lower the T_g by adding plasticizer, a miscible low molar mass liquid that lowers T_g .¹⁹ Plasticizers may offer an additional advantage of cation coordination or charge shielding to facilitate ion dissociation.^{20, 21} Improvement of ionic conductivity by plasticization is well established,^{22, 23} but there have been only a few studies designed to elucidate the ion transport mechanism in plasticized ionomers. A NMR study by Chung *et al.* on plasticized maleic anhydride-styrene copolymer ionomers demonstrated that particular plasticizers weaken the ion-polymer interaction, thus increasing the ionic conductivity.²⁰ Kim and Oh used FTIR to conclude that a polymer's donor number determines their solvating ability: the fraction of free ions was determined to be higher when the polymer has a higher donor number.²⁴ Sekhon *et al.* studied the role of plasticizer dielectric constant and donor number on ionic conductivity of a polymer/salt complex and found that high dielectric constant plasticizers result in large conductivity increases.²⁵⁻²⁷ Choi *et al.* observed a simultaneous increase in ion pair population and ionic conductivity with added plasticizer by measuring the dielectric response of siloxane-based lithium ion conductors.²⁸

In the current investigation, a miscible plasticizer, poly(ethylene glycol) (PEG600, $M_n = 600$ g/mol), was added to a lithium-neutralized PEO single-ion conductor. PEG600 has a low glass transition temperature (-60 °C), low vapor pressure and superior cation solvating ability, which are all desirable properties for electrolyte plasticizers. Additionally, PEG600 shares the same structure with the host ionomer spacer to promote miscibility. We employ FTIR spectroscopy to characterize and quantify ion states of a neat Li-neutralized sulfonate ionomer and its blends with PEG600, while X-ray scattering is used to probe ionomer morphology and results are quantitatively compared with FTIR findings. Electrode polarization (EP) analysis of

dielectric measurements reveals how this oligomeric plasticizer affects ion transport properties. Herein, FTIR, X-ray scattering, and DRS are used quantitatively to explore the dissolution of ionic species in the single-ion conducting polymer.

2. EXPERIMENTAL

2.1. Ionomers and Plasticized Ionomers

The chemical structure of the PEO-based polyester copolymer ionomer, PEO600-85%Li, is illustrated in Figure 1. This ionomer is a random copolymer of oligomeric poly(ethylene glycol) (600 g/mol) separated by isophthalate units wherein 85% of the isophthalate groups are sulfonated and 100% of the sulfonates have lithium counterions. The ionomer synthesis, described previously,²⁹ is a two-step melt condensation reaction between PEG600 and a mixture of dimethyl 5-sulfoisophthalate sodium salt and dimethyl isophthalate. From ¹H-NMR analysis, the structure of the random co-polymer consisted of 85% sulfonated isophthalate and 15% isophthalate. Reagents were obtained from Sigma Aldrich. PEO600-85%Na was ion-exchanged by dialysis (Amicon filter, 1000 MWCO) in an 8 M solution of LiCl dissolved in deionized water to obtain the lithium ionomer. Dialysis was assisted by argon pressure of 10 psi and continued with pure deionized water. Dialysis was considered complete when the conductivity of the dialyzate reached its minimum (~0.7 μ S/cm). The PEO600-85%Li solution was transferred into a rotary evaporator to remove excess water, resulting in a transparent, colorless liquid with high viscosity. The concentrated solution was then dried at 80 °C in a vacuum oven for 24 hours.

Figure 1. Chemical structure of the polyester random copolymer ionomer PEO600-85%Li. 85% is the fraction of random ionic isophthalate groups.

Plasticized ionomer samples were prepared by directly weighing and blending PEG600 with PEO600-85%Li at different weight ratios: 25% and 50% PEG600 for X-ray and FTIR studies, with additional 5% and 10% supplemental samples for dielectric studies. Samples were dried further at 80 °C for a minimum of 24 hours under vacuum prior to characterization.

2.2. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were collected on a Thermo Scientific Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer with wavenumber resolution of 1 cm⁻¹, and 100 scans were signal averaged. Temperature sweeps from 20 °C to 120 °C were conducted with a heating rate of 2 °C/min and stabilization time of 2 minutes. Film thickness was controlled to ensure the absorbance was within the range of the Beer-Lambert law. A custom-designed horizontal sample cell holder was used to contain fluid samples. Samples were prepared by directly spreading onto KBr windows and dried under vacuum at 80 °C overnight to remove residual water and stored in a dry environment. Dry air purge ensured that the samples were dry during spectra collection.

