Ion Transport and Structure in Polymer Electrolytes with Applications in Lithium Batteries

By

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Abstract

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When mixed with lithium salts, polymers that contain more than one chemical group, such as block copolymers and endgroup-functionalized polymers, are promising electrolyte materials for next-generation lithium batteries. One chemical group can provide good ion solvation and transport properties, while the other chemical group can provide secondary properties that improve the performance characteristics of the battery. Secondary properties of interest include non-flammability for safer lithium ion batteries and high mechanical modulus for dendrite resistance in high energy density lithium metal batteries. Block copolymers and other materials with multiple chemical groups tend to exhibit nanoscale heterogeneity and can undergo microphase separation, which impacts the ion transport properties. In block copolymers that microphase separate, ordered self-assembled structures occur on longer length scales. Understanding the interplay between structure at different length scales, salt concentration, and ion transport is important for improving the performance of multifunctional polymer electrolytes.

In this dissertation, two electrolyte materials are characterized: mixtures of endgroup-functionalized, short chain perfluoropolyethers (PFPEs) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt, and mixtures of polystyrene-block-poly(ethylene oxide) (PS-b-PEO; SEO) and LiTFSI. The PFPE/LiTFSI electrolytes are liquids in which the PFPE backbone provides nonflammability, and the endgroups resemble small molecules that solvate ions. In these electrolytes, the ion transport properties and nanoscale heterogeneity (length scale ~1 nm) are characterized as a function of endgroup using electrochemical techniques, nuclear magnetic resonance spectroscopy, and wide angle X-ray scattering. Endgroups, especially those containing PEO segments, have a large impact on ionic conductivity, in part because the salt distribution is not homogenous; we find that salt partitions preferentially into the endgroup-rich regions. On the other hand, the SEO/LiTFSI electrolytes are fully microphase-separated, solid, lamellar materials in which the PS block provides mechanical rigidity and the PEO block solvates the ions. In these electrolytes longer length scale structure (~10 nm – 1 μm) influences ion
transport. We study the relationships between the lamellar grain size, salt concentration, and ionic conductivity using ac impedance spectroscopy, small angle X-ray scattering, electron microscopy, and finite element simulations. In experiments, decreasing grain size is found to correlate with increasing salt concentration and increasing ionic conductivity. Studies on both of these polymer electrolytes illustrate that structure and ion transport are closely linked.
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1 Introduction

1.1 Motivation

Renewable alternatives to fossil-fuel-derived energy such as wind and solar energy, are often intermittent and geographically localized. Energy storage is required for the widespread integration and distribution of renewable energy resources. Lithium batteries are an increasingly popular solution for energy storage in distributed, high energy density applications such as electric vehicles.\textsuperscript{1,2} In order for lithium batteries to further displace fossil fuels, improvements to the energy density are required without sacrificing safety. A major safety concern arises due to the flammability and limited electrochemical stability of organic solvents used as electrolytes in conventional lithium-ion batteries. One approach to improving safety is to use nonflammable materials for the electrolyte.\textsuperscript{3,4}

As lithium battery technology advances from traditional anodes based on lithium graphite (theoretical energy density of 370 mAh/g) to more reactive and higher energy density chemistries based on lithium metal (theoretical energy density of 3900 mAh/g), the issue of safety is even more pressing.\textsuperscript{5} Lithium metal is unstable against traditional organic liquid electrolytes and has a tendency to form dendrites during cycling. Dendrites eventually cause the cell to short circuit, which can result in a catastrophic failure due to the sudden discharge of energy. Using electrolytes with high mechanical modulus has been theorized to prevent the formation of dendrites.\textsuperscript{5} However, mechanical modulus and ionic conductivity are typically antagonistic properties.

It is difficult to produce electrolytes with good ion transport properties in addition to the secondary properties that are required for safer and higher energy density batteries. One approach to producing multifunctional lithium battery electrolytes is to use polymers to solvate and transport ions derived from lithium salts. Polymers have good intrinsic properties for safety: high chemical stability and low vapor pressures. Multiple chemical functionalities can be incorporated through endgroup modification or block architectures. In this dissertation, the ion transport and structure-function properties of two polymer electrolyte materials are examined: mixtures of nonflammable liquid perfluoropolyether (PFPE) and the lithium salt lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) for safer lithium-ion batteries and solid block copolymer electrolytes based on mixtures of polystyrene-\textit{block}-poly(ethylene oxide) (SEO) and lithium salt for high energy density lithium metal batteries.

1.2 Polymer electrolytes

Due to their promising properties, polymer electrolytes have been studied for several decades, most prominently electrolytes consisting of salts dissolved in polyethers.\textsuperscript{7,8} In most polymer electrolytes, ion transport, especially ionic conductivity, is coupled to the motion of the polymer chain. Ions are typically transported by one of two
mechanisms: (1) vehicular transport, where the ions travel with the center of mass of the polymer chain, and (2) segmental motion, where ions travel between solvation sites in the electrolyte. Vehicular transport dominates at low molecular weights below the entanglement limit, and segmental transport dominates at higher molecular weights. Due to the close coupling between the polymer segmental dynamics and ion motion, properties such as ionic conductivity are sensitive to the presence of chemical species that impede or promote segmental mobility. This fact makes it challenging to incorporate chemical groups that improve the secondary properties of a polymer electrolyte without sacrificing the ion transport.

Fortunately, polymers with different chemical functionalities often contain structural heterogeneity due to favorable interactions between similar chemical groups. This heterogeneity can lead to the decoupling of ion transport and secondary properties. In block copolymers, the main focus of this dissertation, two types of heterogeneities occur: disordered concentration fluctuations and microphase separation. In both cases, structural features impact ion transport properties. It is well-documented that microphase-separated block copolymers can self-assemble into ordered morphologies such as hexagonally-packed cylinders of one phase in a matrix of the other phase, or lamellae of different phases. For microphase-separated block copolymers, structural features of relevance to ion transport properties include morphology, the long range ordering of the self-assembled structures, and the grain boundaries between ordered domains. Of these, the effect of morphology on ionic conductivity has been studied, but the effects of long range order on ionic conductivity are not well-understood. For disordered block copolymers, structural features of relevance to ion transport include the intensity and length scale of the concentration fluctuations. To add further complication, salt can influence phase separation and morphological structure. The objective of this work is to understand the interrelationships between salt content, structure and ion transport in polymer electrolytes with multiple functional groups.

1.3 Structure of the dissertation

The body of the dissertation is organized into 6 chapters. Chapters 2-4 focus on nonflammable liquid electrolytes based on short chain PFPE homopolymers and disordered PFPE-PEO block copolymers. Chapter 2 examines the effect of endgroups on the fundamental ion transport of the electrolytes. The addition of PEO segments to the PFPE chains produces significant changes in the ion transport properties. To understand the reason for the strong influence of PEO, chapters 3 and 4 focus on the structure of PFPE and PFPE-PEO polymer electrolytes. In chapter 3, a method based on wide angle X-ray scattering is developed to study the miscibility between PFPE and PEO segments in neat polymers. Though the PFPE-PEO polymers appear to be homogenous liquids, they exhibit concentration fluctuations between PFPE and PEO segments, characteristic of incipient microphase separation. In chapter 4, WAXS is used to determine whether or not salt is evenly distributed among the PFPE and PEO segments, by examining the effect of salt concentration on the shape of the WAXS peak due to concentration fluctuations. It is demonstrated that the LiTFSI preferentially segregates into the PEO domains, which
explains why the addition of PEO segments has a strong influence on ion transport properties.

In chapters 5-7, we examine structure-property relationships at larger length scales through studies on microphase-separated solid block copolymers based on SEO/LiTFSI. In chapter 5, an in situ SAXS experiment is performed to elucidate the effect of lamellar grain size on ionic conductivity. Decreasing grain size is found to correlate with increasing ionic conductivity. In chapter 6, the effect of salt concentration on grain size and ionic conductivity is presented. Decreasing grain size is found to correlate with increasing salt concentration in addition to increasing ionic conductivity. In chapter 7, we attempt to explain the reason for the dependence of ionic conductivity on grain size. By simulating the electric potential distribution in 2D TEM images of electrolytes with large and small grains, we conclude that simulations do not capture all of the relevant phenomena responsible for the experimental results. We speculate that in experiments, ionic conductivity might be controlled by rare grain boundary defects that occur at length scales longer than the TEM images.
2 Relationship Between Conductivity, Ion Diffusion, and Transference Number in Perfluoropolyether Electrolytes†

ABSTRACT

Connecting continuum-scale ion transport properties such as conductivity and cation transference number to microscopic transport properties such as ion dissociation and ion self-diffusivities is an unresolved challenge in characterizing polymer electrolytes. Better understanding of the relationship between microscopic and continuum scale transport properties would enable the rational design of improved electrolytes for applications such as lithium batteries. We present measurements of continuum and microscopic ion transport properties of nonflammable liquid electrolytes consisting of binary mixtures of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and perfluoropolyethers (PFPE) with different end groups: diol, dimethyl carbonate, ethoxy-diol, and ethoxy-dimethyl carbonate. The continuum properties conductivity and cation transference number were measured by ac impedance spectroscopy and potentiostatic polarization, respectively. The ion self-diffusivities were measured by pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR), and a microscopic cation transference number was calculated from these measurements. The measured ion self-diffusivities did not reflect the measured conductivities; in some cases, samples with high diffusivities exhibited low conductivity. We introduce a non-dimensional parameter, $\beta$, that combines microscopic diffusivities and conductivity. We show that $\beta$ is a sensitive function of end group chemistry. In the ethoxylated electrolytes, $\beta$ is close to unity, the value expected for electrolytes that obey the Nernst-Einstein equation, the microscopic and continuum transference numbers are in reasonable agreement. PFPE electrolytes devoid of ethoxy groups exhibit values of $\beta$ that are significantly lower than unity. In these cases, there is significant deviation between microscopic and continuum transference numbers. We propose that this may be due to electrostatic coupling of the cation and anion or contributions to the NMR signal from neutral ion pairs.

2.1 Introduction

Most studies on electrolyte characterization only report ionic conductivity, $\sigma$, a property that is measured by ac impedance using blocking electrodes such as stainless steel or nickel. However, in the continuum limit, complete characterization of electrolytes requires the measurement of two additional transport properties: salt diffusivity, $D$, by restricted diffusion, and cation transference number, $t_+$, by combining concentration cell data with galvanostatic polarization.29–33 These experiments are more challenging because they involve contacting the electrolyte with lithium metal electrodes, which are highly

† This chapter is reported in Chintapalli, M., Timachova, K., et al. Relationship between Conductivity, Ion Diffusion, and Transference Number in Perfluoropolyether Electrolytes. Macromolecules 49, 3508–3515 (2016).
reactive. Rational design of new polymer electrolytes will only be possible when the relationship between these transport properties and molecular structure is established. This requires understanding the state of dissociation, clustering, and diffusion of salt ions in the polymer matrix. One approach for obtaining some of this information is pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR). Other studies have provided insight into ion dissociation and clustering in polymer electrolytes using spectroscopic techniques, molecular dynamics simulations, X-ray and neutron scattering, as well as more recently developed methods such as electrophoretic NMR.

In simple dilute electrolytes containing fully-dissociated species, the Nernst-Einstein equation can be used to relate conductivity and ion diffusivity. This framework does not necessarily apply to concentrated electrolytes or electrolytes that contain ion clusters. There is also a lack of understanding of the relationship between ion self-diffusion coefficients measured in PFG-NMR and the salt diffusion coefficient measured by restricted diffusion. While some papers on polymer electrolytes report on properties beyond conductivity, few studies fully characterize systems at the continuum level, and fewer still attempt to characterize systems at both the continuum and molecular level. To our knowledge, complete characterization of the continuum properties of polymer electrolytes has only been done in two systems, both based on poly(ethylene oxide) (PEO), a widely characterized polymer electrolyte material. While the same electrolytes have been studied by PFG-NMR, the relationship between molecular parameters, e.g. the self-diffusion coefficient of the ions, and continuum transport parameters, e.g. $D$, have not yet been fully established. Furthermore, electrolytes based on PEO mixed with low lattice-energy lithium salts such as lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), are thought to exhibit low ion-pairing at practical concentrations. This simplification may not be generally applicable to concentrated polymer electrolytes.

In this chapter, we measure $\sigma$ by ac impedance and estimate $t_+$ by potentiostatic polarization in a systematic series of electrolytes based on perfluoropolyethers (PFPEs). Specifically, we study binary mixtures of LiTFSI and four PFPEs with different endgroups: diol (PFPE$_{D10}$-Diol), dimethyl carbonate (PFPE$_{D10}$-DMC), ethoxy-diol (PFPE$_{E10}$-Diol) and ethoxy-dimethyl carbonate (PFPE$_{E10}$-DMC). Many ether and carbonate-based molecules have good ion transport characteristics. By incorporating these functional groups into the endgroup moieties of the PFPE electrolytes, we explore their effects on ion transport properties. We find that changes in the end groups have a significant effect on both $\sigma$ and $t_+$. Measurements of the self-diffusion coefficients of the ions by PFG-NMR provide some insight into the relationship between microscopic phenomena and continuum transport. The nonflammable nature of PFPE is a promising characteristic for developing intrinsically safe rechargeable lithium batteries.

2.2 Experimental Section

2.2.1 Materials
The chemical structures of the PFPE electrolytes are given in Table 2.1. The polymers PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{E10}-Diol were purchased from Santa Cruz Biotechnology. However, Santa Cruz Biotechnology no longer sells these polymers. The polymers PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{E10}-Diol were chemically modified to convert the diol groups to dimethyl carbonate. The approach used for synthesis and characterization of these polymers are discussed in references 60 and 64. The PFPE\textsubscript{E10} polymers have backbones that are chemically similar to the PFPE\textsubscript{D10} polymers and ethylene oxide moieties that are chemically similar to PEO. For comparison to the PFPE\textsubscript{D10} and PFPE\textsubscript{E10} electrolytes, we characterize the transport properties of a PEO electrolyte. With the exception of ionic conductivity which was measured at 28 °C, the transport properties of the PFPE electrolytes were measured at 30 °C, at a LiTFSI concentration of 9.1 weight percent, (0.57 M for PFPE\textsubscript{D10} polymers and 0.56 M for PFPE\textsubscript{E10} polymers). The PEO sample used in this chapter was purchased from Sigma Aldrich and had a viscosity-averaged molecular weight of approximately 5,000 kg mol\textsuperscript{-1}. The transport properties of a 12.7 weight percent (0.56 M) LiTFSI/PEO mixture were measured at 90 °C, above the melting point of the electrolyte.

Because LiTFSI is extremely hygroscopic, materials were thoroughly dried prior to use and maintained in an air-free environment during preparation and characterization. Salt was dried at 120 °C and PFPE was dried at room temperature, both for 72 h, in the vacuum antechamber of an Ar glovebox with O\textsubscript{2} and H\textsubscript{2}O levels maintained below 1 ppm. Electrolytes were prepared by directly mixing salt into the PFPE liquid and stirring at 60 °C for 48 h. The as-received PEO contained butylated hydroxytoluene (BHT) inhibitor, which was removed by rinsing 3 g of polymer with 500 mL of acetone. The PEO was dried at 90 °C under vacuum for 24 h. Salt and PEO were dissolved in anhydrous 1-methyl-2-pyrrolidone (NMP) and cast into a polytetrafluoroethylene dish. The NMP was evaporated for 72 h at 90 °C in an Ar environment, and then for an additional 72 h at 90 °C under vacuum. The concentrations of water, solvents, and in the case of PEO, BHT, were below the detection limit of \textsuperscript{1}H NMR in the electrolytes.

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Table 2.1 Perfluoropolyether electrolytes. Functional groups containing ethylene oxide moieties are shown in blue. Dimethyl carbonate groups are shown in red.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>m</th>
<th>n</th>
<th>q</th>
<th>$M_n$ [kg mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPE\textsubscript{D10}-Diol</td>
<td>$\text{HO-CH}_2\text{-CF}_2\text{-O-}[\text{CF}_2\text{CF}_2\text{O}]_m\text{-CH}_2\text{-OH}$</td>
<td>7</td>
<td>3</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>PFPE\textsubscript{D10}-DMC</td>
<td>$\text{HO-CH}_2\text{-CF}_2\text{-O-}[\text{CF}_2\text{CF}_2\text{O}]_m\text{-CH}_2\text{-OH}$</td>
<td>7</td>
<td>3</td>
<td>0</td>
<td>1.1</td>
</tr>
<tr>
<td>PFPE\textsubscript{E10}-Diol</td>
<td>$\text{HO-CH}_2\text{CH}_2\text{O-CH}_2\text{-CF}_2\text{-O-}[\text{CF}_2\text{CF}_2\text{O}]_m\text{-CH}_2\text{-CH}_2\text{O}$</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>PFPE\textsubscript{E10}-DMC</td>
<td>$\text{HO-CH}_2\text{CH}_2\text{O-CH}_2\text{-CF}_2\text{-O-}[\text{CF}_2\text{CF}_2\text{O}]_m\text{-CH}_2\text{-CH}_2\text{O}$</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>PEO 5M</td>
<td>$\text{HO-CH}_2\text{CH}_2\text{O}$</td>
<td></td>
<td></td>
<td></td>
<td>1.14x$10^5 \sim 5000$</td>
</tr>
</tbody>
</table>

Table 2.1 Perfluoropolyether electrolytes. Functional groups containing ethylene oxide moieties are shown in blue. Dimethyl carbonate groups are shown in red.
2.2.2 Electrochemical Characterization

For electrochemical measurements, three samples were measured and averaged, and the standard deviation of the three measurements is reported as the error. The ionic conductivities of the PFPE electrolytes were measured by ac impedance spectroscopy in home-built liquid cells with two stainless steel electrodes of unequal area at 28 °C. Cell constants were determined by modelling the current distribution using Laplace’s equation and calculating the effective cross-sectional area. A description of the cells and the methods used to determine the cell constants are given in reference 65. The amplitude of the ac input signal was 20 mV and the frequency was varied from 1 MHz to 1 Hz using a potentiostat (Bio-Logic VMP3). The conductivity was determined by taking the minimum in a Nyquist plot of the magnitude of the imaginary impedance versus the real impedance.

Potentiostatic polarization was performed on 2325 coin cells, using a potentiostat (Bio-Logic VMP3). Lithium foils 150 μm thick (MTI corporation) were used as the electrodes, and the PFPE electrolytes were contained in a Celgard 2500 separator (a polypropylene film, 25 μm thick and 55 % porosity). The area of the electrodes was 2.38 cm². Samples were annealed at 50 °C for 24 h prior to measurement at 30 °C. The ac impedance and potentiostatic polarization experiments on the PEO electrolyte were measured in hermetically sealed lithium-lithium pouch cells using similar techniques to those described above; samples were annealed at 90 °C for 24 h prior to measurement at 90 °C. The conducting area in the pouch cells was 0.32 cm². AC impedance spectroscopy measurements were performed prior to the potentiostatic polarization. Cells were polarized using potentials, Δ𝑉, of 40 mV and 80 mV to confirm that measured ion transport characteristics were independent of the magnitude of the applied potential. The numbers reported herein are from the experiments using 40 mV; however, data obtained with 80 mV were within the experimental error of the measurements at 40 mV. Current was monitored during polarization using a time interval of 1 s, and potential was applied for 30 min, until steady state was reached. The cell resistances were monitored as a function of time by performing ac impedance spectroscopy at t = 0.5, 15, and 30 min during polarization. The center of the ac signal was offset by Δ𝑉 to minimize the effect of ac impedance measurement on the polarization signal. The input signal for ac impedance was 10 mV, and the frequency was varied from 1 MHz to 250 mHz.

In the absence of concentration polarization, current is given by Ohm’s law (equation 2.1).

\[ I_{Ω} = \frac{Δ𝑉}{R_{Total}} \]  

(2.1)

In equation 2.1, Δ𝑉 is the applied potential and \( R_{Total} \) is the initial total cell resistance measured by ac impedance spectroscopy. Following Bruce and Vincent, the transference number determined by potentiostatic polarization, \( t_{PP}^{+} \), is given by equation 2.2.  

\[ t_{PP}^{+} = \frac{I_{SS}(Δ𝑉−I_{0}R_{i,0})}{I_{0}(Δ𝑉−I_{SS}R_{i,SS})} \]  

(2.2)

Here, the initial current measured at \( t = 1 \) s is \( I_{0} \) and the steady state current measured at \( t = 30 \) min is \( I_{SS} \), the initial interfacial resistance is \( R_{i,0} \), and the steady state interfacial resistance, \( R_{i,SS} \). The interfacial impedance was determined by taking the difference
between the abscissa values of the minima at the bounds of the low frequency semicircle of Nyquist plots.

2.2.3 Diffusivity Measurements

NMR measurements were performed on a Bruker Avance 600 MHz spectrometer with a Z-gradient direct detection broad-band probe. Temperature was maintained throughout the experiments using a variable temperature unit. The isotopes $^7$Li and $^{19}$F were used to probe the diffusion of lithiated and fluorinated species. Lithium-containing ions produced peaks around 233 MHz and fluorine-containing ions produced peaks around 565 MHz. A bipolar pulse longitudinal-eddy-current delay sequence was used to measure the diffusion coefficients $D_{i}^{\text{NMR}}$. The attenuation of the echo $E$ was fit to equation 2.3,

$$E = e^{-\gamma^2 g^2 \delta^2 D_i^{\text{NMR}} (\Delta - \frac{\delta - \tau}{3})}$$

(2.3)

where $\gamma$ is the gyromagnetic ratio, $g$ is the gradient strength, $\delta$ is the duration of the gradient pulse, $\Delta$ is the interval between gradient pulses, $\tau$ is the separation between pulses, and $D_i^{\text{NMR}}$ is the diffusion coefficient of the cation ($D_+^{\text{NMR}}$) or anion ($D_-^{\text{NMR}}$). The $90^\circ$ pulse lengths were optimized for each sample to achieve maximum signal amplitude and $T_1$ relaxation times were independently measured for each sample nuclei using inversion-recovery (180-$\tau$-90-acq.) to insure the choice of an appropriate diffusion time interval $\Delta$. The acquisition parameters were diffusion intervals $\Delta = 0.3$-$0.6$ s, and pulse lengths $\delta = 10$-$20$ ms. For each diffusion calculation, gradient strength was varied up to 0.5 T m$^{-1}$ over 32 separate measurements and the change in amplitude of the attenuated signal as a function of gradient was fit to obtain the parameter $D_i^{\text{NMR}}$. The measured signal attenuations were single exponential decays with fit errors less than 2 % ($^{19}$F) and 4 % ($^7$Li). The gradient strength, $g$, was calibrated using an ethylene glycol standard. Due to the complexity and length of the PFG-NMR measurements at slow diffusion times, single data points are presented for each PFPE measurement. The methods used to validate the ion diffusivity measurements are described in reference 55. Ion diffusivity measurements were performed for a PEO/LiTFSI mixture in addition to the PFPE electrolytes, and the ion diffusivities obtained for the PEO electrolyte are in good agreement with those reported in the literature.53–55 The diffusivity values were found to be independent of $\delta$ and $\Delta$. The cation transference number measured by NMR, which we refer to as $t_+^{\text{NMR}}$, is calculated using equation 2.4.

$$t_+^{\text{NMR}} = \frac{D_+^{\text{NMR}}}{D_+^{\text{NMR}} + D_-^{\text{NMR}}}$$

(2.4)
2.3 Results

![Graph showing ionic conductivity as a function of endgroup.](image)

Figure 2.1 Ionic conductivity as a function of endgroup. Ionic conductivities measured at 28 °C and 9.1 weight percent salt loading (0.56 M for PFPE\textsubscript{D10} and 0.57 M for PFPE\textsubscript{E10}) are plotted for each perfluoropolyether electrolyte. Ionic conductivities were averaged over three samples, and error bars represent the standard deviation of the measurements.

In Figure 2.1, ionic conductivities measured at 28 °C are plotted for each PFPE electrolyte. The ionic conductivity values in Figure 2.1 for the PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{D10}-DMC are in agreement with the values published earlier in reference 60. The ionic conductivities of the PFPE\textsubscript{E10}-Diol and PFPE\textsubscript{E10}-DMC electrolytes are approximately an order of magnitude higher than the ionic conductivities of the PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{D10}-DMC electrolytes. The ethoxylation of the PFPE chain has a significant effect on the ionic conductivity, even though on average, the number of ethoxy repeat units, \( q \), is only two per chain end (see Table 2.1). The ionic conductivity of PEO was found to be \((1.1 \pm 0.3) \times 10^{-3} \) S cm\(^{-1}\) at 90 °C, a value that is similar to previous measurements reported for high molecular weight PEO at similar temperature and LiTFSI concentration.\(^{69}\)

![Graph showing diffusivities of Li and TFSI ions.](image)

Figure 2.2 Diffusivities of Li and TFSI ions. Diffusivities of Li and TFSI ions, measured by \(^7\)Li and \(^19\)F NMR at 30 °C, are plotted for each PFPE electrolyte.
The self-diffusivities of the salt cation and anion in PFPE electrolytes measured at 30 °C are shown in Figure 2.2. Typical $^7$Li and $^{19}$F NMR spectra are given in the Supporting Information (Figure 2.S1). The diffusivities of the ions in PFPE$_{D10}$-Diol, PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC electrolytes are similar (between $1.7 \times 10^{-8}$ and $3.9 \times 10^{-8}$ cm$^2$ s$^{-1}$). Surprisingly, the ions in PFPE$_{D10}$-DMC have the highest diffusivity (both at $8.5 \times 10^{-8}$ cm$^2$ s$^{-1}$). The effect of endgroups on conductivity and ion diffusion are qualitatively different (compare Figures 2.1 and 2.2). PFPE$_{E10}$-Diol is the most conductive electrolyte, while self-diffusion of salt ions is maximized in PFPE$_{D10}$-DMC. For completeness, we also report the diffusivities of ions in PEO: $1.4 \times 10^{-7}$ cm$^2$ s$^{-1}$ for Li$^+$ and $5.6 \times 10^{-7}$ cm$^2$ s$^{-1}$ for TFSI$^-$ at 90 °C. These values are similar to those obtained in the literature.$^{53-55}$

For ideal dilute binary electrolytes, the relationship between ionic conductivity and diffusivity is given by the Nernst-Einstein relationship (equation 2.5).$^{29}$

$$\sigma = \frac{F^2 c (D_+ + D_-)}{RT} \tag{2.5}$$

In equation 2.5, $F$ is Faraday’s constant, $c$ is the bulk molar salt concentration, $R$ is the gas constant, $T$ is temperature, and $D_+$ and $D_-$ are the self-diffusivities of the cation and anion. The cation and anion diffusivities presented in Figure 2.2 are $D_+^{\text{NMR}}$ and $D_-^{\text{NMR}}$, which, in general, are not equivalent to ion self-diffusivities, $D_+$ and $D_-$. We could not distinguish associated and dissociated ions in the $^7$Li or $^{19}$F NMR spectra in this study (Figure 2.S1). Thus, if ion pairing is prevalent in the electrolyte, then the diffusivities measured by NMR, $D_+^{\text{NMR}}$ and $D_-^{\text{NMR}}$, reflect the diffusion of neutral ion pairs, $D_n$, and dissociated ions, $D_+$ and $D_-$. Additional complications arise if the ions form charged clusters. In contrast, conductivity is only affected by the diffusivity of the charged species.$^{48}$

![Figure 2.3 Non-ideality and transference number from NMR measurements. In (a), the non-dimensional ideality parameter, $\beta$, is plotted for each electrolyte. In (b), the transference number determined by NMR measurements is plotted for each electrolyte. The data for PFPE electrolytes were taken at 30 °C, and the data for PEO were taken at 90 °C.](image)

We combine ac impedance and NMR measurements to define an ideality parameter, $\beta$, given by equation 2.6.  

$$\beta = \frac{\sigma}{\sigma_{\text{ideal}}}$$

10
\[
\beta = \frac{\sigma R T}{F^2c (D_{+}^{NMR} + D_{-}^{NMR})}
\]  \hspace{1cm} (2.6)

For an electrolyte that obeys the Nernst-Einstein equation, \( \beta = 1 \). In Figure 2.3a, the value of \( \beta \) is shown for each electrolyte. For PFPE\textsubscript{D10} electrolytes, \( \beta \) is below 0.1, for PEO, \( \beta \) is close to 1, and the values of \( \beta \) of PFPE\textsubscript{E10} electrolytes lie between 0.1 and 1. Equation 2.6 bears resemblance to a model introduced by Boden \textit{et al.},\textsuperscript{35} and some authors label \( \beta \) as the charge dissociation fraction, \( \alpha \).\textsuperscript{36–39} If we assume that the electrolytes contain only dissociated ions and neutral ion pairs, then,\textsuperscript{33,36}

\[
D_{+}^{NMR} = \alpha D_+ + (1 - \alpha)D_n \hspace{1cm} (2.7)
\]

\[
D_{-}^{NMR} = \alpha D_- + (1 - \alpha)D_n \hspace{1cm} (2.8)
\]

Equations 2.7 and 2.8 were proposed by Videa \textit{et al.}\textsuperscript{33,36} These equations illustrate that for an ideal electrolyte with a high degree of charge dissociation (\( \alpha \approx 1 \)), \( D_{+}^{NMR} \) and \( D_{-}^{NMR} \) are equivalent to \( D_+ \) and \( D_- \). For a non-ideal electrolyte with a low degree of charge dissociation (\( \alpha \ll 1 \)), the diffusivity of neutral ion pairs dominates the measured diffusivity, (\( D_{+}^{NMR} \approx D_{-}^{NMR} \approx D_n \)). Based on equations 2.4, 2.7 and 2.8, in the limit of low charge dissociation, the value of \( t_{+}^{NMR} \) should be \( \frac{1}{2} \).