Prior to curve fitting, a linear baseline was set to be 0.001 below the minima of the entire spectrum, to take into consideration the extended tails of possible Lorentzian shaped bands.³⁰

After the baseline is applied, infrared spectra were compared in the characteristic region from 2000 cm^{-1} to 600 cm^{-1} . Information on ion association states is obtained by resolving the FTIR spectra in the region from 1100 cm^{-1} to 1000 cm^{-1} , which includes the bands assigned to the SO_3^- symmetric stretching modes near 1045 cm^{-1} . This region also includes bands from the PEO backbone with dominant bands between 1200 cm^{-1} and 1000 cm^{-1} . These have been previously assigned to a combination of the C-O stretch, C-C stretch, and CH_2 rocking modes from the PEO backbone.³¹ There is also a broad band centered near 1030 cm^{-1} , which is associated with different conformations of $\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2$ species.³¹

Spectral subtraction is required to discern the SO_3^- modes from the PEO modes. PEG600 has a very similar structure as the EO portion of the repeat unit in the PEO600-85%Li ionomer. Therefore, if the spectrum of PEG600 is subtracted from the spectrum of the PEO600-85%Li ionomer and its blends with PEG600, the contribution of the PEO backbone can be largely eliminated, Figure 2. After subtraction, the spectral profile due to sulfonate bands near 1040 cm^{-1} is better resolved. The films used to obtain spectra differ in thickness, so a multiplicative correction factor is used in the subtraction procedure. The subtraction factor is determined when there is no negative band remaining after subtraction and the common contribution to both spectra can be eliminated to the highest extent. Over-subtraction leads to band position shift and shape distortion; under-subtraction fails to make the weak bands of interest more pronounced.¹⁶ This subtraction procedure was also performed for 0% PEG600 and 50% PEG600.

Figure 2. Comparison of the FTIR spectrum of PEO600-85%Li plasticized with 25 % PEG600 (purple), PEG600 plasticizer (green), and the ionomer spectra after PEG subtraction (red).

After spectral subtraction, a program developed by Painter, *et al.*, Spectra Fit, is used to determine the peak position and intensity at maximum absorption, the FWHM, the band shape (Gaussian fraction, f), and calculates the area of the band.³² The experimental IR bands are curve resolved as a sum of a Gaussian and a Lorentzian, which resembles a Voigt profile.³³

$$I(\nu) = fA_0 \exp\left[-\ln 2 \left[\frac{\nu - \nu_0}{\Delta\nu}\right]^2\right] + (1 - f)A_0 / \left\{1 + \left[\frac{\nu - \nu_0}{\Delta\nu}\right]^2\right\} \quad (1)$$

The Gaussian and Lorentzian contributions are assumed to have equal HWHM, $\Delta\nu$, and are present in the proportions of f to $(1 - f)$. A_0 is the peak height, ν_0 is the wavenumber of the peak maximum, and ν is the frequency. Knowledge of the total number of bands in the region to be resolved is determined based on chemical and spectroscopic information.³⁰ Initial parameter

estimates are defined and least-squares fitting determines the best fitting parameters (position ν_0 , intensity A_0 , bandwidth at half-height $2\Delta\nu$, and f).

2.3. Thermal Characterization

Glass transition temperatures (T_g) were measured on a Seiko SSC-5200 differential scanning calorimeter (DSC). Measurements were performed under a high purity nitrogen purge. Samples of ~8 mg were sealed in aluminum DSC pans. Samples were held at 120 °C for 10 min, cooled to -120 °C at 10 °C/min and held for 10 min, then reheated to 120 °C at 10 °C/min. The T_g is defined as the midpoint of heat capacity change in the second heating curve. No crystallization or melting transitions were detected.

2.4. Dielectric Relaxation Spectroscopy (DRS) and Analysis

The complex dielectric spectra were collected by a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in isothermal intervals over a frequency range from 10^{-2} to 10^7 Hz. Temperature was varied from 120 °C to -130 °C in 5 or 10 degree steps. An AC voltage of magnitude 0.1 V was used for all measurements.

Samples for DRS measurements were prepared by sandwiching the sample between two polished stainless steel electrodes. Samples were first loaded onto a 20 mm diameter round stainless steel electrode and dried at 80 °C under vacuum overnight. Two 50 μ m silica spacers beneath a 10 mm diameter electrode were placed on top of the dry sample to construct a sandwich cell, followed by further drying. Before measurements, samples were annealed at 120 °C for 1 hour in the instrument under dry nitrogen gas to eradicate water absorption during

sample transfer. The measurements were performed from high to low temperatures under a flow of dry nitrogen gas.

Dielectric constant, ε' , and loss, ε'' , are obtained directly in DRS experiments and provide insight into ion and polymer dynamics. DC conductivity is taken as the frequency-independent value of the AC conductivity (σ'), where $\sigma'(f)$ is independent of frequency over approximately a three decade range. We can further extract information on static dielectric constant (ε_s), mobile ion concentration (p), and ion mobility (μ) by applying Macdonald's model for electrode polarization³⁴ as described previously.³⁵

Segmental relaxations of polymers are analyzed by fitting their dielectric loss curves with the Havriliak-Negami (HN) relationship,³⁶

$$\varepsilon_{HN}^*(f) = \frac{\Delta\varepsilon}{[1 + (if/f_{HN})^a]^b} \quad (2)$$

where $\Delta\varepsilon$ is the relaxation strength; f_{HN} is the characteristic frequency, which is related to the peak frequency of the relaxation; and a and b are the symmetric and asymmetric broadening parameters. f_{HN} is related to the loss peak maximum f_{max} by³⁷

$$f_{max} = f_{HN} (\sin \frac{a\pi}{2 + 2b})^{1/a} (\sin \frac{ab\pi}{2 + 2b})^{-1/b} \quad (3)$$

At higher temperatures, ion conduction often masks the segmental α relaxation. The logarithmic derivative formalism based on the real part of the dielectric constant is used here to resolve the segmental relaxation at temperatures above T_g :

$$\varepsilon_{der}'' = -\frac{\pi}{2} \frac{\partial \varepsilon'(f)}{\partial \ln f} \quad (4)$$

This approach has been shown to be an excellent approximation to the ohmic-conduction-free dielectric loss, essentially the same as that determined from a Kramers-Krönig transform of ε' .³⁸

2.5. X-ray Scattering

X-ray scattering data used two sample-to-detector distances, 11 cm and 54 cm. Cu K α X-rays were generated by a Nonius FR591 rotating anode source operated at 40 kV and 85 mA. Osmic Max-Flux optics and triple pinhole collimation yield a bright X-ray beam. X-ray counts are detected with a Bruker Hi-Star multi-wire area detector. The beam path is entirely in *vacuo* for minimal beam attenuation from windows and air. The system was fitted with a Linkam temperature controller for stepped temperature collections.

Samples were dried under vacuum at 80 °C for at least 24 hours and loaded into 1 mm glass capillaries. 2D X-ray scattering patterns of the isotropic ionomer are integrated azimuthally and reduced to 1D plots with the Datasqueeze software package.³⁹ Background scattering from an empty capillary was subtracted from ionomer scattering patterns to correct for scattering from the capillary, air, and cosmic radiation. The two angular data sets were combined by using a scaling factor for intensity such that data overlapped smoothly. Scattering data were collected at 25 °C, 75 °C, and 125 °C, with 10 minutes allowed for morphology equilibration at each temperature.

3. RESULTS AND DISCUSSION

3.1. Room Temperature Characterization of Ion States

All samples, including the neat ionomer, display a single glass transition temperature, signifying that the ionomer and plasticizer are miscible over the temperature window studied (Figure 3). No melting transitions were detected in the DSC experiments. T_g decreases with increasing plasticizer content when plotted against Li/EO ratio. The T_g of a series of PEO600 x%

Li ionomers acquired in another study are also plotted in Figure 3.¹³ The ionomer exhibits a lower T_g when the Li/EO ratio is modified with PEG plasticizer than when the sulfonation level of the ionomer is varied, arising from PEG600's lower T_g compared to non-sulfonated PEO-isophthalate.

The glass transition temperature response to ion content was compared to predictions from the Fox equation⁴⁰ (black line in Figure 3),

$$\frac{1}{T_g} = \frac{\varphi_1}{T_{g1}} + \frac{\varphi_2}{T_{g2}} \quad (5)$$

where φ_1 and T_{g1} are the weight fraction and glass transition temperature of PEG600, and φ_2 and T_{g2} are the weight fraction and glass transition temperature of the neat ionomer. The plasticized ionomer data in Figure 3 demonstrate deviations from the Fox prediction. The glass transition depression is captured with the Gordon-Taylor equation⁴¹ (red line in Figure 3),

$$T_g = \frac{\varphi_1 T_{g1} + Z \varphi_2 T_{g2}}{\varphi_1 + Z \varphi_2} \quad (6)$$

where Z is a parameter related to the interaction between the ionomer and plasticizer. It is generally known that the ionic aggregation physically cross-links the ionomer, elevating the glass transition temperature. We suggest that the non-linear response ($Z = 0.13$) originates from excess free volume and favorable interactions between the plasticizer and ionic aggregates, as evidenced by the ion aggregate dissolution discussed shortly.

Figure 3. DSC glass transition temperatures of neat and plasticized PEO600-85%Li with various PEG600 contents. The PEG plasticized ionomer data are fit with the Fox equation (Eq. 5, black line) and the Gordon-Taylor equation (Eq. 6, $Z = 0.13$, red line). For comparison, data from neat ionomers PEO600 $x\%$ Li, are shown (Ref. 13).