In Figure 2.3b, we show \( t_{+}^{NMR} \) of the PFPE and PEO electrolytes. The value of \( t_{+}^{NMR} \) that we measure for the non-ideal PFPE\textsubscript{D10} electrolytes is indeed nearly \( \frac{1}{2} \) (0.49 for PFPE\textsubscript{D10}-Diol and 0.50 for PFPE\textsubscript{D10}-DMC). For the PFPE\textsubscript{D10} system, ion-pairing, \( \alpha \), may contribute to non-ideality, \( \beta \).\textsuperscript{35–40} However, it is evident from equations 2.6, 2.7 and 2.8, that when \( \alpha \) is significantly lower than unity, \( \beta \) is very different from \( \alpha \). Hence a simple interpretation of \( \beta \) and \( D_n \) should be avoided.\textsuperscript{35} Interpretation of the measured values of \( \beta \) in terms of a molecular picture is outside the scope of this chapter.
Figure 2.4 Potentiostatic polarization measurements. In (a), the normalized current is shown as a function of time for PFPE and PEO electrolytes. Gaps in the data occur when impedance spectra were collected. In (b), an alternative normalization is used to show the current as a function of time for PFPE and PEO electrolytes. In (c), the initial and steady state Nyquist plots are shown for each electrolyte. The vertical axis is complex impedance, $-Z''$, and the horizontal axis is real impedance, $Z'$. The results of potentiostatic polarization experiments are shown in Figure 2.4a, where the measured current $I$ normalized by $I_\Omega$ is plotted as a function of time, $t$. Note that the electrolytes covered in Figure 2.4a have widely different conductivities and ion diffusivities. The currents obtained in response to the applied potentials were also widely different. The proposed normalization enables the measured currents from the different systems to be displayed on the same axes. For all samples, $I(t)/I_\Omega$ is unity at short times.
and decays to a steady state plateau in about 30 min. The qualitative differences between PFPE- and PEO-based electrolytes are clearly seen in Figure 4a. In particular, the decay of $I(t)/I_\Omega$ in the PEO-based electrolyte is much larger in magnitude than that observed in PFPE-based electrolytes. The gaps in the data represent times when ac impedance measurements were made. In Figure 2.4b, an alternative normalization, $[I(t) - I_{SS}] / [I_\Omega - I_{SS}]$, is used to plot the current as a function of time. The data in Figure 2.4b demonstrate that for the PFPE and PEO electrolytes, the current reaches steady state in the 30 min window. The initial impedance spectra taken before potentiostatic polarization and those obtained at steady state after 30 min of polarization are shown in Figure 2.4c. Both interfacial and bulk impedances did not change appreciably during the polarization experiment. Impedances obtained in PEO are appreciably lower than those obtained in the other systems. We do not include data obtained from PFPE$E_{10}$-Diol because large changes in impedance spectra were observed during polarization, and no evidence of steady state was found.

![Figure 2.5](image)

Figure 2.5 Estimates of transference number in PFPE electrolytes. Cation transference numbers of PFPE and PEO electrolytes were determined using two methods, PFG-NMR (filled symbols), and potentiostatic polarization (open symbols).

The data in Figure 2.4 enable evaluation of $I_0$, $I_{SS}$, $R_{i0}$, and $R_{iSS}$, and thus the calculation of $t+_{PP}$ (equation 2.2). For PFPE electrolytes, the cell area of 2.39 cm$^2$ was used to obtain resistances from the impedance spectra shown in Figure 2.4c. For PEO, the cell area of 0.32 cm$^2$ was used. The transference numbers measured by potentiostatic polarization, $t+_{PP}$, are shown in Figure 2.5. The values of $t+_{PP}$ of the PFPE$D_{10}$ electrolytes are above 0.9, consistent with previous reports.$^{60}$ The value of $t+_{PP}$ of PFPE$E_{10}$-DMC is significantly lower, 0.36. It is perhaps surprising that adding a few ethoxy groups to PFPEs dramatically affects $t+_{PP}$. The value of $t+_{PP}$ of PEO is 0.16, similar to values found in literature.$^{52,56,70}$ The value of $t+_{PP}$ for PFPE$E_{10}$-DMC is thus between that of PFPE$D_{10}$-DMC and PEO. Also shown in Figure 2.5 are the $t+_{NMR}$ data from Figure 2.3b. For the PFPE$D_{10}$ polymers, $t+_{PP}$ and $t+_{NMR}$ are dramatically different, at approximately 0.9 and 0.5. In contrast, for PEO and PFPE$E_{10}$-DMC, $t+_{PP}$ and $t+_{NMR}$ are both similar, 0.16 and 0.19 for PEO, and 0.36 and 0.39 for PFPE$E_{10}$-DMC.
We observe that for electrolytes with high values of $\beta$ (PEO and PFPE\textsubscript{E10}-DMC), the values of $t^\text{PP}_+$ and $t^\text{NMR}_+$ are similar (Figure 2.5), and for electrolytes with low values of $\beta$ (PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{D10}-DMC), the values of $t^\text{PP}_+$ and $t^\text{NMR}_+$ are dissimilar, and $t^\text{NMR}_+$ is close to $\frac{1}{2}$. In the latter case, $D^\text{NMR}_+$ and $D^\text{NMR}_-$ do not reflect the motion of charged ions. The value of $t^\text{PP}_+$ depends on the mobility of the ions, i.e. the velocity of the ion obtained upon application of an electric field when charge migration is balanced by friction due to interactions between the ions and other molecules in the electrolyte. In the absence of external fields, the measured self-diffusion coefficients of the ions may differ substantially from those inferred from mobility measurements due to intrinsic coupling of the cation and anion; the ion with lower mobility will slow down the diffusion of the ion with higher mobility.\textsuperscript{55,71,72} Quantification of the effect of this coupling on $t^\text{PP}_+$ is outside the scope of this chapter.

The ethoxy groups of PFPE\textsubscript{E10} electrolytes are chemically similar to PEO, but the internal segments are chemically similar to non-ethoxylated PFPE\textsubscript{D10}. As such, the transport properties of the PFPE\textsubscript{E10} electrolytes are related to the transport properties of both the PFPE\textsubscript{D10} and PEO electrolytes. For the PFPE\textsubscript{E10} electrolytes, the measured value of $\beta$ lies between that of PFPE\textsubscript{D10} and PEO. The values of $t^\text{PP}_+$ and $t^\text{NMR}_+$ for PFPE\textsubscript{E10}-DMC is similar to literature values reported for PEO of similar degree of polymerization and LiTFSI concentration,\textsuperscript{53,56} while the values of $D^\text{NMR}_+$ and $D^\text{NMR}_-$ are similar to those of PFPE\textsubscript{D10} electrolytes. It appears that $t^\text{PP}_+$ is strongly influenced by the ethoxy groups while the values of $D^\text{NMR}_+$ and $D^\text{NMR}_-$ are more dependent on the perfluoropolyether groups. The transference number we report for ethoxylated PFPE is slightly higher than what was recently reported for PFPE/PEO blends.\textsuperscript{73} The presence of ethoxy groups, whether chemically bonded to the PFPE (PFPE\textsubscript{E10}) or blended with it (PFPE/PEO blends), reduces the transference number and increases the ionic conductivity compared to non-ethoxylated PFPE\textsubscript{D10}. This observation suggests that anion conduction is promoted by the presence of ethoxy groups. Endgroup functionality has a strong influence on the ion transport properties of PFPE electrolytes. Hence, further improvements to the transport properties might be realized by using more polar endgroup moieties to promote ion dissociation or by using lower molecular weight polymers to increase the concentration of endgroups.

2.4 Conclusions

We report on continuum and microscopic scale ion transport properties in a series of PFPE electrolytes. On the continuum scale, we present conductivity measured by ac impedance spectroscopy and cation transference number measured by potentiostatic polarization, $\sigma$ and $t^\text{PP}_+$. On the microscopic scale, we present ion self-diffusivities and cation transference number measured by PFG-NMR, $D^\text{NMR}_+$, $D^\text{NMR}_-$, and $t^\text{NMR}_+$. For PFPE electrolytes the dependence of $D^\text{NMR}_+$ and $D^\text{NMR}_-$ on the type of endgroup is qualitatively different than the dependence of $\sigma$ on the type of endgroup. We use a non-dimensional parameter, $\beta$, which depends on $D^\text{NMR}_+$, $D^\text{NMR}_-$, and $\sigma$, to compare the continuum and microscopic properties. The value of $\beta$ is unity for electrolytes that obey the Nernst-Einstein relationship. Electrolytes based on PEO and PFPE\textsubscript{E10} have $\beta$ values close to unity, while electrolytes based on PFPE\textsubscript{D10} have $\beta$ values significantly below unity. In electrolytes with high values of $\beta$ (PEO and PFPE\textsubscript{E10}-DMC), $t^\text{NMR}_+$ and $t^\text{PP}_+$ are similar,
whereas in electrolytes with low values of $\beta$ (PFPE$_{D10}$-DMC and PFPE$_{D10}$-Diol), $t^\text{NMR}_+$ and $t^\text{PP}_+$ are dissimilar.

One might expect a simple relationship between ion diffusion measured by NMR and ionic conductivity. The data presented in this chapter clearly show that this is not true in the PFPE electrolytes. Diffusivities measured by NMR are highest in PFPE$_{D10}$-DMC, while conductivity is maximized in PFPE$_{E10}$-Diol. This may be due to electrostatic coupling of the cation and anion or contributions to the NMR signal from neutral ion pairs. This chapter is but one step toward understanding the relationship between microscopic and continuum ion transport properties.

2.5 Supporting Information

In Figure 2.S1, we show representative nuclear magnetic resonance (NMR) spectra for a PFPE$_{D10}$-Diol electrolyte. Figure S1a shows the $^7$Li spectrum and S1b shows the $^{19}$F spectrum. In each plot, the top axis gives the scale in units of MHz, and the bottom axis gives the scale in units of ppm. In Figure S1b, we zoom in on the peak due to the lithium bis(trifluoromethanesulfonyl) imide anion to show that it is a single broad peak (full width at half maximum of 24 Hz). A single broad peak is also observed in the $^7$Li spectrum in S1a (full width at half maximum of 19 Hz). Hence, we cannot discern multiple ionic species such as paired and unpaired ions in the NMR spectra in this study.

Figure 2.S1 Representative NMR spectra. Representative NMR spectra are given for a PFPE$_{D10}$-Diol electrolyte. In (a), the $^7$Li spectrum is given, and in (b), the $^{19}$F spectra is given.
ABSTRACT

Incipient microphase separation is observed by wide angle X-ray scattering (WAXS), in short chain multiblock copolymers consisting of perfluoropolyether (PFPE) and poly(ethylene oxide) (PEO) segments. These materials have several applications including solvents for non-flammable Li battery electrolytes. Two PFPE-PEO block copolymers were studied, one with dihydroxyl endgroups and one with dimethyl carbonate endgroups. Despite having a low degree of polymerization (N ~ 10), these materials exhibit significant scattering intensity, due to disordered concentration fluctuations between the PFPE-rich and PEO-rich domains. The disordered scattering intensity was fit to a model based on a multi-block random phase approximation to determine the value of the interaction parameter, $\chi$, and the radius of gyration, $R_g$. Over the temperature range 30-90 °C, the values of $\chi$ were determined to be very large (~2-2.5), indicating a high degree of immiscibility between the PFPE and PEO blocks. For hydrocarbon-based block copolymers, disordered scattering intensity is typically only detected for larger molecules, at small angles, with the scattering vector, $q$, below 1 nm$^{-1}$. In PFPE-PEO, due to the large electron density contrast between the fluorinated and non-fluorinated block and the high value of $\chi$, disordered scattering was detected at intermediate scattering angles, ($q \sim 2$ nm$^{-1}$) for relatively small polymer chains. In the context of salt-containing PFPE-PEO electrolytes, the finding that PFPE-PEO polymers contain nanoscale heterogeneity raises the question of how salt is distributed in the PFPE-rich and PEO-rich domains.

3.1 Introduction

Perfluoropolyethers (PFPE) are a class of short chain polymers that are traditionally used as lubricants. More recent applications of these materials includes antifouling surface coatings, lithium battery electrolytes, and surfactants. In this chapter, we study the thermodynamic properties of four PFPEs described in Table 3.1. The two versions of diol-terminated PFPEs are commercially available: PFPE$_{D10}$-Diol and PFPE$_{E10}$-Diol (see Table 3.1 for structures). PFPE$_{D10}$-Diol is a random copolymer of CF$_2$CF$_2$O and CF$_2$O groups with diol endgroups. PFPE$_{E10}$-Diol can be thought of as a short triblock copolymer with two short poly(ethylene oxide) (PEO) chains attached to the fluorinated random copolymer. In a previous publication, we demonstrated that simple chemical reactions may be used to convert the diol endgroups into dimethyl carbonate (DMC) endgroups to give PFPE$_{D10}$-DMC and PFPE$_{E10}$-DMC. When viewed by the naked eye, all of these compounds appear to be simple homogeneous liquids. However, hydrocarbons such as PEO have very limited miscibility with fluorinated compounds. There is thus the possibility for the formation of small PEO-rich microphases in PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC.
DMC. The purpose of this chapter is to examine this possibility. Understanding the nanostructure and thermodynamics of phase separation in PFPE-PEO block copolymers is important to improving the performance of these materials.

Whether or not two-component block copolymers undergo microphase separation depends on the linear arrangements of the segments, the volume fraction of one of the components \( \phi \), the average number of statistical segments, \( N \), and the interaction parameter \( \chi \).\(^{13,14} \) In block copolymers, the chain architecture, volume fractions of each phase, and \( N \) are usually known from synthetic characterization of the polymer. However, a separate experiment is needed to determine \( \chi \). In this study, a new \( \chi \) value is reported for linear block copolymers consisting of ethylene oxide (EO) and perfluoroether (PFE) segments.

Several experimental techniques have been employed to measure the interaction parameter between A and B segments in a two-component block copolymer, and these are reviewed in reference \(^82\). In disordered block copolymers, concentration fluctuations between the A and B segments occur at a characteristic length scale, which can be detected via X-ray or neutron scattering experiments.\(^{83,84} \) These concentration fluctuations are described by the random phase approximation (RPA) theory developed by Leibler and later expanded on by Fredrickson and Helfand.\(^{12,85} \) Typically, scattering that occurs due to concentration fluctuations is observed at small angles, where the scattering vector, \( q = \frac{4\pi \sin \theta}{\lambda} \), is below approximately 1 nm\(^{-1} \) (corresponding to fluctuation length scales above ~5 nm). Here, \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the radiation. One method to determine \( \chi \) in block copolymers is to measure the small angle scattering intensity in a disordered block copolymer and to fit the scattering to the RPA model using \( \chi \) and the statistical segment length, \( l \), or radius of gyration, \( R_g \), as adjustable parameters.\(^{83,84} \) For microphase-separated block copolymers, \( \chi \) can be estimated from the domain spacing, by applying strong segregation theory and self-consistent mean field theory.\(^{13,86,87} \) The interaction parameter can also be estimated by comparing theoretical and experimental order-disorder transition temperatures.

In contrast to previous methods reported in the literature, we use a wide angle X-ray scattering (WAXS) configuration to measure the disordered scattering intensity, due to the short chain lengths of the materials studied. Given the relatively large scattering intensity, angle-dependent scattering corrections are developed to reduce and fit the scattering data. In the RPA model, the polymers are assumed to be monodisperse.\(^{12} \) Modifications have been proposed to account for polymers with a unimodal molecular weight distribution described by the dispersity, \( D \).\(^{58} \) The PFPE\(_{10}\) materials used in this study are based on commercial materials which are known to exhibit some degree of chain coupling. Furthermore, the reaction to produce PFPE\(_{10}\)-DMC polymer from the PFPE\(_{10}\)-Diol precursor has been shown to increase chain coupling. In light of the documented chain coupling, we adapt the RPA model to include contributions from the uncoupled ABA triblock, the dimer, an ABABA pentablock, the trimer, an ABABABA heptablock, and the tetramer, an ABABABABA nonablock. Using WAXS measurements and multiblock RPA, we report on the structure and interaction strength in short chain PFPE-PEO block copolymers.
Table 3.1 Structure of polymers used in this study. The average numbers of the tetrafluoroethylene oxide groups, \( m \), the difluoromethylene oxide groups, \( n \), and the ethylene oxide groups, \( q \) are given. The number of ethylene oxide groups per chain is \( 2q \).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure of Uncoupled Component</th>
<th>( m )</th>
<th>( n )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPE(_{D10})-Diol</td>
<td>( \text{[Structure]} )</td>
<td>7</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>PFPE(_{D10})-DMC</td>
<td>( \text{[Structure]} )</td>
<td>7</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>PFPE(_{E10})-Diol</td>
<td>( \text{[Structure]} )</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>PFPE(_{E10})-DMC</td>
<td>( \text{[Structure]} )</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

3.2 Experimental Section

3.2.1 Materials

The polymer PFPE\(_{D10}\)-Diol was purchased from Santa Cruz Biotechnology and PFPE\(_{E10}\)-Diol from Solvay-Solexis. They have since been discontinued from production; however, PFPEs with other endgroups are still commercially available. The polymers PFPE\(_{D10}\)-DMC and PFPE\(_{E10}\)-DMC were synthesized from the respective diols. The synthesis and characterization of the dimethyl carbonate polymers were reported previously.\(^{60,64}\) As a reference, a low molecular weight, liquid PEO was also studied. The PEO was purchased from Polymer Source and the number-averaged molecular weight \( M_n \) of the PEO is 400 g mol\(^{-1}\). All materials were dried prior to use at room temperature for 72 h under vacuum in a glovebox antechamber. Subsequently, materials were handled in an Ar glovebox with water level below 1 ppm and O\(_2\) level below 5 ppm or sealed in air-tight sample holders.

The structures of the polymers used in this study, PFPE\(_{D10}\)-Diol, PFPE\(_{D10}\)-DMC, PFPE\(_{E10}\)-Diol, and PFPE\(_{E10}\)-DMC are shown in Table 3.1. The PFPE chains are random copolymers of CF\(_2\)CF\(_2\)O, tetrafluoroethylene oxide (TFEO), and CF\(_2\)O, difluoromethylene oxide (DFMO), and the average ratios of these components, \( m \) and \( n \), taken from reference Y, are given in Table 3.1.\(^{64}\) In the PFPE\(_{E10}\) polymers, the average number of EO units per chain is given by \( 2q \). In reference 64, a combination of mass spectrometry, nuclear magnetic spectroscopy and gel permeation chromatography were used to elucidate the structures of the PFPE polymers. The PFPE\(_{D10}\) materials were reported to have unimodal molecular weight distributions, while both the as-received and DMC-modified PFPE\(_{E10}\) materials exhibited chain coupling. The volume fractions of the coupled components, \( \phi_1 - \phi_4 \) are shown in Table 3.2. The fraction \( \phi_1 \) represents the uncoupled PFPE\(_{E10}\) chain, which we regard as an ABA triblock copolymer where A is the PEO chain and B is the average PFPE chain. The number average molecular weight and dispersity of the uncoupled polymers, \( M_{n,1} \) and \( D_1 \), are given in Table 3.2. The higher order fractions can
be viewed as ABABA pentablocks ($\varphi_2$), ABABABA heptablocks ($\varphi_3$), and ABABABABA nonablocks, where the internal A blocks are twice as long as the terminal A blocks. The number-averaged molecular weight and dispersity, averaged over all of the coupled components, $M_{n,Ave}$ and $D_{Ave}$, are also given in Table 3.2.

Table 3.2 Composition and molecular weight of polymers. The number average molecular weight and dispersity are given for both the mixtures of coupled components, $M_{n,Ave}$ and $D_{Ave}$, and the simple, uncoupled ABA triblock, $M_{n,1}$ and $D_1$. The volume fractions of each component, the uncoupled, monomeric chain, dimer, trimer and tetramer are given by $\varphi_1$, $\varphi_2$, $\varphi_3$, and $\varphi_4$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{n, Ave}$</th>
<th>$D_{Ave}$</th>
<th>$M_{n,1}$</th>
<th>$D_1$</th>
<th>$\varphi_1$</th>
<th>$\varphi_2$</th>
<th>$\varphi_3$</th>
<th>$\varphi_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPE-Diol</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PFPE-DMC</td>
<td>1.1</td>
<td>1.0</td>
<td>1.1</td>
<td>-</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PFPE-Diol</td>
<td>1.5</td>
<td>1.1</td>
<td>1.3</td>
<td>1.03</td>
<td>0.88</td>
<td>0.09</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>PFPE-DMC</td>
<td>1.9</td>
<td>1.3</td>
<td>1.5</td>
<td>1.03</td>
<td>0.43</td>
<td>0.25</td>
<td>0.05</td>
<td>0.27</td>
</tr>
</tbody>
</table>

### 3.2.2 Wide Angle X-Ray Scattering

Samples for WAXS experiments were prepared in a glovebox and sealed in airtight aluminum cells. To mount the liquid samples, a 0.794 mm thick, chemically-resistant, fluoro-elastomer (tradename Aflas) spacer with a 3.175 mm diameter hole was placed on a 25 μm X-ray transmissive polyimide window. Polymer sample (6 μL) was dispensed into the hole, and a second polyimide window was placed on top without trapping bubbles in the liquid sample. Samples were placed in airtight aluminum holders, which were mounted onto a homebuilt temperature controlled stage, up to 8 at a time. Measurements were taken between 30 °C and 90 °C, at intervals of 15 °C, after waiting 45 min at each temperature. The temperatures of the holders were monitored in an offline heating experiment and found to be within ±2 °C of the set temperature for every temperature and sample position in the heating stage.

Wide angle X-ray scattering (WAXS) experiments were performed at beamline 7.3.3 at the Advanced Light Source synchrotron in Berkeley, California, USA. The X-ray energy was 10 keV, and the detector was a Pilatus 2M camera by Dectris, with a pixel size of 0.172 x 0.172 mm. The incident beam intensity was measured by an ion gauge, and the transmitted intensity was measured by a photodiode on the beamstop. The scattering vector and the sample-detector distance were calibrated with a silver behenate standard, using the first five Bragg diffraction peaks, and the sample-detector distance was determined to be 283 mm. An exposure time of 60 s was used for the polymer samples. Two-dimensional scattering patterns were azimuthally averaged and reduced to one-dimensional scattering profiles using the Nika package for IgorPro.

Wide angle scattering profiles were corrected for scattering due to the polyimide windows and due to beam divergence, and the scattering intensity was calibrated as described in reference 91. In the wide angle regime, background subtraction must account
for the angle-dependent transmission of X-rays through the sample because X-rays scattered at wide angles travel a longer distance through the scattering object than X-rays scattered at smaller angles. In small angle scattering, this effect can be neglected. In addition, intensity due to beam spreading may contribute to the measured signal. To aid in the intensity calibration and background subtraction, WAXS profiles were obtained for air (1 s and 60 s exposures), a blank cell containing polyimide windows but no polymer sample (60 s exposure), and a 1 mm thick glassy carbon standard for intensity calibration (sample M13, Jan Ilavsky, 1 s exposure). Equation 3.1, derived in reference 91, gives the expression used for the background subtraction and beam spreading corrections.

\[
I_{corr}(q) = \frac{1}{T_w T_s(\theta)T_w^0 T_f^0} \times \left\{ \left[ I_{sam}(q) - DC \right] - \left[ \frac{(T_s^0 T_w^0 + T_w T_s)}{(T_s^0 + T_w)} \right] I_{ec}(q) - DC \right\} \left[ T_w^2 [I_b(q) - DC] \right] \tag{3.1}
\]

Here, \(I_{corr}(q)\) is the corrected, measured scattering intensity due to the sample, \(T\) is the total transmission, \(T(\theta)\) is the angle-dependent X-ray transmission for a moderately absorptive object (assuming no multiple-scattering events), \(T^0\) is the path-length-corrected X-ray transmission, \(I_{sam}(q)\) is the uncorrected, measured sample intensity, \(DC\) is the dark current signal, \(I_{ec}(q)\) is the measured empty cell or polyimide blank cell intensity, \(I_b(q)\) is the measured background or air intensity (60 s exposure). The subscript \(w\) represents one window, \(s\) represents the free-standing sample, and \(fp\) represents the post-sample flight path. The total transmission \(T\) is given by equation 3.2, where \(\mu\) is the linear absorption coefficient and \(z\) is the thickness of the scattering object.

\[ T = e^{-\mu z} \tag{3.2} \]

The angle-dependent transmission, \(T(\theta)\) for a moderately absorbing, thick object (assuming no multiple scattering events) is defined by equation 3.3.

\[ T(\theta) \equiv T\left(\frac{r_a(\theta) - 1}{a(\theta) \ln(T)}\right); \quad a(\theta) = \frac{1}{\cos \theta} - 1 \tag{3.3} \]

Path-length-dependent transmission is defined by equation 3.4.

\[ T^\theta \equiv e^{\left(\frac{-\mu z}{\cos \theta}\right)} = T^{\frac{1}{\cos \theta}} \tag{3.4} \]

In our experiments, since detectors with different mechanisms and gains are used to measure the beam intensity before and after the sample (ion chamber and photodiode), we do not directly measure the absolute transmission given by equation 3.2. Instead we measure an apparent transmission \(T^{Obs} = I^{PD}/I^{IC}\), where \(I^{PD}\) is the measured response from the post-sample photodiode and \(I^{IC}\) is the measured response from the pre-sample ion chamber. The absolute transmissions can be estimated from these quantities by the
following relationships (equations 3.5-3.7):

\[ T_s = \frac{T_{\text{sam}}^{\text{Obs}}}{T_{\text{ec}}^{\text{Obs}}} \]  \hspace{1cm} (3.5)

\[ T_w = \left( \frac{T_{\text{ec}}^{\text{Obs}}}{T_b^{\text{Obs}}} \right)^{1/2} \]  \hspace{1cm} (3.6)

\[ T_{fp} \approx \left( \frac{e^{-\mu_b z_b}}{T_b^{\text{Obs}}} \right) \]  \hspace{1cm} (3.7)

where \( T_{\text{sam}}^{\text{Obs}} \) is the apparent transmission from the entire sample including windows, \( T_{\text{ec}}^{\text{Obs}} \) is the apparent transmission from the polyimide blank cell, \( T_b^{\text{Obs}} \) is the apparent transmission from air, \( \mu_b \) is the linear absorption coefficient of dry air at 25 °C (5.65 \times 10^{-3} \text{ cm}^{-1} \), and \( z_b \) is the sample-detector distance, 283 mm. In equation 3.6, the ratio of apparent transmissions is raised to the \( \frac{1}{2} \) power to account for the presence of two polyimide films in the blank cell.

A constant intensity calibration factor was determined using a glassy carbon standard. The measured intensity was corrected for beam spreading by subtracting the scattering from air according to equation 3.8:

\[ I_{\text{corr}}(q) = \frac{1}{T_s(\theta) T_{fp}^\theta} \times \left\{ \frac{[I_{\text{sam}}(q) - DC]}{-T_s[I_b(q) - DC]} \right\} \]  \hspace{1cm} (3.8)

where, in this case, the sample is glassy carbon without polyimide windows, and the scattering from the sample, \( I_{\text{sam}}(q) \), and air, \( I_b(q) \), were measured using a 1 s exposure. A constant calibration factor was determined by scaling the measured, corrected scattering profile from glassy carbon to match the known absolute scattering profile from the M13 glassy carbon sample.
3.3 Results

Figure 3.1 WAXS profiles. In (a), WAXS profiles of PFPE and PEO polymers are shown at 30 °C. Traces are offset for clarity. In (b), intensity-calibrated WAXS profiles are shown for the polymer PFPE_{E10}-Diol at temperatures ranging from 30 to 90 °C. In (c), the first peak of the PFPE_{E10}-Diol scattering profiles is shown in more detail.

In Figure 3.1a, scattering profiles are shown for the PFPE and PEO polymers at 30 °C. The block copolymers PFPE_{E10}-Diol and PFPE_{E10}-DMC have a peak in the vicinity of $q_1 \approx 2 \ \text{nm}^{-1}$, which is not present in the profiles of the pure PFPE or PEO polymers. Because the $q_1$ peak is present only in the block copolymers and its intensity decreases with temperature, we attribute the $q_1$ peak to concentration fluctuations in a disordered block copolymer. The temperature dependence of the $q_1$ peak can be seen in Figures 3.1b and 3.1c. In Figure 3.1b, the temperature dependence of the scattering profiles is shown for the polymer PFPE_{E10}-Diol. The temperature-dependent scattering of the other polymers is included in the Supporting Information. In Figure 3.1c, the temperature-dependence of the $q_1$ peak in the PFPE_{E10}-Diol polymer is shown in more detail. The intensity of the $q_1$ peak
decreases significantly with temperature, despite an apparent increase in the background intensity in the region \( q = 0 - 12 \text{ nm}^{-1} \) (Figure 3.1b). With increasing temperature, the \( q_1 \) peak shifts to higher values of \( q \). The dependence of the shape of the \( q_1 \) peak on temperature is consistent with its attribution to disordered polymer scattering.