Figure 4 shows the curve-resolved difference FTIR spectra of PEO600-85%Li and its plasticized blends in the SO_3^- stretching region. Based on assignments in the literature for polymer-salt complexes based on poly(ethylene oxide)⁴²⁻⁵⁶, three sulfonate bands are possible: free anion vibrations (1032 cm^{-1}) from SO_3^- unassociated with cations, vibrations of ion pairs (1042 cm^{-1}) from SO_3^- associated with only one Li^+ , and vibrations of ion aggregates (1050 cm^{-1}) from SO_3^- associated with multiple Li^+ .⁴⁵ The exact band position may vary slightly depending on the local environment and its effect on ionic interactions. In the ionomers studied here, just two bands are observed at 1042 cm^{-1} and 1050 cm^{-1} , associated with SO_3^- contact ion pairs and aggregates respectively.^{44, 45} Also shown in Figure 4 are residual vibrations from the PEO backbone that were not completely subtracted out (dashed curves).

Figure 4. Curve resolved spectra of PEO600-85%Li ionomer plasticized with (a) 0%, (b) 25% and (c) 50% PEG600 after PEG600 spectral subtraction at 25 °C. Resolved bands for ionic aggregates (blue), ion pairs (red), and PEO vibrations (dashed lines) are shown for each spectra (black lines).

A band near 1032 cm^{-1} was not detected in the spectra of any of the materials under investigation here, suggesting there is a negligible population of free anions or solvent separated pairs present in this system. In contrast, previous studies on PEO/triflate salt complexes present evidence of all three anion states (free, ion pair and aggregates).^{42-45, 48, 50, 53, 57} Based on *ab initio* calculations, the binding energy between CF_3SO_3^- and Li^+ is 8% lower than between benzene sulfonate and Li^+ ,¹⁸ so Li^+ can dissociate from CF_3SO_3^- anions more readily than from the benzene sulfonate anions under consideration here.

The relative amounts of ion pairs and aggregates are determined by comparing band areas. Figure 4 compares the ion association bands for the neat PEO600-85%Li and the ionomer plasticized with 25% and 50% PEG600. The band area occupied by the 1042 cm^{-1} mode increases relative to the sum of the 1050 cm^{-1} and 1042 cm^{-1} band areas, signifying an increase in the number of ion pairs with addition of PEG600. If we assume that the absorption coefficient of these bands are the same, then the number fraction of ion pairs to total SO_3^- ion number in these systems can be determined: 3% of contact ion pairs exist in PEO600-85%Li (and 97% aggregates), 10% ion pairs in the 25% PEG600 blend, and 23% ion pairs in the 50% PEG600 blend. These data show a consistent trend of how the number fraction of a less coordinated ion state increases with added plasticizer, Figure 5, and demonstrate the solvation ability of PEG600. While it is possible for a sulfonate that is coordinated with one cation at the end of a string-like ionic aggregate to contribute to the contact pair population, an increase in these end-type ion pairs still signify a reduction in extent of aggregation.

Figure 5. Percent of sulfonate ions with only one associated lithium (ion pair) as a function of PEG600 composition at 25 °C and 120 °C, as calculated from FTIR band area fitting.

Room temperature X-ray scattering data for the neat PEO600-85% Li ionomer and two plasticized samples are shown in Figure 6. A log scale was chosen for plotting so that fits for each feature are visible. All three blend compositions exhibit comparable scattering at $q \sim 15 \text{ nm}^{-1}$, corresponding to amorphous PEO scattering.¹⁴ The absence of crystalline reflections in the wide angular regime indicates that the morphology is amorphous, consistent with DSC results. Aggregation of lithium sulfonate from the rest of the polymer has been previously reported in PEO600-100% Li ionomers.¹⁴ In this similar system, an interaggregate scattering peak at $q \sim 3 \text{ nm}^{-1}$ is visible in all three curves. Plasticization causes a reduction in aggregate peak intensity and q position, consistent with a reduction in the number of ionic aggregate scattering centers, and thereby an increase in the interaggregate separation.

Figure 6. (a) Room temperature X-ray scattering of PEO600 85% Li ionomer blends with various weight percent of PEG600 plasticizer. The lines are fits using Eq. 7. Curves are shifted vertically for clarity. (b) X-ray scattering fit of neat PEO600 85% Li displaying the four fitting functions.

To evaluate how the peak shape changes with the quantity of PEG added, the scattering curves were fit as the sum of four scattering contributions, shown as solid lines in Figure 6(b):

$$I(q) = L_{agg}(q) + L_{amorph}(q) + PowerLaw(q) + C \quad (7)$$

Prior to fitting, scattering curves were normalized to a fixed maximum intensity of the amorphous halo. The interaggregate and amorphous carbon peaks were each fit with a Lorentzian, $L(q)$, of the form:

$$L(q) = \frac{MK^2}{(q - q_0)^2 + K^2} \quad (8)$$

where M is the amplitude, K is the half-width at half-max, and q_0 is the peak position. A power law captures the low angle scattering upturn generally observed in ionomers, and a constant, C , is added to correct for any experimental discrepancies, such as capillary irregularity.

Table 1. Fitting parameters for Lorentzian fitting of the aggregate scattering peak at 25 °C and 125°C.

Sample	T (°C)	q_0 (nm ⁻¹)	d^* (nm)	M (a.u.)	K	Area
0% PEG	25	2.71 ± 0.03	2.3	3.90 ± 0.07	2.91 ± 0.08	36
25% PEG		2.46 ± 0.08	2.6	2.61 ± 0.10	2.69 ± 0.18	22
50% PEG		2.31 ± 0.08	2.7	1.70 ± 0.08	2.31 ± 0.15	12
0% PEG	125	2.45 ± 0.01	2.6	7.71 ± 0.04	1.51 ± 0.01	36
25% PEG		2.22 ± 0.01	2.8	5.85 ± 0.04	1.76 ± 0.02	32
50% PEG		2.06 ± 0.04	3.0	3.22 ± 0.10	1.87 ± 0.06	19

The position of the interaggregate scattering peak (q_0) shifts to smaller angles as the amount of plasticizer increases, which corresponds to larger separations between aggregates. To corroborate the FTIR data reported above, it is necessary to investigate whether the PEG plasticizer is dissolving aggregates rather than merely diluting them. To this end, the area of the aggregate scattering peak area, as given by πMK , is equated to the total volume of ionic aggregates in a representative volume, V_{agg} . This interpretation assumes that the interaggregate contrast (between ionic aggregates and PEO) is constant at all blend compositions. Figure 7 shows the normalized volume of ionic aggregates, V_{agg}/V_{agg}^0 , where V_{agg}^0 is the volume of ionic aggregates in the unplasticized ionomer, as a function of weight percent PEG plasticizer. If the addition of PEG plasticizer to the ionomer simply increases the separation between ionic aggregates without dissolving ionic aggregates, then the rule of mixtures gives $V_{agg}/V_{agg}^0 = (1 - \Phi_{PEG})$, where Φ_{PEG} is the volume fraction of added plasticizer. The mass densities of PEG600 and the PEO600 85%Li ionomer are similar, so volume fraction and weight fraction are approximately equivalent and the rule of mixtures is shown as a function of weight percent PEG600 in Figure 7 (blue line). The experimental results at 25 °C are lower than given by the

rule of mixtures, indicating that a portion of the ionic aggregates have dissolved with the addition of PEG600 and no longer contribute to the interaggregate scattering peak near $q = 3 \text{ nm}^{-1}$. This dissolution of ionic aggregates upon the addition of PEG plasticizer as determined from the X-ray scattering results is consistent with the increase in isolated ion pairs found by FTIR.

Figure 7. Plasticized ionomer aggregate peak area normalized by neat ionomer peak area as a function of plasticizer content at 25 °C and 125 °C.

The quantitative analysis for determining ionic aggregate population (FTIR) and spatial distribution of ionic aggregates (X-ray scattering) can be combined to estimate the composition of ionic aggregates. The total ion density of the neat ionomer, p_0 , is scaled by the volume

fraction of ionomer in the plasticized blend, $\Phi_{ionomer}$, the fraction of ions in aggregates determined from FTIR, (φ_{agg}) , and scattering volume per aggregate, approximated by $(d^*)^3$, to approximate the average number of lithium ions per aggregate, N_{Li} :

$$N_{Li} = p_0 \cdot \Phi_{ionomer} \cdot \varphi_{agg} \cdot (d^*)^3 \quad (9)$$

Figure 8 reveals how the number of lithium ions per ionic aggregate decreases with increasing plasticizer content. These FTIR and X-ray scattering results about the ion state at room temperature foreshadow an improvement in conducting ion density, p , as the addition of PEG plasticizer dissolves ionic aggregates into lower binding energy ion pairs.

Figure 8. The number of lithium ions per ionic aggregate calculated from Eq. 9 as a function of PEG plasticizer content at 25 °C and 125 °C. Ionic aggregates are compositionally much larger than ion pairs (green dashed line).