In Figure 3.1a, all polymers, both PFPE\(_{E10}\) block copolymers and PFPE\(_{D10}\) and PEO single-phase polymers, show two similar peaks, one in the vicinity of \( q_2 \approx 12 - 15 \text{ nm}^{-1} \), and one in the vicinity of \( q_3 \approx 30 \text{ nm}^{-1} \). These correspond to characteristic spacings, \( d = 2\pi/q \), of \( d_2 \approx 0.4 - 0.5 \text{ nm} \) and \( d_3 \approx 0.2 \text{ nm} \). The \( q_2 \) peak is at significantly different positions between the PFPE-containing polymers and pure PEO, while the \( q_3 \) peak is at similar positions for all of the polymers. The position of the maximum of the \( q_2 \) peak, \( q_{2,\text{max}} \), is reported for the PFPE polymers as a function of temperature in Figure 3.2. The effect of temperature on the \( q_2 \) and \( q_3 \) peaks in PFPE\(_{E10}\)-Diol is qualitatively similar to the that in the other polymers (Figures 3.1b, 3.2 and 3.S1). The intensities of the \( q_2 \) and \( q_3 \) peaks remain relatively constant with temperature. With increasing temperature, the \( q_2 \) peak shifts to lower \( q \), and the \( q_3 \) peak remains nearly constant.

Based on these observations, we attribute the \( q_2 \) peak to interchain correlation lengths and the \( q_3 \) peak to the bond distances in the polymer chains. In Figure 3.2, the value of \( q_{2,\text{max}} \) is slightly higher for the DMC-terminated polymers than the diol-terminated ones, suggesting that for the DMC-terminated polymers, the chain packing is slightly denser. This could be due to hydrogen bonding in the diol-terminated polymers. For PEO, the value of \( q_{2,\text{max}} \) ranges from 14.8 – 15.2 nm\(^{-1} \). These values are considerably lower than the values for the PFPE polymers presented in Figure 3.2, suggesting that the PFPE chains have a larger characteristic spacing than the PEO chains. This is consistent with the fact that the C-F bonds in PFPE are longer than the C-H bonds in PEO, and the fact the perfluoroalkane segments are generally more rigid than non-fluorinated alkane segments.

The \( q_1 \) peak in the block copolymer scattering profiles can be used to determine the
interaction parameter between the PFPE and PEO blocks, as well as the radius of gyration, \( R_g \) of the chain. Given the multimodal molecular weight distributions of the PFPE_{E10} materials (see Table 3.2), we use a multiblock RPA model. Based on the RPA theory of Leibler, the scattering due to a monodisperse disordered block copolymer is given by equation 3.9,\(^{12,24}\)

\[
I_{\text{dis}}(q) = \nu_{\text{ref}} \left( \frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2 \left[ \frac{S(q)}{W(q)} - 2\chi \right]^{-1}
\]  

(3.9)

Here, \( I_{\text{dis}}(q) \) is the disordered scattering intensity, \( \nu_{\text{ref}} \) is a reference volume taken to be 0.1 nm\(^3\) in this study, \( b_i \) is the scattering length of block \( i \), \( v_i \) is the monomer volume for block \( i \), and \( S(q) \) and \( W(q) \) are the determinant and sum of matrix elements of the structure factor matrix, \([S_{ij}]\). The scattering length, \( b_{PFPE} \) of the PFPE block was calculated by taking the average of the scattering lengths of the TFEO and DFMO monomers, weighted by the coefficients \( m \) and \( n \), given in Table 3.1. We neglect any scattering contribution from the diol or DMC endgroups. The monomer volumes were calculated by equation 3.10,

\[
v_i = \frac{M_i}{\rho_i N_A v}
\]

(3.10)

where \( M_i \) is the molar mass of the monomer, \( \rho_i \) is the bulk density of the pure PEO or PFPE phase, and \( N_A \) is Avagadro’s number. The values for \( M_i \) used in this study are 44.05 g mol\(^{-1}\) for EO, and 93.79 g mol\(^{-1}\) for PPE, the weighted average of the masses of the TFEO and DFMO monomers. The density of both components was assumed to be roughly independent of temperature. The values for density used in this study are 1.12 g cm\(^{-3}\) for EO, based on the relationship 1.139 [g cm\(^{-3}\)] – 7.31 x 10\(^{-4}\) [g cm\(^{-3}\) °C\(^{-1}\)] x T at 30 °C, and 1.77 g cm\(^{-3}\) for PFPE, based on the manufacturer’s data on the density of PFPE_{D10-Diol}.\(^{94}\)

The scattering contrast \( c \), is defined by the prefactor in equation 3.9: \( c \equiv \nu_{\text{ref}} \left( \frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2 \), and for the PFPE_{E10} polymers the theoretical value is \( c_{th} = 0.17 \) cm\(^{-1}\).

To account for the polydispersity of our samples, we regard the samples to be mixtures of monodisperse, coupled components. The scattering of the mixture, \( I_{\text{dis, mix}}(q) \), is taken to be the sum of scattering from each coupled component, \( I_{\text{dis,k}}(q) \), weighted by the volume fraction of the component, \( \varphi_k \) (equation 3.11). Here, component \( k \) consists of \( k \) chains, with \( k = 1 \) being the uncoupled chain.

\[
I_{\text{dis, mix}}(q) = \sum_{k=1}^{4} \varphi_k * I_{\text{dis,k}}(q)
\]

(3.11)

The scattering of each component, \( I_{\text{dis,k}}(q) \) is calculated according to equation 3.9, where RPA is used to calculate \([S_{ij}]_k \), \( S_k(q) \) and \( W_k(q) \) for each component by treating component 1 as an ABA triblock, component 2 as an ABABA pentablock, component 3 as an ABABABA heptablock, and component 4 as an ABABABABA nonablock.\(^{95}\) The expressions for \( S_k(q) \) and \( W_k(q) \) are given in equations 3.12 -3.15.

\[
S_k(q) = g_{AA,k}(x) + 2g_{AB,k}(x) + g_{BB,k}(x)
\]

(3.12)
\( W_k(q) = g_{AA,k}(x)g_{BB,k}(x) - [g_{AB,k}(x)]^2 \)  
\hspace{1cm} (3.13)
\[ g_{AB,k}(x) = g_{BA,k}(x) \]
\hspace{1cm} (3.14)
\[ x \equiv q^2 R_{g_1}^2 \]
\hspace{1cm} (3.15)

Here, \( g_{AB,k}(x), g_{AA,k}(x), \) and \( g_{BB,k}(x) \), represent the elements of the structure factor matrix \([S_{ij}]_k\). Expressions for these terms depend on the block architecture, and are given in the supporting information for each coupled polymer, \( k \). The expressions for \( S_k(q) \), \( W_k(q) \), and hence \( I_{dis,k}(q) \), depend on the radius of gyration and degree of polymerization of each component, \( R_{g,k} \) and \( N_k \), and the volume fraction of the PFPE block, \( \phi_{PFPE} \), which is the same for every component. The values \( R_{g,k} \) and \( N_k \) can be expressed in terms of \( R_{g,1} \) and \( N_1 \), the values for the uncoupled component (equations 3.16 and 3.17), by assuming a Gaussian chain. The radius of gyration can also be expressed in terms of the statistical segment length, \( l \).

\[ R_{g,k} = \sqrt{k} R_{g,1} = \sqrt{\frac{k N_k}{6}} l \]  
\hspace{1cm} (3.16)
\[ N_k = k N_1 \]  
\hspace{1cm} (3.17)

The degree of polymerization, \( N_1 \), calculated from equations 3.18 and 3.19, is 10.5.\(^{82}\)

\[ N_1 = N_{PEO} + N_{PFPE} \]  
\hspace{1cm} (3.18)
\[ N_i = \frac{\tilde{N}_i v_i}{v_{ref}} \]  
\hspace{1cm} (3.19)

Here, \( \tilde{N}_i \) is the number of monomers in an uncoupled chain, \( 2q \) for EO and \( m + n \) for PFE (Table 3.1). The volume fraction of PFPE, \( \phi_{PFPE} \), given by equation 3.20, is 0.75.

\[ \phi_{PFPE} = \frac{v_{PFPE}}{v_{PFPE} + \frac{\tilde{N}_{PEO} v_{PEO}}{\tilde{N}_{PFPE}}} \]  
\hspace{1cm} (3.20)

From Figure 3.1b-c, it is apparent that the \( q_2 \) peak and a temperature-dependent background contribute to the disordered scattering intensity at the \( q_1 \) peak. There are several phenomena that contribute to background scattering in the WAXS regime including thermal density fluctuations, incoherent scattering, and Compton scattering.\(^{96,97}\) These contributions are not removed by the empty cell background subtraction, and it is difficult to account for all of them using fundamental models. Vonk et al. treat the background for a disordered polypropylene sample as a function of the form \( a_0 + a_1 q^4 \), which reduces to a simple constant, \( a_0 \) at small and intermediate scattering angles.\(^{98}\) Following the method of Vonk, we fit the background, \( I_{bg}(q) \), with a constant, \( a_0 \), and a Lorentzian due to the contribution of \( q_2 \) (equation 3.21).
Here, $a_0$, $a_1$, and $a_2$ are adjustable parameters, and $q_{2,max}$ is the scattering vector at the maximum of the $q_2$ peak, given in Figure 3.2.

The values of $R_{g,1}$, and $\chi$ are determined by fitting the model for the total scattering intensity, $I_{\text{tot}}(q)$, (equation 3.22) to the scattering profiles for PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC.

\begin{equation}
I_{\text{tot}}(q) = I_{bg}(q) + I_{\text{dis,mix}}(q)
\end{equation}

The term, $I_{\text{dis,mix}}(q)$, can be fit by as few as two adjustable parameters, $R_{g,1}$, and $\chi$. Due to uncertainty in the density of the PFPE block as a function of temperature, $c$ is used as an additional fit parameter. For the values of $R_{g,1}$ and $\chi$ reported herein, $I_{\text{tot}}(q)$ is fit using six parameters, $R_{g,1}$, $\chi$, $c$, $a_0$, $a_1$, and $a_2$, in the $q$ range of 1 - 10 nm$^{-1}$, where the approximation of using a constant background is valid. The values of $R_{g,1}$ and $\chi$, determined using the fixed value of $c = 0.17$ cm$^{-1}$, are reported in the Supporting Information. The values of $R_{g,1}$ and $\chi$ are similar between fits with $c$ as an adjustable or fixed parameter. The fixed parameters using the model in equation 3.22 are summarized in Table 3.3. An example of a fit based on equation 3.22 is shown in Figure 3.3a, in comparison with the experimental data for PFPE$_{E10}$-Diol at 30 °C. In Figure 3.3b, the disordered scattering components from both the experimental data and the fit, $I_{\text{dis,mix}}$, are shown for PFPE$_{E10}$-Diol as a function of temperature. The experimental data is plotted by subtracting the background component of the fits, $I_{bg}$, from the data in Figure 3.1c. Figure 3.3b shows that at all temperatures, the intensity due to disordered scattering decays to zero away from the peak.

Table 3.3 Fixed parameters used in random phase approximation model. The parameters given below are the scattering lengths, $b_1$, monomer molar masses, $M_1$, densities, $\rho_1$, monomer volumes, $v_1$, reference volume, $v_{\text{ref}}$, theoretical contrast, $c_{\text{th}}$, degree of polymerization, $N_1$, and volume fraction of PFPE, $\phi_{\text{PFPE}}$.

<table>
<thead>
<tr>
<th>$b_{\text{PEO}}$ (nm)</th>
<th>$b_{\text{PFPE}}$ (nm)</th>
<th>$M_{\text{EO}}$ (g mol$^{-1}$)</th>
<th>$M_{\text{PFPE}}$ (g mol$^{-1}$)</th>
<th>$\rho_{\text{PEO}}$ (g cm$^{-3}$)</th>
<th>$\rho_{\text{PFPE}}$ (g cm$^{-3}$)</th>
<th>$v_{\text{EO}}$ (nm$^3$)</th>
<th>$v_{\text{PFPE}}$ (nm$^3$)</th>
<th>$v_{\text{ref}}$ (nm$^3$)</th>
<th>$c_{\text{th}}$ (cm$^{-1}$)</th>
<th>$N_1$</th>
<th>$\phi_{\text{PFPE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.76 x 10$^{-4}$</td>
<td>1.28 x 10$^{-5}$</td>
<td>44.05</td>
<td>93.79</td>
<td>1.12</td>
<td>1.77</td>
<td>6.53 x 10$^{-2}$</td>
<td>8.80 x 10$^{-2}$</td>
<td>0.1</td>
<td>0.17</td>
<td>10.5</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Figure 3.3. Comparison of fits based on the random phase approximation (RPA) model and experimental wide angle X-ray scattering data. In (a), a scattering profile from PFPE<sub>E10</sub>-Diol at 30 °C is shown along with the fit to the RPA model. The fit, \( I_{\text{tot}} \), is broken down into the disordered scattering, and background components, \( I_{\text{dis, mix}} \), and \( I_{\text{bg}} \). In (b), the isolated disordered scattering component is shown for PFPE<sub>E10</sub>-Diol as a function of temperature. The markers represent the difference between the experimental data and the background component of the fit \( I_{\text{bg}} \), and the solid lines represent the disordered scattering component of the fit, \( I_{\text{dis, mix}} \).

The values of \( R_{g,1} \), \( \chi \), and \( c \), determined by fitting equation 3.22 to the scattering data, are shown in Figure 3.4. The values of the fit parameters \( a_0 \), \( a_1 \), and \( a_2 \) are given in the Supporting Information. For both PFPE<sub>E10</sub>-Diol and PFPE<sub>E10</sub>-DMC, \( R_{g,1} \sim 1 \) nm, and decreases with temperature, as for most block copolymers. The corresponding values of \( l \) (equation 3.12) are in the vicinity of 0.8 - 0.9 nm, close to the values published by Cotts for various copolymers consisting of EO, TFEO and DFMO segments.\(^99\) In the work of Cotts, values of \( l \) of 0.8 to 1.0 nm were obtained by intrinsic viscosity measurements in conjunction with a worm-like chain model.\(^99,100\) Though the magnitude of \( l \) in Figure 3.4a is consistent with the data of Cotts, the strength of the dependence of \( l \) on temperature is likely overestimated because density and \( N_1 \) were assumed to be temperature-independent. The value of \( R_{g,1} \) is slightly larger for PFPE<sub>E10</sub>-DMC than for PFPE<sub>E10</sub>-Diol.
Figure 3.4 Random phase approximation parameters. In (a), the radius of gyration and statistical segment length, $R_g$ and $l$ are given for PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC as a function of temperature. In (b), the interaction parameter, $\chi$ is shown. The lines through the data in (b) represent fits to equation 3.23. The quantity $\chi N_1$ is also given for reference. In (c), the contrast term, $c$, is shown. The dashed line in (c) represents the theoretical contrast value, $c_{th} = 0.17$ cm$^{-1}$. In (a-c), the error bars give the uncertainty in the fit to the data.

Figure 3.4b shows the temperature dependence of $\chi$. The solid lines are fits based on equation 3.23. In Table 3.4, the values of $A$ and $B$ are reported for both RPA models, the model with $c$ as a variable parameter corresponding to the data reported in Figure 3.4, and the model with fixed $c = c_{th} = 0.17$ cm$^{-1}$, corresponding to the data reported in the Supporting Information (Figure 3.S2).

$$\chi(T) = A + \frac{B}{T}$$  

(3.23)
Table 3.4 Temperature dependence of interaction parameter, $\chi$. The parameters $A$ and $B$ defined in equation 3.23 are given below for values of $\chi$ calculated by the RPA model with varying contrast parameter, $c$ and fixed $c$. The data supporting the RPA model with fixed $c$ is reported in the Supporting Information.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>PFPE$_{E10}$-Diol</td>
<td>2.3</td>
<td>84</td>
<td>2.3</td>
<td>106</td>
</tr>
<tr>
<td>PFPE$_{E10}$-DMC</td>
<td>1.8</td>
<td>180</td>
<td>1.2</td>
<td>355</td>
</tr>
</tbody>
</table>

From Table 3.4, it is evident that the magnitude of $\chi$ determined using the variable $c$ model is comparable to the magnitude of $\chi$ determined using the fixed $c$ model, over the temperature range studied. In the fixed $c$ model, $\chi$ is a stronger function of temperature because all of the temperature dependence is accounted for by the $\chi$ parameter. In the variable $c$ model, $\chi$ is a slightly weaker function of temperature because $c$ and $\chi$ are both allowed to vary with temperature. In both models, values of $\chi$ are lower for PFPE$_{E10}$-DMC than for the PFPE$_{E10}$-Diol, suggesting that endgroups may play a role in miscibility; however, we have not directly accounted for the effects of endgroups on $\chi$ in this study.$^{101,102}$

The high values of $\chi$ in the PFPE$_{E10}$ polymers indicate low miscibility between the PEO and PFPE blocks (see Figure 3.4b). The values of $\chi$ for the PEO-PFPE block copolymers are much higher compared to those for other block copolymer used in electrolytes, for example polystyrene-\emph{block}-poly(ethylene oxide) (SEO).$^{24,103,104}$ Cochran \emph{et al.} found values of $\chi = 0.075$ for SEO of 150 kg mol$^{-1}$ at 30 $\degree$C, and Zhu \emph{et al.} found a similar value of $\chi = 0.063$ for SEO of 18 kg mol$^{-1}$ at 30 $\degree$C. High $\chi$ values have also been reported in other block copolymers with fluorinated and non-fluorinated segments.$^{87,105,106}$ The high values of $\chi$ obtained in this study are somewhat surprising given that there have been previous reports on miscible blends of PFPE and PEO homopolymers; however, this miscibility is not necessarily inconsistent with the high values of $\chi$ measured in the PFPE-PEO block copolymers.$^{73,79}$ The relationship between $\chi$ for homopolymer blends and block copolymers is not well established. Some studies report agreement between values of $\chi$ determined in blends and block copolymers,$^{107}$ while others report discrepancies.$^{108}$ In reference 73, the miscibility between PFPE$_{D10}$-Diol and PEO of similar degrees of polymerization ($N_{PFPE} = 9.48$ and $N_{PEO} = 5.94$, based on equation 3.19) was shown to be highly asymmetric, an indication that the blend does not follow Flory-Huggins thermodynamics. Assuming the phase separation behavior of the PFPE/PEO blend does follow Flory-Huggins theory, the upper limit of $\chi$ can be estimated from equations 3.24 and 3.25, where $N_{Ave}$ is the average degree of polymerization.$^{109}$

$$N_{Ave} = \frac{4}{\left(\frac{1}{\sqrt{N_{PFPE}}} + \frac{1}{\sqrt{N_{PEO}}}\right)^2} \quad (3.24)$$

$$\chi N_{Ave} = 2 \quad \text{at the critical point} \quad (3.25)$$

From equations 3.24 and 3.25, the upper limit for $\chi$ for a symmetric PFPE/PEO blend is approximately 0.27. The discrepancy between $\chi$ in blends and block copolymers
is a nontrivial issue that we do not attempt to resolve herein.

Although in literature, $\chi$ values have been reported for short chain block copolymers with $N$ below 100,\textsuperscript{24,87,110} and as low as 36,\textsuperscript{111} there are limitations to the generality of the $\chi$ values reported in this study due to the short chain lengths of polymers. Both theoretical and experimental work have shown that $\chi$ decreases with increasing $N$.\textsuperscript{24,88,112} Mori \textit{et al.} report an experimental relationship of $\chi \sim N^{-0.5}$ for polystyrene-\textit{block}-polyisoprene ($N = 100$-1000),\textsuperscript{88} and Teran \textit{et al.} report an experimental relationship of $\chi \sim N^{-1}$ for SEO ($N = 20$ – 50).\textsuperscript{24} Given the low molecular weights of the polymers used in this study, it is likely that the values of $\chi$ in Figure 3.4b overestimate $\chi$ for infinitely long PFPE-PEO block copolymers. An investigation of the effect of $N$ on $\chi$ is outside the scope of this study. It should also be noted that the values of $\chi N$, also given in Figure 3.4b, are high compared to the critical values above which microphase separation occurs. These were determined numerically to be: $(\chi N)_{\text{critical}} = 27.51$ for PFPE$_{E10}$-Diol and $(\chi N)_{\text{critical}} = 26.93$ for PFPE$_{E10}$-DMC. The RPA theory is most accurate in the case where $\chi N$ is significantly lower than the critical value. The accuracy of the values obtained herein could perhaps be improved by using the fluctuation-corrected RPA model of Fredrickson and Helfand.\textsuperscript{85}

Figure 3.4c, shows the temperature dependence of the contrast term, $c$. Physically, the contrast in disordered scattering is due to the electron density difference between the A and B segments. The values of $c$ determined by fitting are remarkably similar to the theoretical value $c_{\text{th}} = 0.17$ (dashed line in Figure 3.4c), given the assumptions that went into the calculation of $c_{\text{th}}$. The bulk densities were assumed to be representative of the densities of the relatively short PEO and PFPE blocks, and the electron densities of the endgroups were neglected. For both polymers, $c$ decreases with temperature. A decrease in $c$ with temperature could indicate that the density decrease with temperature is stronger for PFPE segments than for PEO segments. The value of $c$ is higher for PFPE$_{E10}$-Diol than for PFPE$_{E10}$-DMC, consistent with the fact that the electron-rich DMC endgroup reduces the electron density difference between the PEO and PFPE blocks.

In theory, it is possible that scattering intensity of the $q_1$ peak is due to correlation hole scattering instead of concentration fluctuations characteristic of incipient microphase separation.\textsuperscript{113} Correlation hole scattering arises in block copolymers because the correlations between A-type segments on separate polymer chains is reduced due to the presence of the B chains. To verify that the $q_1$ peak is not due to correlation hole scattering, the WAXS data for PFPE$_{E10}$-Diol at 30 $^\circ$C is plotted along with the RPA model from equation 3.22, with $\chi = 0$ (Figure 3.5).\textsuperscript{114} Two limiting RPA-based models are shown, one with the highest and one with the lowest value of $c$ from Figure 3.4c. All other parameters are the same as the values from the variable $c$ fit for PFPE$_{E10}$-Diol at 30 $^\circ$C. Figure 3.5 shows that the correlation hole contribution to scattering is not enough to account for the observed intensity of the $q_1$ peak.
Figure 3.5. Correlation hole scattering. The data for PFPE_{E10}-Diol at 30°C is shown along with two models for correlation hole scattering. The models are based on the RPA fit to the PFPE_{E10}-Diol data with variable contrast, $c$, and interaction parameter, $\chi = 0$. Two bounding values of correlation hole scattering are shown, one with $c$ set to the lowest value found in this study, and one with $c$ set to the highest value.

To our knowledge, this is the first study in which scattering due to incipient microphase separation is detected using a WAXS experimental configuration. Disordered scattering intensity depends on $c$ and $\chi N$, where $N$ is typically much larger than $\chi$. In hydrocarbon-based block copolymers, $c$ is small, making it difficult to detect disordered scattering intensity from polymers with small enough $N$ to scatter in the WAXS regime. In the PFPE-PEO polymers, both $\chi$ and $c$ are large compared to hydrocarbon block copolymers, giving rise to detectable scattering intensity at relatively high scattering angles.

3.4 Conclusion

We present structural and thermodynamic information on PFPE and PFPE-PEO polymers with applications as solvents for nonflammable lithium-ion battery electrolytes, biofouling coatings and surfactants. Because of the short chain lengths of the polymers, WAXS was used to probe the structure. For the PFPE-PEO copolymers, PFPE_{E10}-Diol and PFPE_{E10}-DMC, disordered scattering was observed due to concentration fluctuations between the PEO and PFPE segments, signifying incipient microphase separation between the two phases. Due to the complex molecular weight distributions of the materials used, a model based on the multi-block random phase approximation was used to fit the disordered scattering data to determine the interaction parameter and radius of gyration of the polymers, $\chi$ and $R_g$.

The PFPE-PEO polymers were found to have large values of $\chi$, consistent with reports on other block copolymers consisting of fluorinated and non-fluorinated blocks. It is perhaps surprising that disordered scattering can be observed for such small chain block copolymers. The large values of $\chi$ and contrast factor, $c$ in the PFPE-PEO system allow these observations to be made despite small chain size. The properties of the PFPE-PEO electrolytes giving rise to high scattering contrast could enable measurements of thermodynamic quantities in size regimes that were previously inaccessible due to poor contrast. Though when viewed by the naked eye, the PFPE-PEO block copolymers appear to be homogeneous liquids, WAXS profiles and large values of $\chi$ imply that the PFPE-PEO block copolymers contain PEO-rich and PFPE-rich domains. In the context of lithium
battery electrolytes, large differences have been observed in the ion transport properties between electrolytes containing lithium salts and homopolymer PFPE$_{D10}$ versus those containing block copolymer PFPE$_{E10}$.

The heterogeneity of the PFPE$_{E10}$ materials could impact the ion transport properties of these electrolytes. Further work is needed to examine the structures of salt-containing PFPE and PFPE-PEO polymers.

3.5 Supporting Information

3.5.1 Wide angle X-ray scattering of PFPE polymers

In Figure 3.S1, WAXS profiles are shown for various PFPE polymers, at temperatures between 30 °C and 90 °C. The profiles in Figure 3.S1a and 3.S1b, for PFPE$_{D10}$-Diol and PFPE$_{D10}$-DMC, are qualitatively similar to each other, whereas the profiles in Figure 3.S1c, for PFPE$_{E10}$-DMC, are qualitatively similar to those in Figure 3.1b for PFPE$_{E10}$-Diol.

![WAXS profiles as a function of temperature for PFPE polymers. In (a-c) WAXS profiles are shown for PFPE$_{D10}$-Diol, PFPE$_{D10}$-DMC, and PFPE$_{E10}$-DMC, respectively.](image)

3.5.2 Structure Factors

The RPA structure factor is calculated for an ABA triblock of the sequence $f_1$-$f_2$-$f_3$, an ABABABA pentablock of the sequence $f_1$-$f_2$-$f_3$-$f_4$-$f_5$-$f_6$, an ABABABA heptablock of the sequence $f_1$-$f_2$-$f_3$-$f_4$-$f_5$-$f_6$-$f_7$-$f_8$, and an ABABABABA nonablock of the sequence $f_1$-$f_2$-$f_3$-$f_4$-$f_5$-$f_6$-$f_7$-$f_8$-$f_9$. Here, $f_n$ represents the volume fraction of a specific block in the sequence. For a polymer consisting of $k$ coupled chains ($k=1$ is the uncoupled ABA triblock), the individual block fractions can be related to the overall volume fraction of the B block, $\phi_{PFPE}$, according to the following equations.
\[ f_n = \frac{1 - \phi_{PFPE}}{2k} \] for terminal A blocks \((n = 1 \text{ or } k)\) \hfill (3.51)

\[ f_n = \frac{1 - \phi_{PFPE}}{k} \] for internal A blocks \((\text{odd } n, \text{ and } n \neq 1 \text{ or } k)\) \hfill (3.52)

\[ f_B = \frac{\phi_{PFPE}}{k} \] for B blocks, \((\text{even } n)\) \hfill (3.53)

The following relationships (equations 3.54-3.10) are valid for all of the multiblocks \((k \geq 1)\):

\[ S(q) = g_{AA}(x) + 2g_{AB}(x) + g_{BB}(x) \] \hfill (3.54)

\[ W(q) = g_{AA}(x)g_{BB}(x) - [g_{AB}(x)]^2 \] \hfill (3.55)

\[ g_{AB}(x) = g_{BA}(x) \] \hfill (3.56)

\[ x \equiv q^2R_{g,1}^2 \] \hfill (3.57)

\[ g^0(x) = \exp(-x) \] \hfill (3.58)

\[ g^1(x) = \frac{1 - \exp(-x)}{x} \] \hfill (3.59)

\[ g^2(x) = \frac{2(x + \exp(-x) - 1)}{x^2} \] \hfill (3.60)

In equation 3.511-3.619, \(n\) is the number labelling the specific block in the sequence.

\[ g_{n,n}(x) = f_n^2 g^2(f_n x) \] \hfill (3.511)

\[ g_{n,n+1}(x) = f_n f_{n+1} g^1(f_n x) g^1(f_{n+1} x) \] \hfill (3.512)

\[ g_{n,n+2}(x) = f_n f_{n+1} f_{n+2} g^1(f_n x) g^0(f_{n+1} x) g^1(f_{n+2} x) \] \hfill (3.513)

Equations 3.514-3.515 are used for calculation of the pentablock and larger chains \((k \geq 2)\):

\[ g_{n,n+3}(x) = f_n [f_{n+1} + f_{n+2}] f_{n+3} g^1(f_n x) g^0([f_{n+1} + f_{n+2}] x) g^1(f_{n+3} x) \] \hfill (3.514)

\[ g_{n,n+4}(x) = f_n [f_{n+1} + f_{n+2} + f_{n+3}] f_{n+4} g^1(f_n x) \times g^0([f_{n+1} + f_{n+2} + f_{n+3}] x) g^1(f_{n+4} x) \] \hfill (3.515)

Equations 3.516-3.517 are used for calculation of the heptablock and larger chains \((k \geq 3)\).
\[ g_{n,n+5}(x) = f_n[f_n + f_{n+2} + f_{n+3} + f_{n+4}]f_{n+5} \ g^1(f_n x) \]
\[ \times g^0([f_n + f_{n+2} + f_{n+3} + f_{n+4}]x) \times g^1(f_{n+5}x) \] (3.16)

\[ g_{n,n+6}(x) = f_n[f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5}]f_{n+6} \ g^1(f_n x) \]
\[ \times g^0([f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5}]x) \times g^1(f_{n+6}x) \] (3.17)

Equations 3.21-3.22 are used for calculation of the nonablock \((k = 4)\).

\[ g_{n,n+7}(x) = f_n[f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5} + f_{n+6}]f_{n+7} \ g^1(f_n x) \]
\[ \times g^0([f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5} + f_{n+6}]x) \times g^1(f_{n+7}x) \] (3.18)

\[ g_{n,n+8}(x) = f_n[f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5} + f_{n+6} + f_{n+7}]f_{n+8} \ g^1(f_n x) \]
\[ \times g^0([f_n + f_{n+2} + f_{n+3} + f_{n+4} + f_{n+5} + f_{n+6} + f_{n+7}]x) \times g^1(f_{n+8}x) \] (3.19)

For the triblock \((k = 1)\), the equations 3.20-3.22 are used to calculate the terms \(g_{AA}(x)\), \(g_{BB}(x)\), and \(g_{AB}(x)\). The commas in the subscripts on the right hand side of the equations are removed.

\[ g_{AA}(x) = g_{11}(x) + g_{33}(x) + 2g_{13}(x) \] (3.20)

\[ g_{BB}(x) = g_{22}(x) \] (3.21)

\[ g_{AB}(x) = g_{12}(x) + g_{23}(x) \] (3.22)

For the pentablock \((k = 2)\), the equations 3.23-3.25 are used to calculate the terms \(g_{AA}(x)\), \(g_{BB}(x)\), and \(g_{AB}(x)\).

\[ g_{AA}(x) = g_{11}(x) + g_{33}(x) + g_{55}(x) + 2g_{13}(x) + 2g_{15}(x) + 2g_{35}(x) \] (3.23)

\[ g_{BB}(x) = g_{22}(x) + g_{44}(x) + 2g_{24}(x) \] (3.24)

\[ g_{AB}(x) = g_{12}(x) + g_{14}(x) + g_{23}(x) + g_{25}(x) + g_{34}(x) + g_{45}(x) \] (3.25)

For the heptablock \((k = 3)\), the equations 3.26-3.28 are used to calculate the terms \(g_{AA}(x)\), \(g_{BB}(x)\), and \(g_{AB}(x)\).

\[ g_{AA}(x) = g_{11}(x) + g_{33}(x) + g_{55}(x) + g_{77}(x) + 2g_{13}(x) + 2g_{15}(x) + 2g_{17}(x) + 2g_{35}(x) + 2g_{37}(x) + 2g_{57}(x) \] (3.26)

\[ g_{BB}(x) = g_{22}(x) + g_{44}(x) + g_{66}(x) + 2g_{24}(x) + 2g_{26}(x) + 2g_{46}(x) \] (3.27)

\[ g_{AB}(x) = g_{12}(x) + g_{14}(x) + g_{16}(x) + g_{23}(x) + g_{25}(x) + g_{27}(x) + g_{34}(x) + g_{36}(x) + g_{45}(x) + g_{47}(x) + g_{56}(x) + g_{67}(x) \] (3.28)

34
For the nonablock ($k=3$), equations 3.S29-3.S31 are used to calculate the terms $g_{AA}(x)$, $g_{BB}(x)$, and $g_{AB}(x)$.

\[
g_{AA}(x) = g_{11}(x) + g_{33}(x) + g_{55}(x) + g_{77}(x) + g_{99}(x) + 2g_{13}(x) + 2g_{15}(x) + 2g_{17}(x) + 2g_{19}(x) + 2g_{35}(x) + 2g_{37}(x) + 2g_{39}(x) + 2g_{57}(x) + 2g_{59}(x) + 2g_{79}(x) \tag{3.S29}
\]

\[
g_{BB}(x) = g_{22}(x) + g_{44}(x) + g_{66}(x) + g_{88}(x) + 2g_{24}(x) + 2g_{26}(x) + 2g_{28}(x) + 2g_{46}(x) + 2g_{48}(x) + 2g_{68}(x) \tag{3.S30}
\]

\[
g_{AB}(x) = g_{12}(x) + g_{14}(x) + g_{16}(x) + g_{18}(x) + g_{23}(x) + g_{25}(x) + g_{27}(x) + g_{29}(x) + g_{34}(x) + g_{36}(x) + g_{38}(x) + g_{45}(x) + g_{47}(x) + g_{49}(x) + g_{56}(x) + g_{58}(x) + g_{67}(x) + g_{69}(x) + g_{78}(x) + g_{89}(x) \tag{3.S31}
\]

### 3.5.3 Two Parameter Fits

In Figure 3.S2, the values for radius of gyration, $R_{g,1}$, and interaction parameter, $\chi$, are given as a function of temperature, determined from a two parameter fit to the RPA model. In this fit, the theoretical value was used for the contrast term, $c_{th} = 0.17$. Qualitatively and quantitatively, the values are in good agreement with the values determined from the three parameter fits (Figure 3.4). The intercepts of the fits to the temperature dependence of $\chi$ are shown in Figure 3.S2b. Because the value of $c$ is fixed, the temperature dependence of $\chi$ is stronger in Figure 3.S2b than in Figure 3.4b.

![Figure 3.S2 Random phase approximation parameters using a two-parameter fit. In (a), the radius of gyration, $R_{g,1}$, is given as a function of temperature, and in (b), the interaction parameter, $\chi$, is given as a function of temperature. Linear fits to the data are shown.](image)
3.5.4 Background Fit Parameters

The adjustable parameters in the background scattering function, $a_0$, $a_1$, and $a_2$, are given in Figures 3.S3 and 3.S4. In Figure 3.S3, the background parameters are given for the fit based on the variable $c$ RPA model, and in Figure 3.S4, the background parameters are given for the fit based on the fixed $c$ RPA model. The parameter $a_0$ represents the constant, temperature-dependent offset in scattering intensity, and the parameters $a_1$ and $a_2$ are from the Lorentzian function.

![Figure 3.S3 Background fit parameters for the RPA model with variable contrast, $c$. The values of the parameters $a_0$, $a_1$, and $a_2$ are given in (a), (b), and (c). Error bars represent the fit uncertainty.](image-url)
Figure 3.S4 Background fit parameters for the RPA model with fixed contrast, $c$. The values of the parameters $a_0$, $a_1$, and $a_2$ are given in (a), (b), and (c). Error bars represent the fit uncertainty.
4 Wide Angle X-ray Scattering of Salt-Containing Perfluoropolyether-Based Electrolytes

ABSTRACT

Wide angle X-ray scattering (WAXS) is used to study the distribution of salt in short chain disordered block copolymer electrolytes with concentration fluctuations on the length scale of ~1 nm. WAXS data is presented for electrolytes based on binary mixtures of lithium bis(trifluoromethanesulfonyle) imide (LiTFSI) salt different polymers: homopolymer perfluoropolyethers (PFPEs) and block copolymers with PFPE and poly(ethylene oxide) (PEO) segments. In PFPE-PEO block copolymers, both segments can potentially transport and solvate LiTFSI; thus it is important to determine the salt distribution between the segments and the effect of salt on the structure of the electrolyte. WAXS has been used to measure the scattering due to disordered block copolymer concentration fluctuations in neat PFPE-PEO polymers. In this study, we observe changes in the shape of the disordered scattering peak with salt concentration. With the addition of LiTFSI, the disordered scattering peak shifts to lower scattering vectors, decreases in width, and decreases in intensity. These changes indicate that salt increases the radius of gyration of the polymer electrolyte, salt increases the immiscibility between PFPE- and PEO-rich domains, and salt decreases the electron density contrast between the two domains. The last of these effects is an indication that the electron-rich LiTFSI preferentially segregates to the electron-poor PEO segments. A model for the dependence of contrast on salt concentration is developed and used to estimate the relative affinity between LiTFSI and PEO over LiTFSI and PFPE. The preferential segregation of salt into PEO-rich domains helps explain the observation in chapter 1 that PEO segments have significant impact on ion transport properties of PFPE/LiTFSI electrolytes.

4.1 Introduction

In this chapter, we examine the structure and distribution of salt in perfluoropolyether-based (PFPE) electrolytes using wide angle X-ray scattering. The PFPEs used in this study are the same as those in chapters 2 and 3. The electrolytes used in this study consist of mixtures of lithium bis(trifluoromethane sulfonyle) imide (LiTFSI) salt and PFPEs at different concentrations ranging from 0-1.9 M. PFPEs with four different endgroups were studied: diol, dimethyl carbonate, ethoxy-diol, and ethoxy-dimethyl carbonate, referred to as PFPE_{D10}-Diol, PFPE_{D10}-DMC, PFPE_{E10}-Diol, and PFPE_{E10}-DMC. The PFPE component, a random copolymer of CF₂CF₂O and CF₂O segments, provides nonflammability, while the endgroups have been shown to impact salt solubility and ion transport properties. The PFPE_{E10} polymers consist of a PFPE backbone with several terminal repeat units of non-fluorinated ethylene oxide; they are essentially short chain PEO-PFPE-PEO triblock copolymers. The dimethyl carbonate (DMC)-terminated polymers were synthesized from the commercially available hydroxyl-terminated PFPEs, PFPE_{D10}-Diol and PFPE_{E10}-Diol. The structural characteristics of the polymers are given in Tables 3.1 and 3.2, and the synthesis and characterization was reported in a previous
study.\textsuperscript{64}

The question of how salt is distributed in the block copolymer electrolyte, and how salt impacts the miscibility between phases is non-trivial.\textsuperscript{24–28} Numerous studies have been performed on microphase-separated block copolymer electrolytes in which one phase is mechanically rigid and the other phase is ion-transporting.\textsuperscript{5} Such electrolytes include polystyrene-\textit{block}-poly(ethylene oxide) (SEO), and polyethylene-\textit{block}-poly(ethylene oxide) mixed with lithium salts.\textsuperscript{116–119} In SEO electrolytes, it has been shown that phase separation between the two blocks improves ionic conductivity, and that the salt resides primarily in the PEO phase.\textsuperscript{120,121} The addition of salt increases the value of the thermodynamic interaction parameter between blocks, indicating an increase in block immiscibility.\textsuperscript{24,25,28,122–124} Another block copolymer electrolyte, poly(ethylene oxide)-\textit{block-} polystyrenesulfonyllithium(trifluoromethylsulfonyl)imide (PEO-\textit{b-PSTFSILi}) has attracted attention due to its moderately high conductivity and high transference number.\textsuperscript{125} In this material, the salt anion is covalently bound to and immobilized in the PSTFSILi block, while the PEO block promotes ion dissociation and lithium ion transport. In contrast to SEO, in this material, the ionic species promote miscibility between the two blocks and suppress microphase separation.\textsuperscript{126}

As PFPE\textsubscript{E10} block copolymer electrolytes have some characteristics similar to SEO and others similar to PEO-\textit{b-PSTFSILi}, it is possible that salt could segregate into one of the microphases or that salt could induce miscibility and be evenly distributed. The PFPE electrolytes contain free salt cations and anions, similar to SEO electrolytes. However, unlike SEO electrolytes, in block copolymer PFPE electrolytes based on PFPE\textsubscript{E10}, the constituent homopolymers, PFPE\textsubscript{D10} and PEO, are both known to solvate and conduct ions. Because they are both fluorinated, it has been suggested that there is some affinity between the TFSI anion and the PFPE segments in PFPE electrolytes, similar to PEO-\textit{b-PSTFSILi}, where the anions are bound to the non-PEO block.\textsuperscript{60} However, the presence of the PEO segments in PFPE\textsubscript{E10} electrolytes was shown to promote anion mobility, in chapter 2.\textsuperscript{115} Thus, two scenarios are plausible: salt could segregate into the PEO domains of the PFPE-PEO polymers, or it could remain evenly distributed. Salt may promote or reduce miscibility.

In this chapter, WAXS is used to deduce the distribution of the salt in the electrolyte. In chapter 3, it was shown that scattering due to concentration fluctuations can be observed in the WAXS regime for neat PFPE\textsubscript{E10} polymers. The length scale of the incipient microphase separation is approximately 1 nm, too small to apply elemental mapping techniques that have been used to characterize the salt distributions in other heterogeneous electrolytes.\textsuperscript{120,127} The contrast for X-ray scattering from concentration fluctuations in disordered block copolymers is due to the difference in electron density between the two blocks.\textsuperscript{97} The electron density of LiTFSI is high compared to that of the PEO and PFPE segments. Partitioning of salt into either of the two blocks would produce significant changes in peak intensity. We follow changes in the disordered scattering peak shape with salt concentration to determine the distribution of salt in PFPE/LiTFSI electrolytes.
4.2 Experimental Section

Electrolytes were prepared using the materials and procedures described in section 2.2.1. For the PFPE\textsubscript{D10} materials the ratio of CF\textsubscript{2}CF\textsubscript{2}O to CF\textsubscript{2}O groups is 7:3. For the PFPE\textsubscript{E10} materials, the ratio of CH\textsubscript{2}CH\textsubscript{2}O to CF\textsubscript{2}CF\textsubscript{2}O to CF\textsubscript{2}O groups is 4:5:4. The volume fraction of the PFPE block, $\phi_{PFPE}$, is 0.75. For each PFPE polymer, several salt concentrations were prepared between zero salt and the solubility limit of LiTFSI in the polymer. The published solubility limits of the PFPE\textsubscript{D10} and PFPE\textsubscript{E10} materials were determined by inductively coupled plasma-mass spectrometry.\textsuperscript{64} The solubility limits and salt concentrations used are reported in Table 4.1. Molar concentrations were calculated assuming that the molar volumes of the salt and polymer solvent are additive. The densities used in the calculation were 2.023 g cm\textsuperscript{-3} for LiTFSI, 1.77 g cm\textsuperscript{-3} for PFPE\textsubscript{D10}-Diol and PFPE\textsubscript{D10}-DMC, and 1.73 g cm\textsuperscript{-3} for PFPE\textsubscript{E10}-Diol and PFPE\textsubscript{E10}-DMC. The molar mass of LiTFSI is 287.09 g mol\textsuperscript{-1}.

Table 4.1. Concentrations and solubility limits of electrolytes used in this study. The solubility limits and concentrations are given below in mol L\textsuperscript{-1} (M), weight percent salt, and molar ratio of salt to polymer chains, $n_{\text{LiTFSI}}$. Concentrations in weight percent salt are given in parentheses. Solubility limits are taken from literature.\textsuperscript{64}

<table>
<thead>
<tr>
<th></th>
<th>PFPE\textsubscript{D10}-Diol</th>
<th>PFPE\textsubscript{D10}-DMC</th>
<th>PFPE\textsubscript{E10}-Diol</th>
<th>PFPE\textsubscript{E10}-DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility limit</td>
<td>0.67 11 .43</td>
<td>1.20 19 0.90</td>
<td>1.90 30 1.94</td>
<td>1.97 31 2.35</td>
</tr>
<tr>
<td>Concentration 1</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>Concentration 2</td>
<td>0.31 5 0.18</td>
<td>0.31 5 0.20</td>
<td>0.29 5 0.23</td>
<td>0.30 5 0.28</td>
</tr>
<tr>
<td>Concentration 3</td>
<td>0.57 9 0.35</td>
<td>0.57 9 0.38</td>
<td>0.56 9 0.45</td>
<td>0.56 9 0.52</td>
</tr>
<tr>
<td>Concentration 4</td>
<td>- - -</td>
<td>1.08 17 0.79</td>
<td>1.25 20 1.14</td>
<td>1.25 20 1.31</td>
</tr>
<tr>
<td>Concentration 5</td>
<td>- - -</td>
<td>- - -</td>
<td>1.89 30 1.93</td>
<td>1.90 30 2.24</td>
</tr>
</tbody>
</table>

For WAXS measurements, sample preparation, instrument configuration, data reduction, and background subtraction were performed as described in section 3.2.2. Scattering measurements were performed at beamline 7.3.3 at the Advanced Light Source synchrotron in Berkeley, CA, USA, and 2D scattering images were captured using a Dectris, Pilatus 2M camera.\textsuperscript{89} The sample-detector distance was approximately 30 cm, and the detector pixel size was 0.172 x 0.172 mm\textsuperscript{2}. Intensity was calibrated with a glassy carbon standard (Jan Ilavsky, sample M13), and scattering vector, $q = \frac{4\pi \sin\theta}{\lambda}$, was calibrated using a silver behenate standard.\textsuperscript{93} Scattering vector, $q$, depends on the scattering angle $\theta$, and the wavelength of incident light, $\lambda$, 10 keV, in this experiments. 2D scattering images were reduced to 1D profiles using the Nika package for IgorPro, and angle-dependent background corrections were applied according to section 3.2.2.\textsuperscript{90} Liquid electrolytes were loaded into airtight aluminum sample holders with defined thickness (0.793 mm). Samples were mounted in a homebuilt heat stage, and measurements were taken at 15 °C intervals between 30 °C and 90 °C. Samples were exposed to X-rays for
4.3 Results

Figure 4.1 WAXS scattering profiles of PFPE$_{D10}$-Diol as a function of salt concentration and temperature. In (a-c) scattering profiles are shown for 0.00, 0.31, and 0.57 M LiTFSI in PFPE$_{D10}$-Diol. Color represents temperature.

Figure 4.2 WAXS scattering profiles of PFPE$_{D10}$-DMC as a function of salt concentration and temperature. In (a-d) scattering profiles are shown for 0.00, 0.31, 0.57, and 1.08 M LiTFSI in PFPE$_{D10}$-DMC. Color represents temperature.
Figure 4.3 WAXS scattering profiles of PFPE\textsubscript{E10}-Diol as a function of salt concentration and temperature. In (a-e) scattering profiles are shown for 0.00, 0.29, 0.56, 1.25, and 1.89 M LiTFSI in PFPE\textsubscript{E10}-Diol. Color represents temperature.

In Figures 4.1, 4.2, 4.3 and 4.4, intensity-calibrated WAXS profiles are shown as a function of salt concentration and temperature for each PFPE electrolyte: PFPE\textsubscript{D10}-Diol, PFPE\textsubscript{D10}-DMC, PFPE\textsubscript{E10}-Diol, and PFPE\textsubscript{E10}-DMC. The profiles in Figures 4.1a, 4.2a, 4.3a, and 4.4a are equivalent to those shown in chapter 3. The profiles for the PFPE\textsubscript{D10} electrolytes in Figures 4.1 and 4.2 have two peaks which we refer to as $q_2$ and $q_3$, with $q_2 \sim 10$ nm\textsuperscript{-1}, and $q_3 \sim 30$ nm\textsuperscript{-1}. In chapter 3, these were attributed to interchain and intrachain correlation lengths, respectively. These do not change significantly as a function of temperature or salt concentration. The background intensity in the range $q = 1 – 12$ nm\textsuperscript{-1} increases as a function of temperature. This intensity is due to thermal density fluctuations.\textsuperscript{96,97} In Figure 4.1c, the change in intensity in the range $q = 1 – 12$ nm\textsuperscript{-1} appears to be nonlinear with temperature. This may be due to artifacts introduced through background subtraction. The intensity in the range $q = 1 – 12$ nm\textsuperscript{-1} does not appear to change systematically with salt concentration. The profiles for the PFPE\textsubscript{E10} electrolytes in Figures 4.3 and 4.4 have three peaks, $q_1$, $q_2$, and $q_3$. In chapter 3, the $q_1$ peak was attributed to scattering due to concentration fluctuations between PEO and PFPE segments. As with the PFPE\textsubscript{D10} electrolytes, in the PFPE\textsubscript{E10} electrolytes, the $q_2$ and $q_3$ peaks do not appear to vary systematically with salt concentration or temperature. In the PFPE\textsubscript{E10} electrolytes, the $q_1$ peak decreases significantly in intensity with salt concentration.
Figure 4.4 WAXS scattering profiles of PFPE\textsubscript{E10}-DMC as a function of salt concentration and temperature. In (a-e) scattering profiles are shown for 0.00, 0.30, 0.56, 1.25, and 1.90 M LiTFSI in PFPE\textsubscript{E10}-DMC. Color represents temperature.

In Figures 4.5 and 4.6, WAXS profiles for the PFPE\textsubscript{E10} electrolytes, PFPE\textsubscript{E10}-Diol and PFPE\textsubscript{E10}-DMC, are shown as a function of salt concentration. Profiles in 4.5a and 4.6a were taken at 30 °C, and profiles in 4.5b and 4.6b were taken at 90 °C. Figures 4.5 and 4.6 illustrate the effect of salt on the scattering profiles. As salt concentration increases, the intensity of the $q_1$ peak decreases, and the position of the maximum shifts to lower $q$. In Figure 4.6, the scattering intensity of PFPE\textsubscript{E10}-DMC with 1.90 M LiTFSI appears to be higher than the other electrolytes. This is an artifact caused by discrepancy between the actual and measured thickness of the sample. As with the PFPE\textsubscript{E10}-Diol electrolytes in Figure 4.5, in the PFPE\textsubscript{E10}-DMC electrolytes, the intensity of the $q_1$ peak relative to the background in the vicinity of the peak decreases with increasing salt concentration. The $q_2$ and $q_3$ peaks do not vary systematically with salt concentration.
Figure 4.5. WAXS profiles of PFPE$E_{10}$-Diol electrolytes as a function of salt concentration. In (a), WAXS profiles are shown at 30 °C, and in (b), WAXS profiles are shown at 90 °C. Color indicates different concentrations of LiTFSI.

Figure 4.6. WAXS profiles of PFPE$E_{10}$-DMC electrolytes as a function of salt concentration. In (a), WAXS profiles are shown at 30 °C, and in (b), WAXS profiles are shown at 90 °C. Color indicates different concentrations of LiTFSI.

Scattering due to the concentration fluctuations between segments in a neat disordered block copolymer can be described by the random phase approximation (RPA) theory of Leibler (equation 4.1).

\[
I_{\text{dis}}(q) = v_{\text{ref}} \left( \frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2 \left[ \frac{S(q)}{W(q)} - 2\chi \right]^{-1}
\]  

In equation 4.1, $I_{\text{dis}}(q)$ is the disordered scattering intensity, $v_{\text{ref}}$ is a reference volume, taken to be 0.1 nm$^3$, $b_i$ is the scattering length of block $i$, $v_i$ is the molar volume of block $i$, $S(q)$ is the structure factor, $W(q)$ is the weight factor, and $\chi$ is the Flory-Huggins interaction parameter.
\( S(q) \) and \( W(q) \) are the sum and determinant of the structure factor matrix \([S_{ij}]\), and \( \chi \) is the Flory-Huggins interaction parameter. The values of \( v_i \) and \( b_i \) are given in Table 4.2 for the PEO and average PFPE segments (reproduced from Table 3.3 for convenience). Full expressions for \( S(q) \) and \( W(q) \) for the PFPE materials in this study are given in section 3.5.2. The terms \( S(q) \) and \( W(q) \) depend on additional parameters, the degree of polymerization with respect to the reference volume, \( N \), the radius of gyration, \( R_g \), and the volume fraction of one of the blocks, \( \phi \). The contrast, \( c \), is defined by the prefactor in equation 4.1.

\[
c = v_{\text{ref}} \left( \frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2
\]  

(4.2)

The intensity of the disordered scattering peak is affected by the contrast, \( c \), and the interaction parameter, \( \chi \). As the electron density difference between the blocks increases, \( c \) increases, and the peak height scales linearly with \( c \). As the blocks become more immiscible, \( \chi \) increases. The peak height scales non-linearly with \( \chi \), and the full width at half maximum (FWHM) of the peak decreases with increasing \( \chi \). The position of the peak is determined by the radius of gyration, \( R_g \), of the polymer, which is embedded in the RPA model through the terms \( S(q) \) and \( W(q) \) (see section 3.5.2). As \( R_g \) increases, the peak maximum shifts to lower scattering vectors. The miscibility and radius of gyration are interdependent; as \( \chi \) increases, the chain elongates to minimize contacts between dissimilar segments, causing \( R_g \) to increase.

Table 4.2 PEO, PFPE and LiTFSI properties. The parameters given below are the scattering lengths, \( b_i \), monomer molar masses, \( M_i \), densities, \( \rho_i \), and monomer volumes, \( v_i \) for the species PEO, PFPE, and LiTFSI. The PFPE properties are based on a weighted average of the CF\(_2\)CF\(_2\)O and CF\(_2\)O monomers, with a number ratio of 7:3.

<table>
<thead>
<tr>
<th></th>
<th>PEO</th>
<th>PFPE</th>
<th>LiTFSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_i ) [nm]</td>
<td>6.76 x 10(^{-5} )</td>
<td>1.28 x 10(^{-4} )</td>
<td>3.94 x 10(^{-4} )</td>
</tr>
<tr>
<td>( M_i ) [g mol(^{-1} )]</td>
<td>44.05</td>
<td>93.79</td>
<td>287.09</td>
</tr>
<tr>
<td>( \rho_i ) [g cm(^{-3} )]</td>
<td>1.12</td>
<td>1.77</td>
<td>2.023</td>
</tr>
<tr>
<td>( v_i ) [nm(^3)]</td>
<td>6.53 x 10(^{-2} )</td>
<td>8.80 x 10(^{-2} )</td>
<td>2.36 x 10(^{-1} )</td>
</tr>
</tbody>
</table>

In block copolymers, \( c \) can be calculated from the bulk densities of the blocks, and \( \chi \) is usually determined by fitting the RPA model to small angle X-ray or neutron scattering data using \( \chi \) and \( R_g \) as adjustable parameters.\(^{82-84} \) The RPA model has also been widely used to determine \( \chi \) in salt-containing block copolymers in which salt is selectively solvated by one block.\(^{24,123,124} \) In this case, the RPA model can be adapted by taking the properties of the conductive phase segments to be the weighted average of those of the ion-conducting polymer and the salt. Salt influences the number of segments in the polymer electrolyte solution, \( N \), the volume fraction of the salt-containing block, and the electron density contrast between the two blocks. In many salt-containing block copolymers, it has been found that salt increases \( \chi \) between the two microphases.\(^{24-28} \) The RPA approach is not appropriate for determining \( \chi \) and \( c \) in the PFPE\(_{E10} \) electrolytes because the partitioning of salt between the two blocks is unknown, and properties of average segments cannot be calculated. Instead, we can observe changes in the intensity, FWHM, and position of the \( q_1 \) peak in order to make qualitative conclusions about the distribution of salt and the impact.
of salt on $R_g$, $c$, and $\chi$.

In the PFPE$_{E10}$ electrolytes, the changes in the shape of the $q_1$ peak with salt concentration are shown in Figures 4.7, 4.8 and 4.9. Figure 4.7 shows the change in the position of the peak, Figure 4.8 shows the change in the height of the peak, and Figure 4.9 shows the change in the FWHM of the peak. In Figure 4.7, the shift in the $q_1$ peak with salt concentration is shown for the PFPE$_{E10}$ electrolytes at two temperatures, 30 °C, and 90 °C. The $q_1$ peak position shifts to lower scattering vectors with increasing salt concentration. This change indicates that the length scale of concentration fluctuations, and consequently the $R_g$ of the polymer electrolyte, increases with salt concentration. This effect is likely due to the fact that adding salt increases the total number of segments, $N$, in the system. Though peak position is dependent on both $R_g$ and $\chi$, the data in Figure 4.7 alone cannot be used to draw conclusions on the impact of salt concentration on $\chi$.

Figure 4.7 Position of peak due to disordered block copolymer scattering with salt concentration. The position of the $q_1$ peak is plotted as a function of salt concentration for the PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC electrolytes at the temperatures, 30 °C and 90 °C.