3.2. High Temperature Characterization of Ion States

The temperature dependence of both the neat ionomer and plasticized samples were also studied by FTIR and changes in ion states were evaluated. The spectra shown in Figure 9 compare FTIR fitting at 25°C and 120°C for PEO600-85%Li with 50% PEG600. The band area at 1042 cm⁻¹ (ion pairs) decreases slightly at high temperature while the band area for ionic aggregates increases (1050 cm⁻¹). Similar trends were detected in both the unplasticized ionomer and the 25% plasticized ionomer. Figure 5 compares the fraction of ion pairs to total ion number at 120°C, which is lower than 25°C. These changes in ion states with temperature are completely reversible on cooling and indicate greater ionic aggregation at higher temperature. This counterintuitive phenomenon has been observed in similar PEO-PTMO copolymers^{15, 35} and is attributed to the entropy of lithium solvation favoring ionic aggregation at elevated temperature.⁹

Figure 9. A comparison of FTIR spectra fits for PEO600-85%Li plasticized with 50% PEG600 at (a) 25 °C and (b) 120 °C. Resolved bands for ionic aggregates (blue), ion pairs (red), and PEO vibrations (dashed lines) are shown for each spectra (black lines).

Figure 10 shows elevated temperature X-ray scattering for the 0%, 25%, and 50% PEG compositions. Scattering profiles were collected at 20°C, 75°C, 125°C, and 20°C again. All X-ray samples showed complete thermal reversibility. At wide angles, the amorphous halo shifts to smaller angles, consistent with thermal expansion. The interaggregate scattering peak increases in strength, indicating thermally-induced ionic aggregation, as did the FTIR spectra. The scattering curves were fit using Eq. 7 and fitting parameters are listed in Table 1. Figure 7 shows the normalized aggregate volume at 120°C that decreases with PEG content. At 120°C, V_{agg}/V_{agg}^0 as a function of PEG content is above or comparable to the rule of mixtures, suggesting a few more ionic aggregates than expected by dilution alone. The number of ions per aggregate (Eq. 9) is larger at 120°C and decreases with the addition of PEG600, such that at 50% plasticizer the size is comparable to aggregates in the neat ionomer at room temperature, Figure 8. Overall at 120°C the impact of adding PEG600 plasticizer is smaller than at 25°C, because the reduction in dielectric constant at higher temperatures dictates ionomer morphologies with more ionic aggregation, even when plasticized. These findings suggest more moderate increases in ionic conductivity with the addition of plasticizer above room temperature.

Figure 10. Elevated temperature X-ray scattering data for (a) neat PEO600 85% Li ionomer, (b) 25% PEG600 plasticized ionomer, and (c) 50% PEG600 plasticized ionomer showing full thermal reversibility (20°C-Reverse). The linear intensity scale highlights the growth of the aggregate peak at elevated temperatures. Curves are shifted vertically for clarity.

3.3. Dielectric Relaxations

In ion-conducting polymer systems, segmental motion is generally coupled to ion transport. Previous studies on the segmental relaxation of ion-conducting polymers reveal two high frequency relaxations, α and α_2 . The α relaxation corresponds to the usual segmental motion of the polymer chains^{13, 58, 59}, while the α_2 process usually appears at a lower frequency than the α process and has been attributed to the motion of cations in the vicinity of the anions.^{13, 35} However, in our plasticized PEO600-85%Li ionomer system, only one high frequency relaxation is identified. Since ion conduction dominates the dielectric loss spectra at lower frequency, and EP dominates in derivative loss spectra, α and α_2 cannot be resolved. In addition, the dielectric strength $\Delta\epsilon$ is higher than the typical non-ionic polymer segmental relaxation strength and it is therefore reasonable to conclude that the single segmental relaxation resolved at high frequency is a combination of motions previously identified as α and α_2 .

As shown in Figure 11, with increasing PEG600 content, the segmental relaxations move to higher frequencies, reflecting the decrease in T_g . All the segmental relaxations can be described by the Vogel-Fulcher-Tammann (VFT) equation,

$$f_{max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (10)$$

where f_{max} is the peak frequency, f_0 is a constant, T_0 is the Vogel temperature, and B is a strength parameter that is inversely related to fragility. The VFT fitting parameters for the segmental relaxations are listed in Table 2. The temperature range over which the dielectric loss can be resolved are limited in samples with high plasticizer content due to PEG600 crystallization below room temperature. Meanwhile, the segmental relaxation moves out of the frequency window at low temperatures because of PEG's relatively low T_g . Consequently, the fitting

parameters of samples with relatively high plasticizer content are more uncertain due to the smaller number of points available. Fragility decreases with increased plasticizer content, which has been reported for other plasticized systems.^{60, 61} One proposed mechanism for a less fragile system is a reduction of polymer chain interactions upon the addition of plasticizer, reducing the scale of cooperative segmental motion.^{62, 63} The Vogel temperature (~ 30 K below T_g) also decreases with plasticizer content, attributed to the segmental relaxation acceleration with increasing plasticizer content.