In Figure 4.8, the height of the $q_1$ peak is plotted for the PFPE$_{E10}$ electrolytes as a function of salt concentration, at the temperatures 30 °C and 90 °C. The height of the $q_1$ peak is calculated by subtracting a linear baseline, fit in the vicinity of the $q_1$ peak, and finding the maximum intensity. A linear baseline was used to approximate the scattering contributions from thermal density fluctuations and the neighboring $q_2$ peak. The decrease in the intensity of the $q_1$ peak with salt concentration could be due to a decrease in $c$ or a decrease in $\chi$. A decrease in $c$ could result from the electron-rich LiTFSI partitioning into the electron-poor PEO phase over the electron-rich PFPE phase. A decrease in $\chi$ could result from the balance of interactions between the species Li$^+$/TFSI$^-$, Li$^+$/PEO and TFSI$^-$/PFPE. Analysis of the FWHM of the peak is necessary to determine whether the decrease in peak intensity is due to changes in $c$ or $\chi$. Changes in $c$ do not impact the FWHM of the peak, while changes in $\chi$ do. In Figure 4.9, the FWHM of the $q_1$ peak is plotted for the
PFPE\textsubscript{E10} electrolytes. FWHM, like peak height, was determined after subtracting a linear baseline from the scattering intensity. Figure 4.9 shows that FWHM decreases as salt concentration increases, indicating that $\chi$ increases with the addition of salt. An increase in $\chi$ should be accompanied by an increase in the peak height, opposite of what is observed in Figure 4.5, 4.6 and 4.8. The observed decrease in peak height implies that the addition of salt causes a decrease in $c$ large enough to counteract the increase in $\chi$.

4.8 Height of peak due to disordered block copolymer scattering with salt concentration. The height of the $q_1$ peak is plotted as a function of salt concentration for the PFPE\textsubscript{E10}-Diol and PFPE\textsubscript{E10}-DMC electrolytes at the temperatures, 30 °C and 90 °C.

Figure 4.9 Full width at half maximum (FWHM) of peak due to disordered block copolymer scattering with salt concentration. The FWHM of the $q_1$ peak is plotted as a function of salt concentration for the PFPE\textsubscript{E10}-Diol and PFPE\textsubscript{E10}-DMC electrolytes at the temperatures, 30 °C and 90 °C.
The implication of a decrease in $c$ with increasing salt concentration is that some of the electron-rich LiTFSI preferentially associates with the electron-poor PEO segments. Using equation 4.2, we can construct a model for $c$ as a function of salt concentration, assuming that the molar volumes of the LiTFSI and PEO or PFPE segments are additive, that the scattering lengths of LiTFSI, PEO, and PFPE are additive, and that the bulk densities of LiTFSI, PEO, and PFPE$_{D10}$-Diol, represent the densities of these components in the electrolyte solution (equation 4.3 and 4.4). In equations 4.3 and 4.4, $n_{LiTFSI}$, $n_{EO}$, and $n_{PFE}$ are the number of salt molecules, ethylene oxide (EO) monomers, and perfluoroether (PFE) monomers per chain, $p$ is the proportion of salt molecules associated with the PEO block, and $g$ is the relative affinity of salt for the EO monomer over the PFE monomer (see Tables 3.1, 4.1 and 4.3). Here, the values of $n_{EO}$ and $n_{PFE}$ are 4 and 9, and the values of $n_{LiTFSI}$ are given in Table 4.1. The densities, monomer volumes, and scattering lengths of LiTFSI, PEO, and PFPE are given in Table 4.2. The values of $p$ and $g$ vary between 0 and 1. If $g = 0$, all of the salt resides in the PFPE block, and $p = 0$ (equation 4.4). If $g = 0.5$, the salt has an equal preference for the PEO and PFPE blocks, and $p = 4/13$, based on the values of $n_i$ for the species in this system. If $g = 1$, all of the salt resides in the PEO block, and $p = 1$.

$$c = v_{ref} \left(\frac{b_{PFE} + p (n_{LiTFSI} / n_{EO})}{b_{EO} + p (n_{LiTFSI} / n_{EO})} \times \frac{v_{LiTFSI}}{v_{PFE} + (1 - p) (n_{LiTFSI} / n_{PFE})} \times \frac{b_{LiTFSI}}{v_{LiTFSI}}\right)^2$$ \hspace{1cm} (4.3)

$$p = \frac{n_{EO} g}{n_{EO} g + n_{PFE} (1 - g)}$$ \hspace{1cm} (4.4)

The quantities in equations 4.3 and 4.4 are assumed to be independent of temperature. We neglect the contribution of DMC endgroups to the electron density for the PFPE$_{E10}$-Diol electrolytes. The value of $c$ from the model in equation 4.3 is proportional to the contribution of electron density contrast to the experimentally observed peak height.

In Figure 4.10, the contrast predicted by equations 4.3 and 4.4 is plotted with the heights of the $q_1$ peaks from Figure 4.8 for two cases, $g = 1$ (all of the salt in PEO block), and $g = 0.5$ (even salt distribution). The contrast and the peak heights are normalized by the values for the neat PFPE$_{E10}$ electrolytes to facilitate the comparison of the different quantities. Equation 4.3 yields $c = 0.17 \text{ cm}^{-1}$ when no salt is added to the polymer. The trends in the experimental peak height data are intermediate to the trends predicted by equation 4.3 with $g = 1$ and 0.5, for the electrolytes PFPE$_{E10}$-Diol and PFPE$_{E10}$-DMC, at 30 °C and 90 °C. This indicates that salt is not randomly distributed throughout the sample volume, but has a tendency to associate with the PEO segments. The amount of salt in the PEO and PFPE segments can be estimated by fitting equation 4.3 to the average experimental data in Figure 4.10 using $g$ as an adjustable parameter. The result of such a fit is shown in Figure 4.10. The value of $g$ from the fit is $0.74 \pm 0.01$, and the corresponding value of $p$ is $0.55 \pm 0.01$, indicating that about half of the salt resides in the PEO-rich phase (even though the PEO-rich phase only accounts for 0.25 the volume fraction of the neat polymer). Though the fit provides a qualitative measure of the salt distribution in the electrolyte, a quantitative interpretation should be avoided. The experimental values of
peak height reported in Figure 4.10 are likely to underestimate the strength of the dependence of the experimental contrast on salt concentration for two reasons: (1) some of the \( q_1 \) scattering intensity is due to \( \chi \), and \( \chi \) increases with salt concentration, as concluded from Figure 4.9; and (2) the bulk densities in Table 4.2 may be slightly higher than the actual microscopic densities of the phases in these solutions. Because the electrolyte consists of short polymer chains, the concentration of endgroups is high, and endgroups tend to contribute more free volume than internal polymer segments. Despite these limitations, Figure 4.10 provides evidence that LiTFSI is preferentially solvated by the PEO segments.

Figure 4.10 Normalized trends in theoretical contrast and disordered scattering peak height as a function of salt concentration. The heights of the experimental disordered scattering peaks are shown for the PFPE_{E10}-Diol and PFPE_{E10}-DMC electrolytes, normalized by the heights at 0 M LiTFSI. Data from 30 °C and 90 °C are plotted. The contrast, \( c \), calculated according to equation 4.3 and normalized by the value at 0 M LiTFSI (yellow lines), is plotted as a function of salt concentration for two cases, \( g = 1 \) (all LiTFSI in PEO) and \( g = 0.5 \) (LiTFSI distributed equally between PEO and PFPE). Equation 4.3 is fit to the experimental data with \( g \) as an adjustable parameter (black line). The corresponding value of \( g \) is 0.74 ± 0.01.

4.4 Conclusion

We have demonstrated that WAXS can be an effective tool for studying the distribution of salt in heterogeneous electrolytes where the length scale of concentration fluctuations is too small for traditional elemental mapping techniques. Wide angle X-ray scattering data is presented for electrolytes based on binary mixtures of LiTFSI salt with homopolymer PFPEs, PFPE_{D10}-Diol and PFPE_{D10}-DMC, and block copolymer PFPE-PEOs, PFPE_{E10}-Diol and PFPE_{E10}-DMC. For the homopolymer electrolytes, scattering does not change significantly as a function of salt concentration. For the block copolymer electrolytes, the peak due to concentrations fluctuations between PEO and PFPE segments moves to lower values of scattering vector, \( q \), decreases in intensity, and decreases in full
width at half maximum (FWHM), as a function of increasing salt concentration. Due to the potential affinity between LiTFSI and either of the PEO or PFPE segments, an RPA-based model could not be used to determine the effect of salt on the radius of gyration, $R_g$, the interaction parameter $\chi$, and the electron density contrast, $c$. Instead, the effect of salt on these parameters is qualitatively determined by analyzing the changes in peak position, peak height and peak FWHM. The addition of salt was found to increase the value of $R_g$ for the electrolyte solution, increase the value of $\chi$, and decrease the value of $c$. Comparing the decrease in peak height to a model for the dependence of $c$ on salt concentration and distribution, we conclude that the salt preferentially associates with the PEO segments. It is perhaps surprising that salt segregation can be observed in solutions with concentration fluctuations on a length scale as low as ~1 nm.

In chapter 2, it was shown that the PFPE$_{E10}$/LiTFSI electrolytes have significantly different ion transport properties than the PFPE$_{D10}$/LiTFSI electrolytes. The presence of PEO segments in the PFPE$_{E10}$ electrolytes increases the ionic conductivity and decreases the cation transference number. This study offers evidence that salt segregates into the PEO-rich domains, which can explain why significant changes in ionic transport are observed in PFPE electrolytes with different endgroups. In PFPE$_{D10}$-DMC electrolytes, high cation transference numbers are observed, suggesting that there are strong interactions between the PFPE segments and the TFSI anion. Our results imply that the affinity of LiTFSI for the PEO domains is stronger than the affinity of LiTFSI for PFPE.
5 The Effect of Grain Size on the Ionic Conductivity of a Block Copolymer Electrolyte

ABSTRACT

A systematic study of the dependence of ionic conductivity on the grain size of a lamellar block copolymer electrolyte was performed. A freeze-dried mixture of poly(styrene)-block-poly(ethylene oxide) and lithium bis(trifluoromethylsulfonyl)imide salt was heated in steps from 29 to 116 °C and then cooled back to 29 °C with an annealing time ranging from 30 to 60 min at each temperature. Grain structure and ionic conductivity during these steps were quantified by in situ small angle X-ray scattering and ac impedance spectroscopy, respectively. Conductivity depends both on grain structure and temperature. A normalization scheme to decouple the dependence of conductivity on temperature and grain structure is described. Ionic conductivity at a given temperature was found to decrease by a factor of 5.2 ± 0.9 as the SAXS measure of grain size increased from 13 to 88 nm. The fact that in the system studied, large, well-formed lamellar grains are less conducting than poorly defined, small grains suggests a new approach for optimizing the transport properties of block copolymer electrolytes. Further work is necessary to confirm the generality of this finding.

5.1 Introduction

In block copolymers, coherent order is restricted to small regions of characteristic size, \( L \), which we refer to as grains. Figure 5.1a shows a schematic view of a typical block copolymer electrolyte, which is composed of grains. Here, we show alternating conducting (blue) and non-conducting (red) lamellar domains. In electrolytes created in the absence of external fields, one expects the grains in a macroscopic sample to be randomly oriented, with concomitant defects.\(^{17-24}\) Ion transport in a collection of grains is more complex than transport within an individual grain, as the former depends on the nature of the defects in addition to the intrinsic material properties.\(^{17,134}\) It is customary to use the following expression for the ionic conductivity, \( \sigma \), of randomly oriented block copolymer grains:

\[
\sigma = f \phi_c \sigma_c
\]  

(5.1)

where \( \phi_c \) is the volume fraction of the conducting block, and \( \sigma_c \) is the intrinsic ionic conductivity of the conductive phase.\(^{5,16,116}\) The product \( \phi_c \sigma_c \) gives the conductivity within each grain, accounting for the presence of the non-conducting microphase. The morphology factor, \( f \), accounts for transport between grains and grain orientation, and, in principle, can range between zero and one. In Figures 5.1b and 5.1c we have outlined two

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specific defects that would impact $f$ differently, one that blocks ion transport in the $x$-direction (Figure 5.1c) and one that does not (Figure 5.1b). If the concentration of transport-blocking defects is negligible, then $f$ is $2/3$ for a random collection of lamellar grains.\textsuperscript{116,135} It is conceivable that the value of $f$ and consequently, $\sigma$, could vary with $L$ due to changes in defect structure with grain size.

![Figure 5.1 Schematic of a block copolymer electrolyte. In (a), a lamellar block copolymer electrolyte consisting of many grains is illustrated. An example of a grain is outlined in black. The ion conducting domains are blue, and the non-conducting domains are red. In (b) and (c), two types of grain boundaries are depicted, one in which ions can travel across the boundary (b), and one in which the ions are blocked by the boundary (c). The x-axis indicates the direction of ion transport.](image)

The main objective of this chapter is to quantify the relationship between conductivity, $\sigma$, and average grain size, $L$, in a block copolymer electrolyte. The grain structure of a block copolymer sample depends on both thermodynamic and kinetic factors. The thermodynamic factors reflect the free energy of defect formation that in turn, is governed by the orientation of the adjacent grains (tilt versus screw dislocations, etc).\textsuperscript{19,136–138} Upon annealing, defects can annihilate depending on the availability of complementary defects in the neighborhood, as first seen by Harrison \textit{et al.}\textsuperscript{18,139,140} The distribution of defects in a given sample thus depends not only on the state variables (temperature, pressure, composition) but also on the thermal history. It is thus imperative that in such a study, $\sigma$ and $L$ are measured simultaneously. We have accomplished this by conducting our experiments in a specially-designed air-free X-ray scattering cell that enables \textit{in situ} ac impedance measurements.

5.2 Experimental Section

5.2.1 Electrolyte Preparation

A polystyrene-\textit{block}-poly(ethylene oxide) copolymer was synthesized by living anionic polymerization, and characterized by methods described in previous publications.\textsuperscript{32-34} The polymer used in this chapter was found to have a number-averaged molecular weight of 10.4 kg mol$^{-1}$, and a polydispersity of 1.04. The number-averaged molecular weights of the individual blocks were 4.9 kg mol$^{-1}$ for PS and 5.5 kg mol$^{-1}$ for PEO. The block copolymer was mixed with LiTFSI salt (Novolyte) to create the electrolyte. Due to the highly hygroscopic nature of LiTFSI, all operations involving the salt or salt-containing
materials were carried out in an Ar glove box with O₂ and H₂O levels maintained below 1 ppm. The clean SEO was dried for 24 hrs at 90 °C under vacuum before being introduced into the glove box. SEO was dissolved in benzene, LiTFSI was dissolved in THF, and the two solutions were stirred for 12 hrs. In order to make accurate mass measurements to prepare solutions in the dry glovebox environment, a piezoelectric antistatic gun (Milty Zerostat3) was used to treat the area around the glovebox balance to reduce measurement error due to static electricity. The SEO-benzene solution was spiked with salt solution and stirred for 4 hrs to give an $r$-value (molar ratio of salt molecules to ethylene oxide moieties) of 0.085. This $r$-value was chosen because previously, SEO electrolytes with $r$-values in the vicinity of 0.085 have been shown to have optimal ionic conductivities.¹⁶ The dissolved polymer was transferred to a Millrock LD85 Lyophilizer without exposure to air and freeze dried under approximately 1 mTorr of vacuum. The condenser temperature was maintained at -70 °C, and the sample temperature was raised slowly from -70 °C to 30 °C over the course of one week. The electrolyte was then dried for 24 hrs in the antechamber of a solvent-free glove box, under vacuum, at elevated temperature. The amount of water and residual solvent in the electrolyte was found to be below the detection limit of $^1$H NMR (Figure 5.S1).

5.2.2 Sample Preparation

Samples were prepared for simultaneous characterization by small angle X-ray scattering (SAXS) and ac impedance spectroscopy. Freeze dried electrolyte, in the form of a fluffy powder, was mechanically pressed into a fiberglass, Garolite-10 spacer at room temperature to form a transparent, dense pellet. The spacer was 150 µm thick with a hole 3.175 mm in diameter. Two high purity aluminum foils, 17 µm thick and 15.875 mm in diameter, were pressed on either side of the polymer-containing spacer to form electrodes. The thickness of each polymer pellet was determined by measuring the thickness of the electrode and spacer assembly with a micrometer and subtracting the thickness of the electrode foils. Aluminum tabs were attached to the edges of the foil electrodes to make electrical contact without blocking the path for X-rays to travel through the polymer. The samples were vacuum-sealed in a polyethylene-coated aluminum pouching material (Showa Denko) with the aluminum tabs protruding from the pouch, before being removed from the glovebox. The sample assembly was fixed in place by the 1 atm of pressure acting on the sealed pouch. Blank samples for scattering experiments were made in a similar way, but no polymer was pressed into the spacer, and no tabs were attached to the electrodes. After scattering experiments were performed, the samples were disassembled in a glove box to measure the polymer thickness and inspect the polymer to make sure it did not contain bubbles or macroscopic defects. The difference in sample thickness before and after the annealing experiment was found to be below 10 percent of the total thickness in all cases.

5.2.3 Small Angle X-ray Scattering

In situ small angle X-ray scattering experiments were conducted at beamline 7.3.3 at the Advanced Light Source in Lawrence Berkeley National Lab (Berkeley, CA) using 10 keV monochromatic X-rays.¹⁴³ A Dectris Pilatus 1M detector with a pixel size of 0.172 mm x 0.172 mm was placed approximately 1.8 m from the sample to image the
diffracted X-ray intensity. The distance between the sample and detector and the scattering vector coordinate, \( q \), were determined by calibrating the diffraction images with a silver behenate reference. The magnitude of the scattering vector, \( q \), is given by \( q = \frac{4 \pi \sin(\theta/2)}{\lambda} \), where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the X-rays. Three polymer electrolyte samples and one blank sample were mounted onto a home-built temperature-controlled heating stage. All images were obtained using 60 s exposures. Two dimensional scattering data (images) were reduced to one dimensional intensity, \( I \), versus \( q \) profiles by azimuthally averaging using the Nika macro for Igor Pro.\(^{90}\) For each data point measured, scattering from the blank sample (described above) was subtracted according to equation 5.2, where \( I_{\text{Sample}} \) is the raw scattering intensity from the sample, \( I_{\text{Blank}} \) is the raw scattering intensity of the blank at the corresponding \( q \) value, \( T_{\text{Sample}} \) is the transmission coefficient of the sample, and \( T_{\text{Blank}} \) is the transmission coefficient of the blank.

\[
I = I_{\text{Sample}} - \frac{T_{\text{Sample}}}{T_{\text{Blank}}} \times I_{\text{Blank}} \tag{5.2}
\]

The sample transmission coefficient was measured along with every scattering image by recording the total intensity before and after the sample using two ion gauges.

The samples were heated from 29 to 116 °C and cooled back to 29 °C, holding the temperature constant for 30 to 90 min at each temperature step. The temperature set-point was changed in increments of 5-10 °C during heating, and increments of 30 °C during cooling. Several scattering and conductivity measurements were performed for each temperature step. The maximum sample temperature, 116 °C, is well below the degradation temperature of the polymer. The temperature of the heating stage was controlled using a Watlow EZ zone controller and monitored using a thermocouple. At each temperature step during heating, it took approximately 2 min for the stage temperature to reach the set-point. During cooling, which took place passively, it took 15 min to 1 hr to reach the set-point. A separate calibration experiment was performed to relate the stage temperature to the temperature at each sample location; thin wire thermocouples were attached to the samples and the stage was heated to the same temperatures used in the \textit{in situ} experiment (see Figure 5.S3).\(^{144}\) Temperatures reported herein are sample temperatures (determined via calibration), as opposed to temperature set-points.

### 5.2.4 AC Impedance Spectroscopy

The conductivity of the electrolyte in each sample was measured, \textit{in situ}, by performing ac impedance spectroscopy. A Biologic VMP3 potentiostat was connected to the tabs protruding from the pouch to measure the complex impedance as a function of an ac input signal with frequency varying from 1 Hz to 1 MHz and fixed amplitude of 50 mV. The resistance due to ion transport in the electrolyte was determined from the local minimum in the Nyquist plot of the impedance. The minimum was used to approximate the real axis-intercept, which gives the true resistance. The conductivities of the electrolytes were determined from equation 5.3, where \( R_s \) is resistance, \( w \) is the electrolyte thickness, \( a \) is the area, and \( \sigma \) is conductivity.

\[
\sigma = \frac{w}{R_s a} \tag{5.3}
\]
The inner diameter of the spacer, 3.175 mm, was used to calculate \( a \). For the sample thickness, \( w \), the initial and final thicknesses were averaged.

5.2.5 Transmission Electron Microscopy

Sample structure was verified, \textit{ex situ}, using transmission electron microscopy (TEM). Two bulk samples were prepared using the same procedure for SAXS sample preparation. One was annealed using the same temperature profile and one was maintained at room temperature, both air-free. Samples were briefly exposed to air to section, stain and transfer them to the TEM. Thin sections with thicknesses of approximately 100 nm were obtained by cryo-microtoming using a Leica EM FC6 at \(-120 \, ^\circ C\) and transferred onto a lacey carbon-coated copper grid (Electron Microscopy Sciences). Samples were stained in RuO\(_4\) vapor for 10 min. STEM (scanning transmission electron microscopy) experiments were performed on a Tecnai F20 UT FEG equipped with a high angle annular dark field (HAADF) detector using 200 keV acceleration voltage. PEO domains appear bright in images.\(^{145,146}\)

5.3 Results and Discussion

Simultaneous SAXS and conductivity measurements were performed for three independent samples. Conductivity measurements (without SAXS) were performed on six additional independent samples. All of the results obtained from these experiments were consistent with each other. Due to our interest in studying the dependence of ionic conductivity on grain size, and because grain size is known to be a sensitive function of thermal history,\(^{147}\) we only discuss the results of the simultaneous SAXS and conductivity experiments. For clarity, we begin our discussion by describing one of the samples.

Figure 5.2a shows selected SAXS profiles obtained at representative temperatures between 29 and 116\(^{\circ}\)C. All of the profiles contain a prominent primary scattering peak in the vicinity of \( q = q^* \approx 0.38 \, \text{nm}^{-1} \) and higher order peaks at \( 2q^* \) and \( 3q^* \), indicating that the block copolymer morphology is lamellar over the entire temperature window. The primary and higher order peaks obtained from the as-prepared, freeze-dried sample are broad. Increasing sample temperature above 63 \(^{\circ}\)C results in a decrease in the widths of primary and higher order peaks (heating data in Figure 5.2a). At a given temperature, peak width decreases with annealing time, albeit at a rate that is highly temperature dependent. This is illustrated in Figures 5.2b and 5.2c, where data collected over a 40 min time interval at 68 and 116 \(^{\circ}\)C are shown. Changes in peak width with time are more readily seen at 68 \(^{\circ}\)C.
Figure 5.2 SANS profiles. SANS intensity as a function of the magnitude of the scattering vector, $q$, is shown during heating and cooling. In (a), SANS profiles are shown for representative temperatures during heating and cooling, after at least 30 min at each temperature. Profiles are offset for clarity and plotted on a log scale to emphasize the $2q^*$ and $3q^*$ peaks. In (b) and (c), time evolution of profiles is shown at 68°C and 116°C, respectively, plotted on a linear scale.

The SANS peak widths are affected primarily by variation in domain spacing and finite grain size. We assume that the variation in domain spacing arises from the polydispersity in the polymer sample and is thus independent of temperature and annealing history. The dependence of peak width on temperature and annealing history is assumed to arise from changes in the average grain size. As expected, average grain size increases irreversibly with annealing. Cooling the sample from 116 to 29°C has virtually no effect on peak width (Figure 5.2a). The SANS profiles obtained at 116°C are essentially independent of time, except for data obtained at 33 min (Figure 5.2c). We do not know the reason for the outlier. In addition to peak width, the value of $q^*$ also changes irreversibly, as documented in the supporting information (Figure 5.S4). In our analysis of morphology, we focus on changes in the FWHM (full width at half maximum) of the primary peak and ignore changes in $q^*$. The validity of our approach is confirmed by TEM. Electron micrographs of an as-prepared freeze-dried sample and a sample annealed from 29 to 116°C are shown in Figure 5.3. The average size of the coherently ordered grains in the freeze-dried sample is much smaller than that in the annealed sample. A variety of distinct
defect structures including low and high angle tilts (v patterns) and twists (x patterns) are discernible in the annealed sample (Figure 5.3b). The geometries of the defects in the freeze-dried sample are less clear (Figure 5.3a).

![Figure 5.3. STEM images of electrolyte samples before and after annealing. In (a), the electrolyte was cold pressed after freeze-drying, and in (b), the electrolyte was freeze-dried, cold pressed and then annealed from 29 to 116 °C before cooling to room temperature. The samples were stained with RuO₄, and images were obtained using an HAADF detector. PEO domains appear bright.](image)

The FWHM of the primary SAXS peak of each scattering profile was determined in two steps. First, the SAXS peak intensity was calculated by subtracting a linear baseline, fit in the vicinity of the primary peak. Second, linear interpolation between the two data points closest to the half maximum, on each side of the scattering peak, was used to determine FWHM. Grain size, $L$, is approximated by $L \approx \text{FWHM}^{-1}$, based on the Scherrer equation. Typical samples contain grains of a distribution of shapes and sizes, and the relationship between $L$ as defined here and the average grain size determined by other approaches such as quantitative analysis of TEM images or depolarized light scattering is unclear. In Figure 5.4, the average grain size, $L$, determined by SAXS is plotted against inverse temperature. Inverse temperature is used for ease of comparison with conductivity data, which is generally plotted using the same abscissa (the top abscissa in Figure 5.4 shows sample temperature in °C). Heating the sample from 29 to 63 °C has very little effect on $L$. As the temperature is increased beyond 63 °C, the grain size begins to grow with time and temperature. The average grain size is a much weaker function of temperature during the cooling run (Figure 5.4). Cooling the electrolyte below this temperature results in only a slight decrease in $L$. 

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Figure 5.4 Dependence of grain size, $L$, on temperature, $T$. The grain size is plotted as a function of temperature with the color scale indicating the amount of time the sample spent at a given temperature. Lines are drawn to guide the eye.

In Figure 5.5a, we show the observed grain growth as a function of time, $t$, at selected temperatures. The ordinate in Figure 5.5a is $L/L_0$ where $L_0$ is the grain size at $t = 0$ for a given temperature. The temperature dependence of $L_0$ is given in Figure 5.4 (t = 0 hr data during the heating run). The slope of the linear fit through each data series in Figure 5.5a gives the history-dependent non-dimensional grain growth rate, $m$, defined as $m = d(L/L_0)/dt$, at the temperature of interest. It is worth noting that the grain growth is approximately linear in the time window of our experiment. One expects power law behavior or saturation at long times. At 53 °C, $L/L_0$ increases slowly with time with a growth rate of 0.055 hr$^{-1}$. Increasing the temperature to 68 °C results in a much larger growth rate of 0.44 hr$^{-1}$. Increasing the temperature to 87 °C results in a significant slow-down of growth rate, and a value of 0.16 hr$^{-1}$ is obtained. Figure 5.5b shows the temperature dependence of $m$ observed during the annealing process. The largest growth rate occurs around 72 °C, which is very close to 71 °C, the glass transition temperature of PS, the structural block, ($T_g$,$\text{PS}$; see Figure 5.S2 for differential scanning calorimetry data). The as-prepared, freeze-dried sample contains a high concentration of defects. At temperatures lower than $T_g$,$\text{PS}$, chain mobility is limited, and this limits defect annihilation. In the vicinity of $T_g$,$\text{PS}$, the chains have sufficient mobility, and the most unstable defects are rapidly consumed. We posit that the normalized grain growth rate decreases beyond 72 °C because the remaining defects are more stable (lower free energy), and their concentration is lower. Ryu et al. have shown that annealing block copolymers results in the preferential elimination of certain kinds of defects. This may be related to the free energy of defect formation as calculated by Matsen et al. In addition, the barrier for defect annihilation, which will depend on defect concentration, will play an important role in the dependence of grain growth rate on temperature. It is evident that $m$ depends on $L_0$.
(which is inversely related to defect density), and \( T \). As anticipated in the introduction, the grain structure of our sample is dependent on both the temperature of the system and on thermal history.

Figure 5.5 Grain growth as a function of temperature. In (a), dimensionless grain size is plotted against time for three representative temperatures during sample heating. Linear fits through the data are shown. In (b), the grain growth rate, determined from the slope of the fits in (a), is plotted as a function of temperature. A line is drawn to guide the eye.

Figure 5.6 Conductivity as a function of temperature and time. Conductivity data are shown for a representative sample during heating (filled triangles) and cooling (open triangles). Heating data below 68 °C and all of the cooling data are both fit to the VTF model (solid and dashed curves). The color scale represents the time spent at each temperature.
In addition to scattering (data shown in Figures 5.2 and 5.4), conductivity was also monitored with time and temperature. In Figure 5.6, conductivity data is shown for the same representative sample discussed in Figures 5.2-5.5. Upon heating, at temperatures between 29 and 63 °C, the conductivity increases with temperature but does not change significantly with time. When the sample is heated from 53 to 63 °C, the conductivity first increases and then decreases with increasing time. Each subsequent step along the heating curve results in the same qualitative behavior: a discontinuous increase in conductivity at early times followed by a decrease in conductivity at longer times. After completing the last heating step from 106 to 116 °C, the sample was cooled in steps as shown in Figure 5.6. Data obtained at different temperatures during the cooling run were independent of time; the open symbols in Figure 5.6 representing cooling data are superpositions of several conductivity measurements as a function of time at each temperature.

There are two regimes wherein the grain structure is a relatively weak function of temperature: (1) during the heating run between 29 and 63 °C, and (2) during the cooling run between 116 and 29 °C (see Figure 5.4). We use the term "stable grain structure" to describe the sample during these two regimes as it is clear that grain growth does not occur in spite of rapid molecular motion. The Vogel-Tammann-Fulcher (VTF) model is often used to describe ionic conductivity in homogenous polymer systems, or heterogeneous polymer systems with fixed microstructure.\(^5\)\(^6\)\(^9\) We use the VTF equation to fit conductivity obtained in the two regimes described above:

\[
\sigma_{\text{VTF}}(T) = AT^{-1/2}\exp\left(\frac{-E_a}{R(T-T_0)}\right)
\]

In equation 5.4, \(\sigma_{\text{VTF}}(T)\) is the VTF fit to the conductivity as a function of temperature, \(A\) is a prefactor that, in theory, is related to the number of charge carriers, \(E_a\) is the effective activation energy for ion transport, \(R\) is the gas constant, and \(T_0\) is a reference temperature. In all VTF fits used in this chapter, \(T_0\) was taken to be -40 °C, which is the glass transition temperature of the ion-conducting block, PEO. The parameters \(E_a\) and \(A\) obtained from the fits are shown in Table 5.1. In addition, we also show \(\sigma_{120}\), which is the conductivity at 120 °C predicted by the VTF fit. The quantities reported in Table 1 represent the average and standard deviation of the values for three independent samples studied simultaneously by SAXS and ac impedance.

<table>
<thead>
<tr>
<th>Condition</th>
<th>(E_a [\text{kJ mol}^{-1}])</th>
<th>(A [\text{S cm}^{-1} \text{K}^{1/2}])</th>
<th>(\sigma_{120} [\text{S cm}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>4.3 ± 0.1</td>
<td>0.35 ± 0.09</td>
<td>7×10^{-2} ± 1×10^{-4}</td>
</tr>
<tr>
<td>Cooling</td>
<td>4.3 ± 0.2</td>
<td>0.07 ± 0.03</td>
<td>1.4×10^{-4} ± 0.4×10^{-4}</td>
</tr>
<tr>
<td>Heating / Cooling (unitless)</td>
<td>0.99 ± 0.03</td>
<td>5.2 ± 1.3</td>
<td>5.2± 0.9</td>
</tr>
</tbody>
</table>

The VTF parameters are given for the fit to the stable grain structure during the heating and the cooling run. The value of each fit at 120 °C is given in the last column. The last row gives the dimensionless ratio of the parameters obtained during the heating
run to those obtained during the cooling run. The values represent the average and standard deviation of parameters for three separate samples.

The VTF parameters obtained during heating represent conductivity through the as-prepared, freeze-dried sample with small grains, while the VTF parameters obtained during cooling represent conductivity through the well-annealed, large grains. Comparing the conductivities of these two systems at fixed temperature (e.g., 120 °C) enables quantification of the effect of grain structure on ion transport. It is evident that increasing \( L \) from 13 to 88 nm (Figure 5.4) results in a decrease in conductivity by a factor of 5.2 (Table 5.1). It is perhaps interesting to note that the activation energies obtained during heating and cooling are within experimental error (Table 5.1). The change in conductivity is mainly due to a difference in the prefactor \( A \) (Table 5.1). In homogeneous electrolytes, it is normally assumed that the magnitude of \( A \) reflects the concentration of charge carriers. One, however, does not expect the grain size to affect the number of charge carriers. We are thus not sure of the origin of the observed relationship between \( L \) and \( A \).

In Figure 5.7, we establish an explicit relationship between conductivity and structure by plotting the conductivity against grain size. In Figure 5.7a, raw conductivity, \( \sigma \), obtained during heating is plotted against grain size for the representative sample used in the previous Figures. This \( \sigma \) vs. \( L \) plot does not reveal a clear relationship because \( \sigma \) depends on both \( L \) and \( T \). To isolate the dependence of \( \sigma \) on \( L \), the raw conductivity was normalized by the VTF fit to the cooling data. This serves as a reference conductivity corresponding to the stable grain structure of the well-annealed sample. In Figure 5.7b, normalized conductivity, \( \sigma/\sigma_{\text{VTF}} \) is plotted against \( L \), and a clear relationship is revealed between the two. Normalized conductivity data from three samples studied simultaneously by SAXS and ac impedance were binned into groups of five adjacent data points and averaged. The averaged data is shown in the inset in Figure 5.7b, with error bars representing one standard deviation in each direction. It is important to note that the trends seen in Figure 5.7b would also be obtained if we were to use the VTF fit through the conductivity data obtained from the stable grains obtained during the heating run because the \( E_a \) value is similar and \( T_0 \) is identical. The values of \( \sigma/\sigma_{\text{VTF}} \) would be reduced by a factor of about five due to differences in \( A \) between the heating and cooling fits (see Figure 5.S5).

We can use equation 5.1 to study the effect of increasing \( L \) on the morphology factor, \( f \), for the three samples used in the simultaneous SAXS and ac impedance experiments. In order to do this, we need estimates of \( \sigma_c \) and \( \phi_c \). Based on the characterization data given above, we assume \( \phi_c = 0.58 \) (independent of temperature). To estimate \( \sigma_c \), a straightforward approach is to assume that \( \sigma_c \) is equal to the conductivity of a mixture of PEO homopolymer and LiTFSI at \( r = 0.085 \) (the same value as for the block copolymer).\(^{11}\) The conductivity of PEO/LiTFSI mixtures at \( r = 0.085 \) is independent of homopolymer molecular weight when it exceeds about 5 kg mol\(^{-1}\).\(^{65}\) As discussed in previous publications,\(^{149}\) obtaining pure PEO microphases by self-assembly of block copolymers requires strong segregation, which, in the case of symmetric SEO copolymers, occurs when the total molecular weight of the copolymer exceeds 100 kg mol\(^{-1}\). The SEO used in this chapter (4.9 kg mol\(^{-1}\) PS and 5.5 kg mol\(^{-1}\) PEO) is clearly not in this regime.
Since the extent of mixing of PS segments in the PEO-rich microphases has not been measured directly, we use the conductivity of PEO/LiTFSI at a given temperature to estimate $\sigma_c$. To quantify the effect of $L$ on $f$, conductivity measurements obtained at 63 °C (heating run) and at 65 °C (cooling run) were used. At 63 °C, $\sigma_c = 5.95 \times 10^{-4}$ S cm$^{-1}$, and at 65 °C, $\sigma_c = 6.55 \times 10^{-4}$ S cm$^{-1}$. Values of $\sigma_c$ were calculated at the temperatures of interest based on the published work of Yuan et al.$^{11}$ and Teran et al.$^{65}$ During heating, at 63°C, when the samples are composed of small grains ($L=15$ nm), we obtain $f = 0.36 \pm 0.05$, and during cooling, at 65 °C, when the samples are composed of large grains ($L=85$ nm), $f = 0.058 \pm 0.013$. The values of $f$ reported here are the average and standard deviation of the $f$ values for the three samples. Increasing $L$ causes $f$ to decrease. The value of $f$ in both regimes is considerably smaller than the ideal value of 0.67 for lamellar structures due to the aforementioned mixing of glassy PS segments in the PEO-rich microphases.$^{11,150}$

![Figure 5.7](image)

**Figure 5.7** Dependence of conductivity on grain size. In (a), raw conductivity of a representative sample is plotted against grain size, and in (b), normalized conductivity is plotted. The color scale represents the temperature at each data point for both plots. The inset in (b) shows normalized conductivity data averaged for three samples. The vertical and horizontal error bars represent one standard deviation in each direction.

It is clear from Figure 5.7b that conductivity decreases as grain size increases. This result indicates that poor long-range order is desirable in block copolymer electrolytes. It also sheds light on previously published data on the effect of molecular weight on the conductivity of block copolymer electrolytes; increasing molecular weight resulted in an increase in conductivity.$^{11,16}$ We expect defect annihilation to slow down with increasing molecular weight. Trapped defects and small grain sizes may be one of the reasons why high molecular weight block copolymer electrolytes exhibit high conductivities. The passage of ions through defective lamellar phases of the kind pictured in Figure 5.3 is non-trivial, and we have not identified the particular defects in the well-annealed sample (Figure 5.3b) that impede ion motion. It is conceivable that annealing block copolymers results selectively in the formation of defects pictured in Figure 5.1c, which in turn reduce ionic conductivity.
5.4 Conclusions

We have performed a systematic study of the influence of grain size on the ionic conductivity of a lamellar block copolymer electrolyte. As the electrolyte was heated in steps from 29 to 116 °C, the grain size increased with time and temperature, with a maximum in the normalized grain growth rate in the vicinity of the $T_g$ of the structural block, PS. After the heating run was complete, a stable structural state was reached, and the grain structure did not change appreciably when the polymer was cooled. The dependence of the conductivity on temperature followed VTF behavior in temperature regimes where the structure did not change significantly; however, when grain size increased, conductivity decreased in all cases. Typically, it is difficult to deconvolute the effects of microstructure and temperature on conductivity because the three quantities are interrelated and because microstructure and conductivity are both history-dependent. By normalizing the conductivity with the conductivity in a reference state with constant microstructure, the grain size-dependence of the conductivity was isolated. It was observed that conductivity decreases with increasing grain size. This chapter points to long range order as a parameter that should be considered when designing block copolymer electrolytes. All other characteristics being equal, block copolymers with small grains are better electrolytes than those with larger, well-defined grains. It is possible that in other block copolymer systems, the kinetics of grain growth and the types of grain boundaries formed upon annealing may not be the same as in this system. More work is needed to confirm the generality of the finding that large grains impede conductivity. The fact that the poorly defined lamellae pictured in Figure 5.3a are five times more conductive than the clearly defined lamellae in Figure 5.3b may, at first, appear counterintuitive. We hope to identify the underpinnings of this surprising observation in future studies.

5.5 Supplementary Information

5.5.1 Electrolyte Characterization
Electrolyte purity and thermal properties were assessed by nuclear magnetic resonance spectroscopy (NMR) and differential scanning calorimetry (DSC), respectively. To confirm that the freeze-dried electrolyte was free of water and solvent, $^1$H NMR was performed on a Bruker AVB400 instrument (400 MHz) using dry CDCl$_3$ solvent. The electrolyte was transferred to a sealed NMR tube without exposure to air. The resulting spectrum is shown in Figure 5.S1. Features from CHCl$_3$, PS, and PEO can be seen. Two small peaks appearing at shifts of 3.37 and 3.08 ppm arise from the isopropyl alcohol-terminated PEO chain ends. No trace of water, which would appear as a sharp peak near 1.56 ppm, is observed.

The glass transition temperature, $T_g$, of PS and the melting point of PEO were determined by DSC. Electrolyte was transferred to an aluminum pan and hermetically sealed in an Ar glovebox. The data shown in Figure 5.S2 were obtained on the second heating run at a heating rate of 10 °C min$^{-1}$. The range of temperatures scanned was -40 to 140 °C. The $T_g$ of PS was found to be 71 °C, and a weak melting peak was observed for PEO around 36 °C. The $T_g$ of PEO was outside the range of the scan. Interestingly, the melting of PEO apparently did not affect the observed ionic conductivity; however, a strong conclusion cannot be drawn because in the vicinity of 36 °C, conductivity and SAXS measurements were made with large temperature steps.
the design of the stage. A separate calibration experiment was performed to correlate the sample temperature to the temperature setpoint. The sample temperature is given by: 

$$T_{\text{Sample}} = 0.96 \, T_{\text{Setpoint}} - 0.037.$$ 

The sample temperature is reported throughout the chapter.

![Sample temperature calibration](image)

Figure 5.S3 Sample temperature calibration. Sample temperature, measured by a wire thermocouple, is plotted as a function of controller setpoint temperature.

### 5.5.3 Additional Results

In SAXS experiments, the main change in scattering profiles that was observed for temperatures between 63 °C and 116 °C was the narrowing of the FWHM. In this temperature regime, $q^*$ also shifted irreversibly with time and temperature. The domain spacing, $d$, of the polymer is related to $q^*$ as follows: 

$$d = \frac{2\pi}{q^*}.$$ 

Figure 5.S4 shows the dependence of $d$ on temperature and time during heating. During cooling, $d$, did not change significantly from its value at 116 °C. Overall, the domain spacing changed by about 1 nm during annealing. It is possible that changes in $d$ could affect the ionic conductivity; however, we do not believe that a 1 nm (or six percent) change can entirely account for a five-fold change in ionic conductivity, as we have observed.
Figure 5.S4 Domain spacing as a function of temperature during heating. Domain spacing, determined from the $q^*$ position in SAXS data, is plotted against temperature for the heating run. The color scale represents the amount of time spent at each temperature.

In Figure 5.7b, we presented conductivity as a function of grain size, $L$, with the conductivity normalized by the VTF fit to the stable cooling data. Alternatively, one could normalize the conductivity by a VTF fit to the stable heating data collected in the temperature range 29 to 63 °C (Figure 5.S5). As in Figure 5.7b, the data in Figure 5.S5 collapse onto a single line as with values approximately five times smaller than those in Figure 5.7b. The factor of five comes from the difference in the values of the prefactor, $A$, in the two VTF fits. The five-fold change in conductivity is commensurate with the approximately five-fold change in $L$ over the course of annealing.

Figure 5.S5 Normalization of conductivity data by Vogel-Tammann-Fulcher fit to heating data. Conductivity during heating is normalized by the VTF fit to the initial, time-invariant heating data and plotted against $L$. Color indicates the temperature at which the data point was collected.
6 Structure and Ionic Conductivity of Polystyrene-Block-Poly(Ethylene Oxide) Electrolytes in the High Salt Concentration Limit§

ABSTRACT

In this chapter, we explore the relationship between the morphology and ionic conductivity of block copolymer electrolytes over a wide range of salt concentrations for the system polystyrene-block-poly(ethylene oxide) (PS-b-PEO, SEO) mixed with lithium bis(trifluoromethanesulfonyl) imide salt (LiTFSI). Two SEO polymers were studied, SEO(16-16) and SEO(4.9-5.5), over the salt concentration range $r = 0.03$ to 0.55. The numbers x and y in SEO(x-y) are the molecular weights of the blocks in kg mol$^{-1}$, and the $r$ value is the molar ratio of salt to ethylene oxide moieties. Small angle X-ray scattering was used to characterize morphology and grain size at 120 °C, differential scanning calorimetry was used to study the crystallinity and the glass transition temperature of the PEO-rich microphase, and ac impedance spectroscopy was used to measure ionic conductivity as a function of temperature. The most surprising observation of our study is that ionic conductivity in the concentration regime $0.11 \leq r \leq 0.21$ increases in SEO electrolytes but decreases in PEO electrolytes. The maximum in ionic conductivity with salt concentration occurs at about twice the salt concentration in SEO ($r = 0.21$) as in PEO ($r = 0.11$). We propose that these observations are due to the effect of salt concentration on the grain structure in SEO electrolytes.

6.1 Introduction

Ion transport in block copolymers is determined both by the properties of the ion conducting block and by the nano- and meso-scale structure of the electrolyte. The crystallinity and ion transport of PEO homopolymer mixed with LiTFSI, as well as with other salts, have been thoroughly investigated in the literature.

PEO/LiTFSI mixtures, it is known that ionic conductivity reaches a maximum with salt concentration around an $r$ value of 0.1, where $r$ is the molar ratio of salt to ethylene oxide (EO) moieties.\textsuperscript{69} Ionic conductivity rapidly decreases at higher salt concentrations due to ion-pairing and transient cross-linking of the PEO chains.\textsuperscript{41,45,158–160} Due to the low ionic conductivity of PEO/LiTFSI mixtures at high $r$ values, with a few isolated exceptions, the high concentration regime has largely been ignored in studies on block copolymers such as SEO/LiTFSI.\textsuperscript{16,28,116} Recently, Bates et al. studied mixtures of LiTFSI and PS and PEO chains grafted onto a polynorbornene backbone over the salt concentration range $0.05 \leq r \leq 0.5$ and showed that conductivity was maximized at a salt concentration of $r = 0.1$, similar to that in homopolymer PEO/LiTFSI mixtures.\textsuperscript{163} However, Hudson showed that the maximum in conductivity in a particular SEO/LiTFSI mixture occurred at $r = 0.14$, significantly higher than the salt concentration that maximizes conductivity in PEO.\textsuperscript{70} Thus it is important to further investigate the behavior of SEO electrolytes at high salt concentrations. This chapter examines morphology, crystallinity, and ionic conductivity of SEO over a wide range of salt concentrations using small angle X-ray scattering (SAXS), differential scanning calorimetry (DSC) and ac impedance spectroscopy. In PEO, salt precipitation occurs at $r$ values around 0.5.\textsuperscript{69} In this chapter, we probe SEO/LiTFSI mixtures with salt concentrations over the entire solubility range, with $r$ varying from 0.03 to 0.55.

6.2 Experimental Section

6.2.1 Electrolyte Preparation

The polymers used in this chapter, their number-averaged molecular weights, $M_n$, dispersity, $D$, and PEO volume fraction, $\phi_{\text{PEO}}$, are given in Table 6.1.

<table>
<thead>
<tr>
<th>Name</th>
<th>$M_{n, \text{PS}}$ kg mol(^{-1})</th>
<th>$M_{n, \text{PEO}}$ kg mol(^{-1})</th>
<th>$D$</th>
<th>$\phi_{\text{PEO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEO(16-16)</td>
<td>16</td>
<td>16</td>
<td>1.09</td>
<td>0.49</td>
</tr>
<tr>
<td>SEO(4.9-5.5)</td>
<td>4.9</td>
<td>5.5</td>
<td>1.04</td>
<td>0.52</td>
</tr>
<tr>
<td>PEO(5)</td>
<td>-</td>
<td>5.0</td>
<td>1.06</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Block copolymers were synthesized by sequential anionic polymerization.\textsuperscript{141,142} The PS block was synthesized first using a sec-butyllithium initiator. An aliquot was
removed from the reaction to characterize the absolute molecular weight of the intermediate product using gel permeation chromatography (GPC; Viscotek GPCMax) in tetrahydrofuran (THF), with triple detection (viscometry, low angle light scattering, and refractive index detection). The PEO block was synthesized using P4 phosphazene base to promote and isopropyl alcohol to terminate the polymerization. The ratio of PEO to PS was determined by $^1$H NMR (Bruker Avance 500), and the block copolymer dispersity was determined by GPC using $N,N$-dimethylformamide solvent and PS standards. SEO in benzene solution was passed through a neutral alumina column to remove trace P4 base and then lyophilized (Millrock LD85 lyophilizer) to produce a white powder. Pure PEO (PEO(5), $M_n = 5$ kg mol$^{-1}$) was purchased from and characterized by PolymerSource, Inc. The ionic conductivity of PEO(5) is similar to that of higher molecular weight PEO.$^{9,65}$

Electrolytes of varying salt concentrations were prepared from the three polymers, SEO(16-16), SEO(4.9-5.5) and PEO(5). LiTFSI was purchased from Novolyte. Due to the hygroscopic nature of LiTFSI, electrolyte materials were dried and handled in an Ar glovebox with the H$_2$O level maintained below 0.1 ppm. Polymers were dried under vacuum at 90 °C for 24 hrs and LiTFSI was dried at 120 °C for 72 hrs before being brought into the glovebox by air-free transfer. LiTFSI was dissolved in anhydrous THF and added to solutions of SEO in anhydrous benzene. For ease of lyophilization, the concentration of the LiTFSI-THF stock solution was adjusted so that the final solutions contained less than five percent THF by volume. Solutions were lyophilized without exposure to air for one week. Fifteen salt concentrations were prepared for each SEO polymer spanning the range $r = 0.03$ to $r = 0.55$. PEO solutions were prepared by dissolving both the polymer and salt in tetrahydrofuran and evaporating on a hot plate at 45 °C for 72 hours. Eight concentrations were prepared between $r = 0.06$ to $r = 0.55$. Both PEO and SEO solutions were dried under vacuum at 90 °C for 24 hr to remove trace solvents. In all samples, solvent and water content was below the detection limit of $^1$H NMR.

6.2.2 Sample Preparation

Samples for conductivity measurements were prepared by heat-pressing the polymer at 130 °C into a 150 μm-thick fiberglass-epoxy annular spacer (Garolite-10). The diameter of the electrolyte was taken to be the size of the hole in the annulus, 3.175 mm. High-purity aluminum foils, 17.5 μm thick, were pressed onto either side of the polymer as electrodes, and aluminum tabs (MTI corporation) were attached to the electrodes with polyimide tape. The sample assembly was vacuum-sealed in an air-tight aluminum-reinforced polypropylene pouch (Showa Denka) with tabs protruding out so the sample could be electrically probed. The thickness of the polymer sample was measured after conductivity measurements were performed using a precision micrometer.
Samples for SAXS measurements were made using a similar method to those prepared for conductivity measurements. No tabs or aluminum electrodes were attached. Polyimide film 20 μm thick was heat-pressed to either side of the sample at 130 °C to prevent electrolyte from flowing out of the spacer when heated. The samples were vacuum-sealed in a modified airtight pouch. To improve X-ray transmission through the pouch, holes were punched through the material, and 20 μm polyimide windows were glued over the holes using a low vapor pressure epoxy sealant. The modified pouches were dried at 120 °C for 24 h prior to use to remove trace solvents from the sealant. A blank sample for subtraction of the scattering background was produced in a similar manner to the other samples but without electrolyte.

6.2.3 Small Angle X-ray Scattering

SAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source synchrotron (Berkeley, CA). Samples were annealed for 24 hours at 130 °C prior to measurement and were measured at 120 °C, above the glass transition temperatures of all of the constituents of the samples. Scattering was performed using 10 keV X-rays, and transmission was monitored using pre- and post-sample ion chambers. Two-dimensional diffraction images were captured with a Dektris Pilatus 2M camera with a pixel size of 0.172 x 0.172 mm, and images were calibrated using a silver behenate standard. The distance between the sample and detector was 3.8 m and the exposure time was 10 s. Two-dimensional images were azimuthally integrated to produce one-dimensional scattering profiles using the Nika package in Igor Pro. Scattering of the pouch material was subtracted according to equation 6.1:

\[ I_{\text{Corrected}} = I_{\text{Sample}} - \frac{T_{\text{Sample}}}{T_{\text{Blank}}} I_{\text{Blank}} \] (6.1)

where \( I_{\text{Corrected}} \) is the corrected scattering intensity, \( I_{\text{Sample}} \) is the scattering profile from the sample, \( T_{\text{Sample}} \) is the transmission of the sample, \( I_{\text{Blank}} \) is the scattering from the blank, and \( T_{\text{Blank}} \) is the transmission of the blank.

6.2.4 AC Impedance Spectroscopy

Ionic conductivity was measured using ac impedance spectroscopy, and sample temperature was controlled using a home-built heat stage. Prior to making conductivity measurements, samples were annealed at 130 °C for three hours. After annealing, the conductivities of the samples were invariant over the period of an hour. For SEO electrolytes, temperature-dependent conductivity measurements were taken at 10 °C increments as the samples were cooled from 130 °C to 30 °C. For PEO electrolytes, measurements were taken at 5-10 °C increments as the samples were cooled from 90 °C to
The samples were held at constant temperature for 1 h prior to each measurement. AC impedance measurements were performed using a potentiostat (BioLogic VMP3), and the amplitude of the probe signal was 20 mV and the frequency was varied from 1 MHz to 1 Hz. An example Nyquist plot is given in Figure 6.S1 of the Supporting Information. The minimum in the Nyquist plot of impedance was taken as the bulk resistance of the electrolyte, \( R \). The spacer area, \( a \), and the measured sample thickness, \( t \), were used to calculate the conductivity according to equation 6.2.

\[
\sigma = \frac{t}{R \cdot a}
\]

6.2.5 Differential Scanning Calorimetry

Thermal transitions were measured using DSC (TA Instruments Q2000). Samples were hermetically sealed in aluminum pans in an argon glovebox. Samples were heated at 10 °C min\(^{-1}\) from 40 °C to 130 °C (first heating), quickly equilibrated to -80 °C, and then heated at 10 °C min\(^{-1}\) from -80 °C to 130 °C (second heating). The glass transitions temperatures of PEO and PS, \( T_{g, \text{PEO}} \) and \( T_{g, \text{PS}} \), and the melting temperature of nearly-pure PEO, \( T_{m, \text{PEO}} \) are reported from the second heating. Melting peaks of intermediate PEO compounds are reported from the first heating as they were not observed in the second heating.

6.2.6 Transmission Electron Microscopy

Selected samples of SEO(16-16) were imaged using scanning transmission electron microscopy (STEM) after annealing at 130 °C for 24 hrs, the same heat treatment used for preparing SAXS samples.\(^{151}\) Samples were cryo-microtomed (Leica FC6) to an approximate thickness of 100 nm, stained with RuO\(_4\) for 10 min, and transferred to a lacey carbon-coated copper grid. Dark field images were obtained on a Tecnai F20 UT FEG instrument using a high angle annular dark field detector (HAADF) and 200 keV acceleration voltage. Bright regions are PEO.\(^{164}\) Samples were briefly exposed to air during microtoming and transfer to the microscope.

6.3 Results and Discussion

In Figure 6.1, SAXS profiles taken at 120 °C are shown for SEO electrolytes. The intensity is plotted as a function of scattering vector, \( q \), where \( q = 4\pi \sin \theta / \lambda \), \( 2\theta \) is the scattering angle, and \( \lambda \) is the wavelength of the X-rays. Data for SEO(16-16) is shown in Figure 6.1a. At all salt concentrations, SEO(16-16) exhibits lamellar morphology. All of
the scattering profiles contain a primary scattering peak at \( q = q^* \), and higher order scattering peaks that index to a lamellar morphology. At \( r = 0.06 \) and above, higher order peaks at \( 2q^*, 3q^*, 4q^* \), etc. are seen. The expected locations of the higher order peaks for the \( r = 0.55 \) sample are indicated by arrows in Figure 6.1a. At \( r = 0.03 \) and 0.00, the even order peaks are suppressed indicating a nearly-symmetric lamellar structure. Even order peaks are also suppressed at high salt concentrations. SAXS data for SEO(4.9-5.5) is shown in Figure 6.1b. The neat SEO(4.9-5.5) \( (r = 0) \) is disordered. The decrease in scattering intensity at low \( q \) for neat SEO(4.9-5.5) is an artifact due to slight errors in background subtraction. The SAXS patterns of SEO(4.9-5.5) electrolytes at low salt concentrations \((0.03 \leq r \leq 0.11)\) are similar to those of SEO(16-16); the expected locations of the \( 2q^* \) and \( 3q^* \) peaks in the \( r = 0.11 \) sample are shown in Figure 6.1b. We conclude that these samples have a lamellar morphology. The SAXS patterns at high concentrations \((r \geq 0.24)\) are qualitatively different. At the highest salt concentration studied \((r = 0.55)\), higher order peaks at \( \sqrt{3}q^*, 2q^*, \sqrt{7}q^* \), etc. are seen; the arrows near the \( r = 0.55 \) SAXS pattern in Figure 6.1b indicate the expected locations of higher-order peaks corresponding to hexagonally-packed cylinders. We conclude that this sample contains PS cylinders in a PEO/LiTFSI matrix. The SAXS patterns of samples with the range \( 0.27 \leq r \leq 0.55 \) are qualitatively similar indicating the presence of hexagonally-packed PS cylinders. In the salt concentration range \( 0.18 \leq r \leq 0.24 \), SAXS signatures of both lamellar and cylindrical phases are present. This is most clearly seen in the \( r = 0.18 \) sample (Figure 6.1b), where the \( q^* \) peak appears to be composed of two overlapping Gaussian peaks. We conclude that lamellar and cylindrical phases coexist in the range \( 0.18 \leq r \leq 0.24 \). The data in Figure 6.1b are consistent with those reported in reference 24. It was shown in reference 24 that pure SEO(4.9-5.5) has an order-disorder transition near room temperature; hence, no microphase separation is observed at 120 °C. Morphological changes are seen in the weakly segregated electrolyte (SEO(4.9-5.5)). This is anticipated from well-established theories on microphase separation of neat block copolymers.\(^{14,165}\) The difference in morphology behavior with salt concentration between the two polymers can be explained by the fact that in SEO(4.9-5.5), \( \phi_{PEO} \) (Table 6.1) is greater and the number of statistical segments, \( N, \) is less than in SEO(16-16). Both of these parameters make the lamellar-cylinder transition more accessible in SEO(4.9-5.5) than SEO(16-16).\(^{12,85}\)
Figure 6.1 Small angle X-ray scattering profiles of SEO electrolytes at 120 °C. Scattering intensity is plotted as a function of the magnitude of the scattering vector \( q \). In (a) profiles are shown for SEO(16-16), and in (b) profiles are shown for SEO(4.9-5.5). The salt concentration of each profile is indicated on the right. Profiles are shifted vertically. Diamonds indicate peaks due to lamellar order (\( q^*, 2q^*, 3q^*, 4q^*, 5q^* \)), and triangles indicate peaks due to cylindrical order (\( q^*, \sqrt{3}q^*, 2q^*, \sqrt{7}q^*, 3q^* \)).