Figure 11. Relaxation frequencies of the segmental relaxations as a function of inverse temperature. Solid lines represent fits to the VFT equation, Eq. 10.

Table 2. VFT fitting parameters (Eq. 10) for the segmental relaxations plotted in Figure 11.

Sample	$\log f_0$ (Hz)	B (K)	T_0 (K)	T_g (K)	$T_g - T_0$ (K)
PEO600-85%Li	7.3	740	222	253	31
5% PEG600	7.6	785	217	251	34
10% PEG600	8.0	775	208	238	30
25% PEG600	7.9	710	207	235	28
50% PEG600	10.9	1250	194	221	27

3.4. Ion Dynamics

The DC conductivity increases by up to two orders of magnitude with increasing plasticizer content, Figure 12. The significance of dissolving ionic aggregates into ion pairs is reflected in the depression of the glass transition temperature. When normalized by their T_g s, the conductivity data fall approximately on the same curve, as shown in Figure 12(b). This indicates the ion motion exhibits a similar compositional dependence as the segmental motion in the plasticized PEO600-85%Li ionomer system. Conductivity data below 0 °C for the 50 wt% PEG600 sample are discontinuous due to crystallization of PEG600. Crystallinity is only observed in DRS because of the long dwell times associated with the dielectric measurements.

Figure 12. (a) DC conductivity as a function of inverse temperature for plasticized PEO600-85%Li ionomers. The DC conductivity of PEO600-100%Li from ref. 13 is included for comparison. (b) DC conductivity of plasticized PEO600-85% Li ionomers as a function of T_g/T .

Ion mobilities obtained from the electrode polarization analysis are displayed in Figure 13 as filled symbols. Extended mobility is also plotted in Figure 13 as open symbols, which are obtained by dividing the DC conductivity by the product of the elementary charge, e , and the Arrhenius fits of conducting ion data in Figure 14 to Equation 12.⁶⁴ This extension allows us to

fit the ion mobility at low temperatures near T_g to extract a more accurate value for T_0 . Ion mobility in our ionomer blends increases with PEG600 content and its temperature dependence can be fit with the VFT equation,

$$\mu = \mu_{\infty} \exp\left(-\frac{B}{T - T_0}\right) \quad (9)$$

where μ_{∞} is the mobility at infinitely high temperature. The VFT equation fitting parameters shown in Table 3 demonstrate how segmental relaxation dictates ion mobility. Both Figure 11 and Figure 13 may be fit with the same Vogel temperature, and we observe that as plasticizer content increases, T_0 decreases. Fits are poor at high temperature when ion mobility becomes saturated, similar to ethylene carbonate and propylene carbonate plasticized ionomers at high temperature.⁶⁵

Figure 13. Ion mobility determined from the EP model (filled symbols) and extended mobility (open symbols) as a function of inverse temperature. Data are fit with the VFT function, Eq. 11, and fitting parameters are given in Table 3.

Table 3. Fitting parameters of VFT equation (Eq. 11) for ion mobility and Arrhenius equation (Eq. 12) for mobile ion concentration

Sample	$\log \mu_{\infty}$ (cm ² /V s)	B (K)	T_0 (K)	E_a (kJ/mol)	p_0 (cm ⁻³)
PEO600-85%Li	-3.1	595	222	17.2	7.6×10^{20}
5% PEG600	-2.9	605	217	17.1	7.2×10^{20}
10% PEG600	-2.5	600	208	16.2	6.9×10^{20}
25% PEG600	-2.5	600	207	14.9	5.7×10^{20}
50% PEG600	-2.3	630	194	13.0	3.8×10^{20}

Mobile ion concentration, p , is also calculated from EP fitting and compared in Figure 14. The value of p/p_0 increases with temperature and plasticizer content. The temperature dependence may be described by an Arrhenius equation

$$p = p_0 \exp\left(-\frac{E_a}{kT}\right) \quad (10)$$

where p_0 is the mobile ion concentration at infinitely high temperature, and E_a is the activation energy. The fits to Eq. 12 are performed by defining the high temperature limit, p_{∞} , as the stoichiometric ion content, p_0 . The activation energy E_a decreases with increased plasticizer content, reflecting the decrease in the energy needed to separate an ion pair in the presence of higher EO:Li ratio.¹¹ There is only a small fraction of simultaneously mobile ions detected in the neat ionomer (less than 1% of p_0). These results are comparable to those obtained for other single ion conductors,¹¹⁻¹³ and agree well with the ion state study by FTIR where the majority of the ions are in a bound state. The calculated p is an instantaneous representation of ions participating in electrode polarization, so only a small fraction of mobile ions are detected. However, throughout the lifetime of the experiment, the majority of ions do contribute to ion conduction by exchanging between different ion states.