As salt concentration increases, both SEO(16-16) and SEO(4.9-5.5) show changes in the primary peak position, \( q^* \), and full width at half-maximum, \( F \). As salt concentration increases, \( q^* \) shifts to lower values, indicating swelling of the domains. The characteristic domain spacing, \( d \), is given by the equation \( d = \frac{2\pi}{q^*} \) and is plotted against \( r \) in Figure 6.2a. The data in Figure 6.2 are derived from SAXS profiles obtained at 120 °C. For SEO(16-16), \( d \) increases from 31 nm at \( r = 0.03 \) to 51 nm at \( r = 0.55 \) (61% increase), and for SEO(4.9-5.5), \( d \) increases from 15 nm at \( r = 0.03 \) to 21 nm at \( r = 0.55 \) (70% increase). For both polymers \( d \) increases more or less smoothly over the entire range of \( r \) values despite the morphology change in the SEO(4.9-5.5) system.
Figure 6.2 Domain spacing and grain size as a function of salt concentration for SEO(16-16) and SEO(4.9-5.5). In (a) domain spacing, $d$, is plotted as a function of salt concentration, $r$. In (b) and (c), grain size, $L$, and reduced grain size, $L_r$, are plotted versus salt concentration. The data in Figure 6.2 are based on SAXS profiles measured at 120 °C.

In both polymers, $F$ becomes larger with increasing salt concentration indicating a decrease in grain size. $F$ was measured by fitting a linear baseline in the vicinity of the primary peak, and using linear interpolation between data points to find the width at half of the peak maximum. Assuming the primary contribution to peak broadening is finite grain size, according to the Scherrer equation, the average grain size, $L \approx 1/F$. We neglect contributions of instrumental peak broadening and grain anisotropy in estimating $L$. Lamellar and hexagonally-packed cylinder morphologies are periodic in one and two dimensions respectively. We note that for lamellae, $L$ corresponds to the average height of a lamellar stack, and for hexagonally-packed cylinders, $L$ corresponds to the average width of the grain in the radial plane of the cylinders. Grain size is plotted as a function of $r$ in Figure 6.2b. For both polymers, below $r = 0.11$, $L$ is relatively large and
scattered around 90 nm. Between \( r = 0.11 \) and \( r = 0.21 \), the value of \( L \) reaches a minimum plateau. From the average and standard deviation of the data for \( L \) above \( r = 0.21 \), the plateau value is \( 39 \pm 2 \) nm for SEO(16-16) and \( 24 \pm 2 \) nm for SEO(4.9-5.5). These minimum values of grain size are close to the values of domain spacing for each polymer, indicating a high degree of disorder at high salt concentrations. In theory, the smallest possible grain size is on the order of one domain; hence the lower limit of grain size has been reached.\(^{147,169}\) It is thus instructive to examine the dependence of reduced grain size defined as \( L_r = L/d \) on salt concentration. The reduced grain size represents the average number of repeated structures (lamellae or cylinders) in a grain. In Figure 6.2c we plot \( L_r \) vs \( r \). Unlike \( L \), \( L_r \) does not depend on the polymer domain spacing or molecular weight. Figure 6.2c shows that for \( r \geq 0.21 \), the reduced grain size reaches unity for both polymers. At salt concentrations below 0.21, on average, SEO(4.9-5.5) electrolytes contain more lamellae per grain than SEO(16-16) electrolytes do.

Transmission electron microscopy (TEM) was used to confirm our conclusions regarding the morphology of the electrolytes. Micrographs obtained from SEO(16-16) at selected salt concentrations are shown in Figure 6.3. A reduction in grain size with increasing salt concentration is clearly seen in Figure 6.3. The lack of long range order at \( r = 0.55 \), suggests that our assignment of \( L = 39 \) nm \( \approx d \) is correct.

In fully ordered block copolymers, grain growth occurs via defect annihilation.\(^ {18,20}\) Defects such as grain boundaries are metastable and will be annihilated given sufficient time and thermal activation.\(^ {18,137}\) As the samples were all annealed at the same temperature (130 °C) and for the same amount of time (24 h) prior to SAXS measurements, the fact that grain size is smaller at larger salt concentrations is an indication that annealing kinetics are slower at these concentrations. In lamellar and hexagonally-packed cylinder systems, grain boundary morphology has been extensively characterized.\(^ {19,130,133,170}\) Ryu et al. proposed that grain growth kinetics in lamellar block copolymers are influenced by the types of grain boundaries present in a sample, as some structures such as low angle tilt boundaries have a low energetic barrier to annihilation, whereas other structures such as twist boundaries have a high barrier to annihilation.\(^ {18,137,138}\) Low energy barrier defects can be annihilated without requiring the polymer chains to diffuse across incompatible domains, while high barrier defects are annihilated either by long-range collective diffusion of polymer chains or diffusion of chains across incompatible domains.\(^ {18,137}\) Similar principles have been found to apply to the annealing of hexagonally-packed cylinder thin films.\(^ {171–173}\) Diffusion of block copolymer chains in the direction perpendicular to the lamellar plane decreases as an exponential function of \( \chi N \), where \( \chi \) is the Flory-Huggins interaction parameter and \( N \) is the number of statistical segments.\(^ {174–176}\) Dissolving salt selectively in one of the blocks
Figure 6.3 Dark field STEM images of SEO(16-16) at several salt concentrations. Salt concentration increases from (a) through (d). Polymers were stained with RuO$_4$ and PEO domains appear bright. The scale bar in (a) represents 100 nm, and it applies to all images.

of a block copolymer increases the effective incompatibility between blocks. While the effective $\chi$ increases linearly with salt concentration in the low concentration limit, more complex behavior is obtained at high salt concentrations.$^{24}$ In addition to thermodynamic effects, slowing down of segmental motion due to interactions between the PEO block and salt may also influence grain growth.$^{41,45,69,158–160}$ It follows that grain growth and defect annihilation would be slower in block copolymers containing higher salt concentration.

In addition to influencing the block copolymer morphology, salt concentration influences microscopic structure and dynamics of the PEO domains. The homopolymer PEO/LiTFSI system has been the subject of numerous studies.$^{44,45,56,69,159–162}$ Several salt concentration-dependent effects have been documented such as suppression or inhibition of PEO crystallinity, shifting of the PEO glass transition temperature ($T_{g,\text{PEO}}$) and melting point ($T_{m}$), formation of intermediate crystalline compounds, and changes in crystallization kinetics.$^{69,159–161}$ We explore the impact of salt concentration on the PEO block of SEO. To explore the effect of salt concentration on PEO, $T_{g,\text{PEO}}$ and $T_{m,\text{PEO}}$ were measured using DSC for PEO(5), SEO(4.9-5.5) and SEO(16-16) (second heating data). For the block copolymers, $T_{g,\text{PS}}$ was also measured and was nearly invariant with salt concentration.
Between \( r = 0.06 \) and \( 0.15 \), the \( T_g, PS \) for SEO(4.9-5.5) increased from 73.9 °C to 81.9 °C. The average value of \( T_g, PS \) for SEO(4.9-5.5) above \( r = 0.15 \) was 82.1 ± 0.2 °C, and the average value for SEO(16-16) at all concentrations was 95.0 ± 0.1 °C. Unlike \( T_g, PS \), \( T_g, PEO \) varies significantly with salt concentration for all three polymers. The \( T_g, PEO \) for PEO(5), SEO(16-16), and SEO(4.9-5.5) are shown as a function of salt concentration in Figure 6.4. As SEO(16-16) is highly crystalline below \( r = 0.09 \), reliable \( T_g, PEO \) values could not be obtained in that concentration regime. Below \( r = 0.27 \), the values of \( T_g, PEO \) for all three polymers coincide. Above \( r = 0.27 \), the values of \( T_g, PEO \) are only similar for the block copolymers. At high salt concentrations (\( r = 0.45 \) and 0.55), \( T_g, PEO \) for homopolymer PEO reaches a plateau. Our result is similar to that of Lascaud et al., who showed that for salt concentrations above \( r = 0.4 \), pure LiTFSI precipitation occurs, and \( T_g, PEO \) saturates.\(^69\) At the highest salt concentration, \( r = 0.55 \), we found evidence of macrophase separation in PEO(5)/LiTFSI mixtures using the naked eye. For the block copolymers, \( T_g, PEO \) increases over the entire concentration range, which is evidence that after initial heating to 130 °C, LiTFSI remains dissolved over the time scale of the DSC scan (30 min).

It appears that solubility of LiTFSI in SEO electrolytes is greater than that of PEO electrolytes; this may be due to thermodynamic or kinetic reasons. Microphase separation distorts the PEO chains, which may influence thermodynamic interactions between the polymer and salt. Precipitation kinetics could be slower in block copolymers due to confinement effects.\(^180,181\) In a homogenous polymer, dissolved ions can diffuse from any part of the volume to deposit on a growing precipitate nucleus, whereas in a block copolymer, ions can only diffuse to a nucleus within a continuous domain. Several studies have shown that in lamellar SEO, PEO crystallizes in an oriented manner.\(^104,145,182\) Oriented crystallization could occur in SEO/LiTFSI mixtures, which may slow the crystallization kinetics. Due to uncertainty about LiTFSI solubility at high salt concentrations, the conductivity data in this chapter are limited to \( r \leq 0.40 \), and the line in Figure 6.4 is fit to data for SEO and PEO electrolytes with \( r \leq 0.40 \).
The glass transition temperatures of PEO-rich microphases and PEO homopolymer, $T_{g,\text{PEO}}$, are shown as a function of salt concentration, $r$. The line represents a least-squares fit through the data, excluding the two highest PEO(5) salt concentrations.

The crystallization behavior of the PEO blocks in SEO(16-16) and SEO(4.9-5.5) was also measured by DSC. In Figures 6.5a and 6.5b, representative DSC heating scans are presented for SEO(16-16). Figure 6.5a shows second heating data. In Figure 6.5a, an endothermic peak at 55 °C is observed for the sample with $r = 0.03$, which we attribute to $T_{m,\text{PEO}}$, the melting of nearly-pure PEO. Similar peaks were observed in samples with $r \leq 0.09$. At higher salt concentrations, a glass transition is observed at temperatures between -40 and 10 °C, reflecting $T_{g}$ of the salt-containing PEO-rich phase, $T_{g,\text{PEO}}$. The $T_{g,\text{PEO}}$ is also observed in all traces, though it is very weak in semi-crystalline samples with $r \leq 0.09$.

Figure 6.5b shows first heating data. Prior to first heating, DSC samples were in the lyophilized state. At salt concentrations $r \geq 0.11$, endothermic peaks were observed upon first heating (but not on second heating) as seen in Figure 6.5a. We attribute these peaks to slowly crystallizing intermediate compounds formed by PEO and LiTFSI. At several salt concentrations, such as $r = 0.35$, two peaks were observed, indicating the coexistence of multiple crystalline phases. Changes in phase coexistence were observed in the vicinity of integer values of $1/r$; at $1/r = 6$, 3, and 2. It is known that PEO/LiTFSI mixtures form crystalline complexes at these salt concentrations. Following the literature, we label these complexes C$_6$, C$_3$, and C$_2$ respectively.

Figure 6.5c shows the phase diagram of the PEO microphases in SEO(16-16)/LiTFSI mixtures, deduced from the DSC peaks observed in the first and second heating. The melting of crystalline solids in electrolytes with $r \leq 0.09$ (open symbols in Figure 6.5c) were determined from second heating runs. The melting of crystalline solids and their mixtures in electrolytes with $0.15 \leq r \leq 0.55$ (closed symbols in Figure 6.5c) were determined from first heating runs.
vertical lines in Figure 6.5c represent locations expected for C$_2$, C$_3$ and C$_6$. The phase diagram in Figure 6.5c bears close resemblance to the phase diagrams reported by Vallée et al. and Lascaud et al. for homopolymer PEO/LiTFSI. The phase diagram of Lascaud was used to aid in assigning the species in the coexistence regions of Figure 6.5c; however, separate characterization of the crystal structures is necessary for unambiguous assignment. The PEO-rich microphase of SEO(4.9-5.5) polymers exhibit crystallinity similar to that of SEO(16-16) electrolytes, with corresponding phase transitions occurring at lower temperatures. Data from SEO(4.9-5.5) are included in the Supporting Information (Figure 6.S2).

Ionic conductivity, $\sigma$, was measured as a function of salt concentration and temperature for SEO(16-16), SEO(4.9-5.5), and PEO(5). Conductivity as a function of salt concentration and temperature is given in the Supporting Information for each electrolyte in Tables S1-S3. In Figure 6.6, ionic conductivity at 90°C is shown for the three polymers. The data at each point in Figure 6.6 are averaged for three samples and the error bars represent the standard deviations of the measurements. The ionic conductivity of PEO(5) exhibits a maximum at $r = 0.11$; this value is in reasonable agreement with previously reported values for the optimum salt concentration in PEO/LiTFSI mixtures. The dependence of conductivity on salt concentration is much richer for SEO(16-16) and SEO(4.9-5.5). Conductivity increases in the range $0 \leq r \leq 0.09$, decreases in the range $0.09 \leq r \leq 0.11$, before increasing again in the range $0.11 \leq r \leq 0.21$ to obtain a global maximum at $r = 0.21$. Due to the limited range of salt concentrations explored in previous studies on block copolymer electrolytes, only the local maximum at $r = 0.09$ was captured. Our results show that the trend in conductivity with salt concentration for a homogenous system such as PEO is qualitatively different than for a nanostructured system such as SEO.

The temperature dependence of ionic conductivity in PEO-based electrolytes has been shown to follow Vogel-Tammann-Fulcher (VTF) behavior. The VTF model for ionic conductivity is given by equation 6.3:

$$\sigma(T) = A T^{-1/2} e^{-E_a / R (T - T_0)}$$  \hspace{1cm} (6.3)

where $A$ is a prefactor, $E_a$, is a pseudo-activation energy, $R$ is the gas constant, and $T_0$ is the Vogel temperature, which is related to the glass transition temperature of the salt-containing microphase ($T_0 = T_{g,\text{PEO}} - 50$ °C). The temperature-dependent ionic conductivity data for SEO(16-16), SEO(4.9-5.5), and PEO(5) are shown for different salt concentrations in Figures 6.7a-c. We restrict our attention to temperatures above $T_{m,\text{PEO}}$. These data were fit to the VTF model using $A$ and $E_a$ as adjustable parameters (Figure 6.8a and b); $T_0$ is determined by the $T_{g,\text{PEO}}$ data in Figure 6.4 ($T_{g,\text{PEO}}$ is approximated as a linear
Figure 6.5 Differential scanning calorimetry and phase diagram of SEO(16-16)/LiTFSI. Data is shown for electrolytes with different salt concentrations, $r$. In (a) and (b), thermograms obtained by differential scanning calorimetry are offset along the vertical axis, with endothermic peaks down. In (a) thermograms from the second heating are shown, and in (b), thermograms from the first heating are shown. In (c) a phase diagram is constructed from the endothermic peaks observed during first and second heating. Open circles indicate peaks from second heating; solid symbols indicate peaks from first heating. Vertical lines are drawn at stoichiometric ratios between LiTFSI and ethylene oxide (EO) moieties. The symbols C$_6$, C$_3$ and C$_2$ represent stoichiometric ratios of 6, 3 and 2. The symbol L denotes the liquid phase.
Ionic conductivity, $\sigma$, is plotted against salt concentration, $r$, for the block copolymers SEO(16-16), SEO(4.9-5.5) and homopolymer PEO(5). Data were obtained at 90 °C.

Function of $r$, $T_g\text{PEO} = -51.4 + 131\ r\ [\text{°C}]$. In Figure 6.8a, $E_a$ is plotted against $r$ for PEO(5), SEO(16-16) and SEO(4.9-5.5). Values represent the average of $E_a$ calculated for three samples, and error bars show the standard deviation. For PEO(5), $E_a$ exhibits a sharp maximum at $r = 0.11$. For the SEO electrolytes, $E_a$ exhibits two shallow maxima, one near $r = 0.09$ and one near $r = 0.27$, which are close to but not coincident with the maxima in ionic conductivity at 90 °C. In Figure 6.8b, $A$ is plotted against $r$ for all three types of electrolytes. For PEO(5), $A$ exhibits a sharp maximum at $r = 0.15$. For SEO electrolytes, $A$ exhibits a local maximum at $r = 0.09$, and a shallow global maximum at $r = 0.27$. It is believed that $E_a$ is related to the activation energy associated with ion hopping while $A$ is related to the fraction of dissociated ions (charge carrier concentration)\(^{156}\). The data in Figure 6.8 indicate that at high salt concentrations, both the activation energy for ion hopping and charge carrier concentration are higher in SEO electrolytes relative to PEO. These parameters have opposing effects on ionic conductivity. As a result, the conductivities of SEO and PEO electrolytes at high salt concentrations are not significantly different (Figure 6.6).
Figure 6.7 Vogel-Tammann-Fulcher (VTF) plots of ionic conductivity for SEO and PEO electrolytes. Dependence of conductivity, $\sigma$, of SEO(16-16), SEO(4.9-5.5) and PEO(5) on temperature, $T$, shown on a VTF plot are presented in a-c. Each data set represents data at a different salt concentration, and the color scale indicates the $r$ value. The Vogel temperature, $T_0$ is $T_{g, PEO} - 50$ K, where $T_{g, PEO}$ at the salt concentration of interest is given by the line in Figure 6.4 and converted to units of Kelvin. Data points are connected for clarity.

The volume fraction of the conducting domains in the SEO electrolytes is a function of salt concentration. To account for this, we compute normalized conductivity, $\sigma_n$, defined as:

$$\sigma_n = \frac{\sigma_{SEO}(r)}{\phi_c \sigma_{PEO}(r)}$$

(6.4)

where $\sigma_{SEO}$ is the ionic conductivity of SEO measured at 90°C (the data shown in Figure 6.5a), $\sigma_{PEO}$ is the ionic conductivity of PEO(5) measured at 90 °C, and $\phi_c$ is the volume fraction of the combined PEO/LiTFSI domain. The volume fraction, $\phi_c$, at a given $r$
value was estimated according to equation 6.5, which assumes that the partial molar volumes of LiTFSI, \( v_{\text{LiTFSI}} \), and PEO, \( v_{\text{PEO}} \), are unchanged upon mixing.\(^\text{24}\)

\[
\phi_c = \frac{v_{\text{PEO}} + r v_{\text{LiTFSI}}}{v_{\text{PEO}} + r v_{\text{LiTFSI}} + n_{\text{PS}} v_S}
\]

In equation 6.5, \( n_{\text{PS}} \) is the number of monomers in the PS block and \( n_{\text{PEO}} \) is the number of the monomers in the PEO block. The number of monomers were calculated from \( n = M_{\text{Polymer}} / M_{\text{Monomer}} \), where \( M \) is the molar mass. The molar volume of each species was calculated from \( v = M / \rho \), where \( \rho \) is the bulk density of the polymer or salt. The molar masses used were: 44.05 g mol\(^{-1}\) for EO (ethylene oxide monomer), 104.15 g mol\(^{-1}\) for S (styrene monomer) and 287.09 g mol\(^{-1}\) for LiTFSI. The densities of PEO and PS were calculated to be 1.12 g cm\(^{-3}\) and 1.07 g cm\(^{-3}\) at 25\(^\circ\)C from Orwoll,\(^\text{82}\) and the density of LiTFSI was taken to be 2.023 g cm\(^{-3}\).\(^\text{24}\) The conductivity of PEO used in equation 6.3, \( \sigma_{\text{PEO}} \), was estimated by linearly interpolating the conductivity data for PEO(5) onto the \( r \) values corresponding to the conductivity data for SEO(16-16) and SEO(4.9-5.5).

![Graph](image)

**Figure 6.8** Vogel-Tammann-Fulcher (VTF) parameters for SEO and PEO electrolytes. The VTF pseudo-activation energy, \( E_a \), and prefactor, \( A \), are plotted against salt concentration, \( r \), in (a) and (b). See equation 6.3 for definitions of \( E_a \) and \( A \). Curves are drawn to guide the eye.

In Figure 6.9, we plot \( \sigma_n \) versus \( r \) for both SEO(16-16) and SEO(4.9-5.5). The data in Figure 6.9 are derived from ionic conductivity data obtained at 90 \(^\circ\)C (Figure 6.6). In Figure 6.9, error is calculated by propagating the error from the PEO and SEO conductivity data in Figure 6.6. The error from interpolating the values for \( \sigma_{\text{PEO}} \) is not accounted for in the figure. Figure 6.9 shows that both SEO(16-16) and SEO(4.9-5.5) behave similarly with \( \sigma_n \) increasing as a function of \( r \). At concentrations below \( r = 0.11 \), \( \sigma_n \) of both polymers is around 0.1. Between \( r = 0.11 \) and \( r = 0.21 \), \( \sigma_n \) increases from 0.1 to about 0.6. At
concentrations above \( r = 0.21 \), \( \sigma_n \) reaches a plateau of about 0.6. For ideal lamellar samples, \( \sigma_n = 2/3 \), while for ideal cylindrical samples with PEO/LiTFSI in the matrix, \( \sigma_n = 1 \).\textsuperscript{5,16,135} The term ideal implies that our samples are composed of randomly oriented grains with negligible resistance between grains. In other studies, the denominator in equation 6.5 is scaled by a constant morphology factor.\textsuperscript{5,16,135} We omit the morphology factor in equation 6.5 because for salt concentrations of 0.18 \( \leq r \leq 0.24 \), SEO(4.9-5.5) exhibits coexisting morphologies, and the relative volume fraction of each phase is unclear. Hence the morphology factor is unknown for several electrolytes in this chapter. The dashed lines in Figure 6.9 show the expected values of \( \sigma_n \) for ideal morphologies. It is evident that \( \sigma_n \) of both SEO(16-16) and SEO(4.9-5.5) approaches the expected value for ideal lamellae in the high salt concentration limit. The SAXS and conductivity data (Figure 6.1a and Figure 6.9) suggest that ideal lamellar grains are obtained in SEO(16-16) in the high salt concentration limit. On the other hand, the SAXS and conductivity data (Figure 6.1b and Figure 6.9) suggest that non-ideal cylindrical grains are obtained in SEO(4.9-5.5) in the high salt concentration limit. Previous studies that explored a lower range of salt concentrations (\( r \leq 0.1 \)) reported that \( \sigma_n \) of 2/3 was only reached in lamellar SEO/LiTFSI when the molecular weights of the PS and PEO blocks were each above 60 kg mol\(^{-1}\).\textsuperscript{16,116} The present chapter shows that at sufficient salt loading, even low molecular weight SEO polymers can exhibit \( \sigma_n \) values as high as 0.6.

Qualitatively, Figure 6.2c and Figure 6.9 are mirror-images of each other, suggesting a relationship between normalized conductivity and reduced grain size. We thus plot \( \sigma_n \) vs. \( L_r \) of both SEO(16-16) and SEO(4.9-5.5) in Figure 6.10. The data for SEO(16-16) and SEO(4.9-5.5) collapse on the same trend line. The solid curve in Figure 6.10 is an exponential fit through the data (\( \sigma_n = 0.012 + 1.25 \exp[-0.83L_r] \)). The error in \( \sigma_n \) in Figure 6.10 is the same as in Figure 6.9. The reason for apparent exponential relationship between normalized conductivity and reduced grain size is not known at this time. The correlation between increasing conductivity and decreasing grain size has been demonstrated in the previous chapter.\textsuperscript{151} The reason for this correlation is, however, not well-established. It appears that defects obtained in well-annealed samples with large grains impede the transport of ions, although the particular defects that are responsible for this have not yet been identified. Diederichsen \textit{et al.} suggest that having smaller grains increases the number of nodes in the conductive path, reducing the importance of any particular node.\textsuperscript{23} The result in reference 23 was obtained in thin films of block copolymers, \textit{i.e.} in two-dimensional samples. Further work is required to establish the underpinnings of the dependence of conductivity on grain size in three-dimensional samples.
Figure 6.9 Normalized conductivity with salt concentration. Normalized conductivity, $\sigma_n$, is plotted against salt concentration, $r$. Dashed lines indicate the ideal values of $\sigma_n$ for ideal lamellae (0.66) and for ideal hexagonally-packed PS cylinders in a PEO-rich matrix (1). Open, downward triangles represent compositions of SEO(4.9-5.5)/LiTFSI with entirely lamellar structure, filled, upward triangles indicate lamellae-cylinder coexistence, and open, upward triangles indicate pure cylinder morphologies. Data in Figure 6.9 are derived from ionic conductivity data taken at 90 °C (Figure 6.6).

Figure 6.10 Normalized conductivity versus reduced grain size. The normalized conductivity, $\sigma_n$, is plotted against reduced grain size, $L_r$, for both SEO(16-16) (squares) and SEO(4.9-5.5) (triangles). The salt concentration, $r$, is represented by the color of the marker. The curve is an exponential fit through the data. The normalized conductivity is calculated from ionic conductivity data obtained at 90 °C.
The most surprising observation of our study is that in SEO electrolytes, ionic conductivity increases in the concentration regime \(0.11 \leq r \leq 0.21\), but in PEO(5), ionic conductivity decreases in the same regime. We believe that this is due to the effect of salt concentration on the grain structure in SEO electrolytes.

6.4 Conclusions

The morphology, crystallinity, and ionic conductivity of SEO/LiTFSI electrolytes were determined over a wide range of salt concentrations. The morphology of SEO(16-16) remains lamellar at all salt concentrations studied. The SEO(4.9-5.5) electrolytes undergo morphology transitions from lamellae to coexisting lamellae and majority-PEO cylinders at \(r = 0.18\) and from coexistence to cylinders at \(r = 0.24\). The crystallinity of the PEO-rich microphase of SEO was found to be similar to that of homopolymer PEO/LiTFSI mixtures, and the glass transition temperature of the PEO block was similar for both SEO and PEO electrolytes for \(r \leq 0.27\). In block copolymer electrolytes that were annealed for a fixed amount of time, the grain size was shown to decrease with increasing salt concentration and then plateau to a value close to the domain spacing of the polymer, indicating a highly defective structure. The effect of salt concentration on grain size of SEO(16-16) and SEO(4.9-5.5) collapses when reduced grain size (grain size normalized by the domain spacing) is plotted as a function of salt concentration.

We show that the dependence of ionic conductivity on salt concentration is qualitatively different for SEO and PEO electrolytes. The maximum in ionic conductivity with salt concentration occurs at about twice the salt concentration in SEO \((r = 0.21)\) as in PEO(5) \((r = 0.11)\). This result cannot be anticipated from previous systematic studies of conductivity of SEO electrolytes as a functions of salt concentration.\(^{16,116}\) The electrolytes based on SEO(16-16) and SEO(4.9-5.5) reach similar maximum values of ionic conductivity at 90 °C, 2.3\(\times\)10\(^{-4}\) S cm\(^{-1}\), and 2.2\(\times\)10\(^{-4}\) respectively. For both SEO(16-16) and SEO(4.9-5.5), the normalized conductivity calculated at 90 °C, which takes into account the volume fraction and conductivity of PEO at a given \(r\) value, approaches 0.6 in the high salt concentration limit. We show that normalized conductivity decreases exponentially as reduced grain size increases. Increasing salt concentration slows the kinetics of grain growth, which in turn increases block copolymer ionic conductivity.
6.5 Supporting Information

6.5.1 Sample Nyquist Plot

Nyquist plots were used to determine the bulk resistance and ionic conductivity of the electrolyte from ac impedance data. A sample Nyquist plot is given in Figure 6.S1 for SEO(16-16), \( r = 0.21 \) at 60 °C. The minimum at 3.7 kΩ cm\(^2\), represents the bulk resistance of this electrolyte multiplied by the cell area, 0.079 cm\(^2\). The real component of the complex impedance, \( Z' \), is plotted on the abscissa, and the imaginary component of the complex impedance, \( Z'' \), is plotted on the ordinate.

![Nyquist plot](image)

Figure 6.S1 Sample Nyquist plot. A representative Nyquist plot is given for the electrolyte, SEO(16-16), \( r = 0.21 \), at 60 °C. The real impedance, \( Z' \), is plotted on the abscissa and the complex impedance, \( Z'' \), is plotted on the ordinate. The impedances are scaled by the area of the cell, 0.079 cm\(^2\).

6.5.2 Phase Diagram for SEO(4.9-5.5)

Crystallinity of PEO-rich microphases in SEO(4.9-5.5) electrolytes is given in Figure 6.S2. The phase diagram is constructed from endothermic peaks observed using DSC. The vertical lines in Figure 6.S2 represent locations expected for C\(_2\), C\(_3\) and C\(_6\), which are identical to those in the phase diagram in SEO(16-16) phase diagram (Figure 6.5c). The melting temperatures are slightly lower for SEO(4.9-5.5) than for SEO(16-16).
Figure 6.5.2 The phase diagram of the SEO(4.9-5.5)/LiTFSI electrolytes. The phase diagram is constructed from the endothermic peaks observed during first and second heating. Open circles indicate peaks from second heating; solid symbols indicate peaks from first heating. Vertical lines are drawn at stoichiometric ratios between LiTFSI and ethylene oxide (EO) moieties. The symbols C₆, C₃ and C₂ represent stoichiometric ratios of 6, 3 and 2. The symbol L denotes the liquid phase.