Figure 14. Number densities of simultaneously conducting ions, p , determined from fitting EP as a function of inverse temperature. Solid lines are Arrhenius fits (Eq. 12) with the high temperature limit fixed as the total ion content (p_0); fitting parameters are given in Table 3.

Static dielectric constant, ϵ_s , may be calculated either from the dielectric strength found by fitting the segmental relaxation ($\Delta\epsilon = \epsilon_s - \epsilon_\infty$, where ϵ_∞ is the dielectric constant at infinitely high temperature), or by the EP analysis. In these materials, the results are approximately equal and agree with the values determined directly from plots of ϵ' vs. frequency. The temperature dependence of ϵ_s for neat ionomer and mixtures with PEG (not shown) follow expectations from Onsager, decreasing as $\sim 1/T$.⁶⁶ Figure 15 shows the composition dependence of ϵ_s at 40 °C calculated from the EP analysis. Interestingly, the static dielectric constants first increase somewhat at low plasticizer content, then decrease at higher plasticizer content, as observed previously for plasticized ionomers.²⁸ At temperatures above T_g , it is important to recognize that there are two contributions to the dielectric constant for the ionomers: PEO segmental relaxation and ionic relaxation (the motion of cations in the vicinity of the anions). Mixing of these two dielectric constants can be described by the Landau and Lifshitz mixing rule:⁶⁷

$$(\epsilon_s^{mix})^{1/3} = (1 - \Phi_{PEG600})(\epsilon_s^{ionomer})^{1/3} + (\Phi_{PEG600})(\epsilon_s^{PEG600})^{1/3} \quad (11)$$

Figure 15 shows that the experimental dielectric constant of PEO600-85% Li is ~20% lower (~18) than the dielectric constant (~22) obtained by a best fit of the Landau-Lifshitz equation to the mixture compositions (blue dashed line). The difference between the experimental and the best fit dielectric constant of pure PEO600-85% Li arises from an increase in the contribution from ion pair motion upon addition of PEG600, consistent with the higher ion pair fraction observed by FTIR (Figure 5). Without additional ion dipoles induced by PEG plasticizer, no increase in ϵ_s is expected, and the dielectric constant would follow the ideal mixing behavior between pure ionomer and pure PEG600 (red dashed line). At higher plasticizer contents, ϵ_s becomes more strongly influenced by the dielectric constant of PEG600, which is lower than the dielectric constant provided by the ion dipoles. With the competing effects of more ion pairs and more PEG plasticizer, ϵ_s first increases, then decreases with increased plasticizer compared to the neat ionomer.

Figure 15. Static dielectric constants as function of PEG600 content for plasticized PEO600-85% blends, as determined from the EP analysis. The Landau Lifshitz mixing rule is plotted for ideal mixing (red) and best fit mixing (blue). Data was collected at 40°C.

4. SUMMARY

The morphology and dynamics of a single-ion conducting polymer plasticized with PEG were investigated with the objective of distinguishing and quantifying three plasticization effects: (1) lower the glass transition temperature to enhance ion mobility, (2) increase the dielectric constant to promote ion solvation, and (3) reduce ionic aggregation to increase mobile ion content. Enhanced segmental dynamics are reflected in a reduction in glass transition temperature, as measured by DSC. FTIR spectroscopy and X-ray scattering were used in tandem to quantify the number of isolated ion pairs and the total volume of ionic aggregates present in plasticized blends, respectively. The two techniques conclude that at room temperature, PEG plasticizer dissolves ionic aggregates in the PEG-based ionomer to substantially increase the

fraction of ions in isolated ion pairs. At elevated temperature, this effect is less pronounced due to thermally-induced ionic aggregation.

As previously reported for the ionomer alone, the ionic conductivity of the plasticized ionomers is strongly coupled to their segmental relaxation, as ionic conductivity data collapse when plotted against T_g/T . At a fixed temperature the ionic conductivity shows a non-linear increase with PEG600 concentration due to the competing effects of (i) lowering the total ion content and (ii) increasing the number of isolated ion pairs by dissolving ionic aggregates. These changes in polymer and ion dynamics with increasing PEG600 content are readily understood in terms of the changes in ion association states, as determined by FTIR and X-ray scattering. This paper demonstrates that PEG600 can significantly improve the ionic conductivity of solid-state PEO-based single-ion conductors, because PEG600 behaves as both a plasticizer to lower T_g and as a solvent to produce more mobile ions by disrupting ionic aggregation.

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