6.5.3 Tabular Conductivity Data

In Tables 6.S1-S3, raw conductivity data [mS cm⁻¹] is given as a function of temperature [°C] and r-value for the electrolytes in this study. In Table 6.S1, data for electrolytes made with SEO(16-16) are given, in Table 6.S2, data for electrolytes made with SEO(4.9-5.5) are given, and in Table 6.S3, data for electrolytes made with PEO(5) are given.
Table 6.1 Conductivity as a function of temperature for SEO(16-16) electrolytes. Conductivity is given in mS cm\(^{-1}\). For each sample three measurements were made. The averages of the measurements are reported below, and the standard deviations are given in parentheses. In (a), the data for 0.03 \( \leq r \leq 0.24 \) are given, and in (b), the data for 0.27 \( \leq r \leq 0.55 \) are given

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Table 6.53 Conductivity as a function of temperature for PEO(S) electrolytes. Conductivity is given in mS cm⁻¹. For each sample three measurements were made. The averages of the measurements are reported below, and the standard deviations are given in parentheses.

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ABSTRACT

A method is presented to relate local morphology and ionic conductivity in a solid, lamellar block copolymer electrolyte for lithium batteries, by simulating conductivity through transmission electron micrographs. The electrolyte consists of polystyrene-block-poly(ethylene oxide) mixed with lithium bis(trifluoromethanesulfonyl) imide salt (SEO/LiTFSI), where the polystyrene phase is structural phase and the poly(ethylene oxide)/LiTFSI phase is ionically conductive. The electric potential distribution is simulated in binarized micrographs by solving the Laplace equation with constant potential boundary conditions. A morphology factor, \( f \), is reported for each image by calculating the effective conductivity relative to a homogenous conductor. Images from two samples are examined, one annealed with large lamellar grains and one unannealed with small grains. The average value of \( f \) is 0.45±0.04 for the annealed sample, 0.37±0.03 for the unannealed sample, both close to the value predicted by effective medium theory, 1/2. Simulated conductivities are compared to published experimental conductivities. The value of \( f_{\text{Unannealed}}/f_{\text{Annealed}} \) is 0.82 for simulations and 6.2 for experiments. Simulation results correspond well to predictions by effective medium theory but do not explain the experimental measurements. Observation of nanoscale morphology over length scales greater than the size of the micrographs (~1 μm) may be required to explain the experimental results.

7.1 Introduction

In block copolymers, microphase separation gives rise to ordered morphologies with characteristic dimensions in the 5 to 50 nm range. Coherent order is limited to another characteristic length scale that is often referred to as the grain size, \( L \). The influence of

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**This chapter is reported in Chintapalli, M., Higa, K., et al. Simulation of Local Ion Transport in Lamellar Block Copolymer Electrolytes Based on Electron Micrographs. Journal of Polymer Science Part B: Polymer Physics 55, (2017).**
nanoscale morphology and defects on the transport of chemical through block copolymer domains is not yet well understood. While techniques used for morphology characterization such as scattering and microscopy are inherently local (i.e. sensitive to structure on the nanometer or micron length scale), transport measurements are typically performed across length scales of hundreds of microns. In this study, we present a method to relate local morphology and ionic conductivity in a block copolymer electrolyte.

Sax and Ottino developed a widely-adopted model based on effective medium theory to relate structure and transport at the bulk scale in randomly-oriented morphologies relevant to block copolymer materials. Within this model, the ionic conductivity of a block copolymer electrolyte, $\sigma$, is given by

$$\sigma = f \phi_c \sigma_c$$

(7.1)

where $f$ is the morphology factor, $\sigma_c$ is the intrinsic conductivity of the bulk ion-transporting microphase phase, and $\phi_c$ is the volume fraction of the ion-transporting microphase. Others have proposed modifications to the model in equation 7.1 to account for additional structural details such as tortuosity and the non-conducting interfacial volume between microphases. For randomly-oriented lamellae in a bulk three-dimensional material, $f$ is $2/3$; two out of three principle orientations lead to conduction. By similar logic, for a one-dimensional morphology in two dimensions such as a cross section through bulk lamellae, $f$ is $1/2$.

One of the benefits of the effective medium model is its simplicity, as it only requires knowledge of the block copolymer morphology. However, a number of recent publications have noted deviations between experiments and the ideal morphology factor predicted by effective medium theory, suggesting that defects such as grain boundaries may affect ion transport, either positively or negatively. Majewski et al. compared ionic conductivities of electrolytes consisting of randomly oriented and single-grain, aligned hexagonally-packed cylinders and showed that the ratio of morphology factors $f_{\text{Random}}/f_{\text{Aligned}}$ is around 0.10 instead of 0.33, as predicted by effective medium theory. Young et al. found that as the conductive phase becomes more networked, progressing from lamellae to hexagonally-perforated lamellae to hexagonally packed cylinders with a majority conductive phase, the morphology factor increases and becomes closer to the effective medium theory prediction. Meek et al. provide a review of several other examples of deviations that have been observed between experiment and effective medium theory in materials based on polymerized ionic liquids. These studies all suggest that defects decrease the conductivity of the block copolymer by decreasing the connectivity of the conductive phase. In contrast, Diederichsen et al. showed that as the number of node-like defects in a conducting network increases, the conductivity increases. Similarly, in reference 151, it was shown that as $L$ increases from 13 nm to 88 nm, a factor of 6.5, $f$ decreases from 0.36 to 0.058, a factor of 6.2. As $L$ increases, the
number of grain boundary defects decreases. Improving the connection between local structure and ion transport could help clarify which defects enhance transport and which ones inhibit it.

Recently, several authors have made progress toward relating local structure and transport in thin film block copolymers. In the study by Diederichsen et al., block copolymers films were used to template an electronically conductive gold network. The authors use scanning electron microscopy (SEM) to characterize the local structure and directly probe the conductivity of the gold network. Using this approach, the authors could relate the network topology to the electrical conductivity. In another study, Arges et al. use electrodes deposited on a silicon wafer to probe the ionic conductivity of an anion-conducting thin film block copolymer based on a polymerized ionic liquid. This experimental design enables the direct measurement of ionic conductivity by ac impedance spectroscopy and structure by SEM. In both of these experiments, the thin film configuration facilitates the measurement of local structure and transport on the same system.

While previous studies have shed light on the relationship between charge transport and morphology in some idealized systems, the challenge of establishing the relationship between these quantities in block copolymer electrolyte films remains. In an attempt to address this challenge, we simulate ion conduction through scanning transmission electron microscopy (STEM) images of a microtomed bulk lamellar block copolymer electrolyte for lithium metal batteries. The electrolyte consists of polystyrene-block-poly(ethylene oxide) (SEO) mixed with a lithium salt, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). The polystyrene (PS) block provides high modulus, and the poly(ethylene oxide) (PEO) block solvates the LiTFSI. Together, the PEO/LiTFSI mixture forms the ion-conducting phase. Conductivity was simulated in two sets of images, one from an annealed sample with grains and one from an unannealed sample with small grains. The samples used in this study are the same ones used in reference 151, where we reported on the effect of annealing on ionic conductivity. This enables a direct comparison between simulation and experiment. While our conductivity measurements are made on samples that are 100 μm thick, the STEM experiments are restricted to length scales of about 1 μm. The main question that we answer is the following: Can morphological characterization on the local scale (1 μm) can be used to predict ion transport in bulk?

7.2 Experimental Section

7.2.1 Materials
An SEO polymer was synthesized using sequential anionic polymerization, as described previously.\textsuperscript{141,142} The number-average molecular weight, $M_n$, of the PS block is 4.9 kg mol\(^{-1}\) and that of the PEO block is 5.5 kg mol\(^{-1}\). All steps of the electrolyte preparation were conducted in argon glovebox.\textsuperscript{11,151} Polymer was dried under vacuum at 90 °C for 24 h, and LiTFSI was dried under vacuum at 120 °C for 72 h, both in the antechamber of an argon glovebox. The electrolyte was prepared by mixing a 10 mL solution of SEO in anhydrous benzene with a 200 μL solution of LiTFSI salt in anhydrous tetrahydrofuran and freeze drying. The sample was freeze dried without exposure to air using a homebuilt transfer apparatus and then dried under vacuum for 24 h in the antechamber of an argon glovebox. The molar ratio of Li to ethylene oxide moieties, or $r$-value was 0.085.

For both the annealed and unannealed samples, the freeze dried electrolyte was pressed into a 150 μm thick fiberglass-reinforced epoxy spacer (Garolite G10) at room temperature and vacuum-sealed in an air-tight laminated aluminum pouch (Showa-Denko). After sealing, the annealed sample was heated to 120 °C on a hotplate for 24 h, and the unannealed sample was maintained at room temperature. The electrolyte used in this study is the same as the electrolyte used in reference 151. Immediately prior to imaging by STEM, samples were removed from their pouch. Sections of each sample, 100 nm thick, were prepared by cryo-microtoming the bulk electrolyte at -120 °C using a Leica EM FC6 microtome. The samples were placed on lacey carbon-coated copper grids and stained with RuO\(_4\) vapor for 10 min. The electrolytes were imaged with a Tecnai F20 UT FEG instrument using a high angle annular dark field detector, with the PEO domains appearing bright.\textsuperscript{164} The acceleration voltage was 200 keV.

7.2.2 Simulation Domain Preparation

STEM images were converted to binary, black and white images for simulations. Small variations in magnification of the 8-bit grayscale STEM images were eliminated by cropping the images to a consistent physical size (0.985 x 0.985 μm) and compressing them to a consistent resolution (1024 x 1024 pixels). To eliminate noise and long-range intensity fluctuations due to variations in sample thickness, a bandpass filter was applied using the ImageJ software package. The lower cutoff was set to 4 pixels and the upper cutoff set to 20 pixels. The images were segmented to produce binary images. The segmentation threshold was adjusted so that the area fraction of the conducting phase (represented as white), $\phi$, was as close as possible to the volume fraction of the conducting phase in the bulk electrolyte, $\phi_c$, 0.58. Circular regions were extracted from segmented microscopy image data using a custom ImageJ script, and a commercial software package (Avizo, FEI) was used to convert the circular regions into surface meshes.

7.2.3 Modeling
The surface meshes were imported into a commercial simulation package (STAR-CCM+, CD-adapco) and transformed into surface meshes in annular regions, with the inner and outer edges of these regions virtually embedded into circular electrodes of small but finite width. These regions were refined with a custom mesh repair algorithm, and transformed into simulation domains, on which the Laplace equation with potential boundary conditions was then solved. Conductivity ratios were computed from the simulation results. Different boundary conditions and image regions could be used for the simulations. For example, a square image region could be used with potential boundary conditions on two parallel sides and insulating boundary conditions on the other two sides. In this configuration, some paths through the electrolyte would terminate on the insulating boundaries, rendering them non-conducting. Annular image regions with circular electrodes were chosen for this study in order to maximize the number of conductive paths between electrodes and to avoid directional bias in the plane. In Figure 7.S1, electric potential distribution is shown for the image Annealed 2 in both annular and square geometry.

The conductivity ratio is a characteristic of the material. However, in order to obtain these values through simulation, selected spatial domains must be representative of the material. They must be sufficiently large to make the effect of local variation unimportant; in this work, the outer diameters of the annular regions were taken as the image widths. Also, an inner electrode that is too small will be connected to rest of the spatial domain by only a small number of conductive paths, producing a spatial domain that is not representative of the segmented image data. For each segmented image, a suitable inner electrode size was chosen by constructing several domains from the image, each using a different inner radius. As discussed, the conductivity ratios tend to vary with inner electrode size when the inner electrodes are small, as well as when the inner electrodes are too large, making the area of the domain too small. However, the conductivity ratios tend to reach a plateau at intermediate sizes of the inner electrode. The values reported in this article are based on these intermediate sizes, for which variation of effective conductivity with electrode size is within approximately 5%. The effect of inner radius on effective conductivity is reported in Figure 7.S2 in the supporting information.

Direct numerical simulations were performed on planar spatial domains constructed from microscopy images. In the annular region used, the inner and outer boundaries represent electrodes held at different potentials. As a baseline, the potential of an annular region consisting entirely of conductive material is given by Laplace’s equation (equation 7.2).

$$\nabla^2 V = 0$$  \hspace{1cm} (7.2)
The potential is held at 1 V at the inner boundary at radius $R_i$ and at 0 V at the outer boundary at radius $R_o$. The potential as a function of radial position $r$ is then given by equation 7.3.

$$V(r) = \frac{\ln(r/R_o)}{\ln(R_i/R_o)}$$  \hspace{1cm} (7.3)

Though a dc potential is applied to the electrolyte, polarization effects are ignored. This treatment is representative of conditions during a low-amplitude ac impedance experiment.

The total current flowing between the two electrodes may be determined from the current density at some radial position and the circumference of the circle associated with that position, but is independent of radial position. The current density $j$ can be obtained from the potential as $j = \sigma_c E$, where $\sigma_c$ is the bulk conductivity of the conductive material and $E = \nabla V$ is the electric field. The total current per unit depth (assuming no variation of the spatial domain out of the plane) is then given by equation 7.4.

$$I_{\text{analytical}} = 2\pi r |j(r) \cdot \hat{r}| = 2\pi r |\sigma_c E| \left| \frac{dV}{dr} \right| = \frac{2\pi \sigma_c}{|\ln(R_i/R_o)|}$$  \hspace{1cm} (7.4)

This analytical result may be compared against the current per unit depth computed in simulations involving similar spatial domains based on microscopy images. Unlike in the baseline case, these spatial domains consist of complex arrangements of both conductive and insulating regions. However, the total current passing between the electrodes can be computed through any surface represented by a closed, non-intersecting curve encircling the inner electrode in the simulation domain. Based on the computed current, one can assign a conductivity, $\sigma$, to the simulation domain through the analytical relationship obtained earlier (equation 7.5).

$$I_{\text{sim}} = \frac{2\pi \sigma}{|\ln(R_i/R_o)|}$$  \hspace{1cm} (7.5)

Rearranging this expression and reintroducing the bulk conductivity of the conductive material gives equation 7.6, which is a conductivity ratio that reflects only the arrangement of conductive and insulating regions in the image data.

$$\frac{\sigma}{\sigma_c} = \frac{I_{\text{sim}} |\ln(R_i/R_o)|}{2\pi}$$  \hspace{1cm} (7.6)

This conductivity ratio is related to $f$, where $\phi$ is the area fraction of the conductive phase in the image, or $\phi_c$, the conductive phase volume fraction in a bulk sample (equation 7.7).

$$f = \frac{\sigma}{\sigma_c \phi_c}$$  \hspace{1cm} (7.7)
7.3 Results

In Table 7.1, the properties of the annealed and unannealed samples at the bulk and local scale are summarized. The bulk properties, average grain size, $L_{SAXS}$, and domain spacing, $d_{SAXS}$, measured by small angle X-ray scattering (SAXS), are taken from reference 151. The bulk volume fraction of the conductive PEO/LiTFSI domain, $\phi_c$, is estimated to be 0.58 based on a rule of mixtures (equation 7.8).

$$\phi_c = \frac{v_{EO} + r v_{LiTFSI}}{v_{EO} + r v_{LiTFSI} + n_{PS} v_{PS}}$$

In equation 7.8, $v_{EO}$ is the molar volume of the ethylene oxide monomer, calculated from the molar mass of 44.05 g mol$^{-1}$ and bulk PEO density, 1.12 g cm$^{-3}$, $v_S$ is the molar volume of the styrene monomer, calculated from the molar mass of 104.15 g mol$^{-1}$ and bulk PS density of 1.07 g cm$^{-3}$, $v_{LiTFSI}$ is the molar volume of the salt, calculated from the molar mass of 287.09 g mol$^{-1}$ and bulk density of 2.02 g cm$^{-3}$, $n_{PEO}$ is the number of monomers in the PEO block, and $n_{PS}$ is the number of monomers in the PS block.$^{94}$

Table 7.1 Bulk and local properties. Bulk properties are taken from reference 151. The bulk properties conductive phase volume fraction, $\phi_c$, grain size measured by SAXS, $L_{SAXS}$, and domain spacing measured by SAXS, $d_{SAXS}$, are reported along with the local properties, conductive phase area fraction, $\phi$, grain size measured by STEM, $L_{TEM}$, domain spacing measured by STEM, $d_{TEM}$, alignment parameter, $a$, electric potential standard deviation at mid-radius, $S_{V(286)}$, and morphology factor, $f$. 

<table>
<thead>
<tr>
<th>Bulk Properties</th>
<th></th>
<th>Local Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi_c$</td>
<td>$L_{SAXS}$</td>
</tr>
<tr>
<td>Annealed 1</td>
<td>0.59</td>
<td>88</td>
</tr>
<tr>
<td>Annealed 2</td>
<td>0.59</td>
<td>85</td>
</tr>
<tr>
<td>Annealed 3</td>
<td>0.58</td>
<td>48</td>
</tr>
<tr>
<td>Annealed 4</td>
<td>0.58</td>
<td>42</td>
</tr>
<tr>
<td>Average</td>
<td>0.58</td>
<td>88</td>
</tr>
<tr>
<td>Unannealed 1</td>
<td>0.58</td>
<td>10.9</td>
</tr>
<tr>
<td>Unannealed 2</td>
<td>0.58</td>
<td>11.6</td>
</tr>
<tr>
<td>Unannealed 3</td>
<td>0.59</td>
<td>11.9</td>
</tr>
<tr>
<td>Unannealed 4</td>
<td>0.58</td>
<td>11.7</td>
</tr>
<tr>
<td>Average</td>
<td>0.58</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure 7.1 Raw and processed images. Raw and processed images are shown for an annealed sample, Annealed 2, (a)-(c), and an unannealed sample, Unannealed 1, (d)-(f). The scale bar in (a) represents 100 nm and applies to all of the images. Images (a) and (d) show the raw, RuO4-stained STEM images, (b) and (e) show the images after applying a bandpass filter, and (c) and (f) show the images after binarization. The light domains represent the conductive phase.

Binarized STEM images were analyzed to obtain the local properties reported in Table 7.1: conductive phase areas fraction, $\phi$, local grain size, $L_{TEM}$, local domain spacing, $d_{TEM}$, anisotropy factor, $a$, electric potential standard deviation at a radius of 286 nm, $S_{V(286)}$, and morphology factor, $f$. In Figure 7.1, a series of images illustrating the image processing steps are shown for an annealed sample (Figure 7.1a-c), and an unannealed sample (Figure 7.1d-f). The annealed images correspond to Annealed 2 in Table 7.1, and the unannealed images correspond to Unannealed 1. Figures 7.1a and 7.1d show the raw stained STEM images, Figures 7.1b and 7.1e show the images after applying a bandpass filter, and Figures 7.1c and 7.1f show images after binarization. Images such as Figures 7.1c and 7.1f were converted to circular surface meshes and used as inputs to the conductivity simulation. The light domains in the images represent the conductive phase. The area fraction of the conducting phase in each image, $\phi$, is reported in Table 7.1. The values for $\phi$ are very close to those of $\phi_c$ due to the approach used in the analysis (see Simulation Domain...
Preparation) but they are not identical. During the binarization of images, small variations occur in $\phi$ due to the discrete nature of the raw 8-bit grayscale STEM images.

Local grain size, $L_{\text{TEM}}$, and domain spacing, $d_{\text{TEM}}$ were computed using an open-source macro for the ImageJ software program, ADAblock, written by Murphy et al.\textsuperscript{189} Figures 7.2a and 7.2b show false-color orientation maps produced using the ADAblock program, with color representing the orientation of the lamellar domains. In Figure 7.2, black regions represent conducting domains. The values for $L_{\text{TEM}}$ were determined for each image by using the orientation map to calculate the orientational correlation length at a subset of 4000 points in the image, and averaging. The orientational correlation length is taken to be the grain size, $L_{\text{TEM}}$. Values for $L_{\text{TEM}}$ reported in Table 7.1 represent the average of results from three different sets of 4000 points, and the standard deviations between measurements were all within 7 %. The values of $L_{\text{SAXS}}$ and $L_{\text{TEM}}$ are in reasonable agreement for both the annealed and unannealed samples: 65 ± 22 nm (TEM) and 88 nm (SAXS) for the annealed sample, and 11.5 ± 0.4 nm (TEM) and 13 nm (SAXS) for the unannealed sample. The values of $d_{\text{SAXS}}$ and $d_{\text{TEM}}$ are also in good agreement for both the annealed and unannealed samples: 16.0 ± 0.2 nm (TEM) and 16.8 nm (SAXS) for the annealed sample, and 16.2 ± 1.1 nm (TEM) and 16.0 (SAXS) for the unannealed sample. The values of grain size and domain spacing measured by TEM are close to the values measured by SAXS, indicating that the regions of electrolyte in the images are representative of the bulk electrolytes.

![Figure 7.2 Orientation maps](image)

Figure 7.2 Orientation maps. Orientation maps based on STEM images are shown for an annealed sample, Annealed 2, (a) and an unannealed sample, Unannealed 1, (b). The scale bar in (a) represents 100 nm. Black regions are conducting domains. The color scale indicates orientation angle. Images and color scale were produced using the ADAblock program for ImageJ.\textsuperscript{189}
An assumption of effective medium theory is that grains are randomly oriented. To check if grain orientation was random on the length scale of the images, an alignment parameter, \( a \), was calculated for the images according to equation 7.9:

\[
a = \langle \cos^2 \{ \theta_{\text{Domain}}(x, y) - \theta(x, y) \} \rangle
\]  

(7.9)

In equation 7.9, \( \theta_{\text{Domain}} \) is the orientation angle of the domain tangent, and \( \theta \) is the azimuthal angle at a given point \((x, y)\) in the image. The data for \( \theta_{\text{Domain}}(x, y) \) is obtained from the color scale in domain orientation maps such as those in Figure 7.2. The alignment parameter is calculated by averaging the correlation between \( \theta_{\text{Domain}} \) and \( \theta \) over all points in the conductive regions of the annular simulation domain. Both angles are restricted to vary between 0 and 180°, and \( a \) varies between 0 and 1, where the value 0.5 indicates random grain orientation and 1 indicates grain alignment along the radial, conductive direction. For all but one image, the values of \( a \) are very close to 0.5, indicating that the assumption that grains are randomly oriented is valid for the simulation domains. For the image Unannealed 4, \( a \) is 0.44, below 0.5, indicating that the grains are preferentially aligned in the direction perpendicular to conduction.

The local properties \( S_{V(286)} \) and \( f \) were determined from the simulated electric potential. In Figure 7.3, representative electric potential maps are shown for an annealed sample (Figure 7.3a) and an unannealed sample (Figure 7.3b). The simulation results shown in Figure 7.3 are based on the images in Figure 7.1c and 7.1f. In Figure 7.3a, the change in potential with radius is anisotropic. Regions where the lamellae are aligned in the radial direction appear to be different from regions where the lamellae are aligned in the azimuthal direction. Not all conductive paths between the inner and outer electrodes are equivalent. In Figure 7.3b, the change in potential with radius appears to be more isotropic indicating that the conductive paths are networked and roughly equivalent through the image.

The difference in potential distribution between annealed and unannealed samples is illustrated in Figure 7.4. In Figure 7.4a, the azimuthally-averaged potential, \( V_{\text{Ave}}(r) \), is averaged over the four images and plotted as a function of radius, \( r \). The error bars represent the standard deviation of the average over four images. The analytic solution for the potential distribution in a homogenous conducting phase (equation 7.4) is included for comparison. The potential distributions for both annealed and unannealed samples are similar to the analytic solution. In Figure 7.4b, the standard deviation of the azimuthally-averaged potential, \( S_V \) (magnitude of error bars in Figure 7.4a) is plotted as a function of radius. Each point shown in Figure 7.4b is averaged over four images. Because the potential at the inner and outer radii, \( R_i \) (121 nm) and \( R_o \) (493 nm), are fixed, the standard deviations at the boundaries are nearly zero for all samples; the standard deviations are not exactly zero due to numerical error in the image analysis. The value of \( S_V \) at radii between \( R_i \) and \( R_o \) gives a measure of the anisotropy of the images, with higher \( S_V \) indicating
greater anisotropy. In Table 7.1, values of $S_V$ at the mid-radius of 286 nm, $S_{V(286)}$, are reported. On average the images from the annealed sample have higher values of $S_{V(286)}$ than images from the unannealed sample (0.16 ± 0.05 V vs 0.10 ± 0.03 V). However, given that the value of $L_{TEM}$, is approximately four to eight times higher for the images from the annealed sample, the difference in $S_{V(286)}$ is small by comparison. It is perhaps surprising that $L_{TEM}$ and $S_{V(286)}$ do not appear to be strongly linked. One explanation could be that $S_{V(286)}$ is more sensitive to local grain size at a radius of 286 nm than the image-average grain size, $L_{TEM}$.

Morphology factor, $f$, was calculated based on the simulated current, $I_{Sim}$, (equations 7.5-7.7). The values of $f$ for the annealed samples are between 0.40 and 0.50 with an average of 0.46 ± 0.04, and the values of $f$ for the unannealed samples are between 0.33 and 0.39 with an average of 0.37 ± 0.03. Though on average the annealed images have a higher value of $f$, according to Table 7.1, $f$ is not strongly correlated with $L_{TEM}$ or $S_{V(286)}$ on the level of individual images. For example, in the set of annealed images, the values of $S_{V(286)}$ and $L_{TEM}$ are similar for Annealed 3 and Annealed 4, but Annealed 3 has the lowest value of $f$ at 0.40 and Annealed 4 has the highest at 0.50. The ideal value of $f$ in two dimensions is 0.5. This prediction is remarkably consistent with the morphology factors calculated for the annealed samples but higher than the morphology factors calculated for the unannealed samples. For the image Unannealed 4, the low value of $f$ corresponds to a low value of $a$, however, for the other images from the unannealed sample, the reason for the

Figure 7.3 Simulated electric potential maps for an annealed sample. Maps are given for an annealed sample, Annealed 2, (a) and an unannealed sample, Unannealed 1, (b). The color scale indicates the electric potential, $V$, and white regions are non-conducting. The scale bar is indicated in the bottom right.
low value of $f$ is not known. Given the variation in $f$ from sample to sample, the primary conclusions of the analysis of the STEM micrographs are that $f$ is a weak function of grain size and that annealing results in a slight increase in $f$. The ratio $f_{\text{Unannealed}}/f_{\text{Annealed}}$ obtained by using the average values of the two quantities is 0.82.

![Graph](image)

Figure 7.4 Average electric potential. Azimuthally-averaged electric potential, $V_{\text{Ave}}(r)$, is shown in (a), and standard deviations of electric potential, $S_V$, averaged among images from annealed and unannealed samples, are shown in (b). In (a) the analytic solution for a homogenous conductor in an annular geometry, equation 7.4, is also plotted.

The main objective of this study is to compare the local ion transport characteristics determined by simulation with macroscopic measurement of bulk conductivity. There are two main differences between the two approaches:

1. The local transport characteristics were determined in 2D simulations while the bulk measurements were obtained in 3D samples.
2. The local characteristics were determined from analysis of a very small subset of the grains that were sampled in the bulk measurements.

The ratio $f_{\text{Unannealed}}/f_{\text{Annealed}}$ does not depend on the dimension of the system. We can thus use this ratio to account for difference (1) above. The simulated and experimental values of $f_{\text{Unannealed}}/f_{\text{Annealed}}$ are reported in Table 7.2. It is clear that the local analysis provides no explanation for the observation that in bulk measurements, $f_{\text{Unannealed}}/f_{\text{Annealed}}$ in this sample is 6.2. The discrepancy in Table 7.2 suggests that accurate determination of bulk transport requires determination of nanoscale morphology over a significantly larger region than that employed in the present study (approximately 1 μm).
Table 7.2 Morphology factor ratio from simulation and experiment. The experimental result is taken from reference 151.

<table>
<thead>
<tr>
<th></th>
<th>$f_{\text{Unannealed}}/f_{\text{Annealed}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>0.82</td>
</tr>
<tr>
<td>Experiment</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Finally, we note that in our simulation, the intrinsic conductivity of the PEO/LiTFSI phase is assumed to be constant. If annealing induces any changes in intrinsic conductivity, such effects would not be captured by the simulation. Annealing could change the intrinsic conductivity of the PEO/LiTFSI phase in two ways:

1. The interfacial mixing between the non-conducting and conducting phase could change with annealing.
2. The intrinsic conductivity at grain boundaries could be different from that in the interior of a lamellar grain.

As the electrolyte is annealed from a less ordered, freeze-dried state to a more ordered state, we expect the intermixing to either decrease or stay constant. This should result in an increase in conductivity upon annealing; however, the opposite is observed in experiment. Hence, it is unlikely that the first factor can account for the discrepancy between simulation and experiment.

It is possible that non-equilibrium structures such as grain boundaries have different intrinsic conductivities from the interior of a grain. The experimental morphology factor ratio and discrepancy between simulation and experiment could be explained if conductivity is higher at grain boundaries than in the interior of a grain. To date, most characterization of SEO/LiTFSI electrolytes has been performed on annealed samples. Further experimental work is needed to determine if segmental dynamics and intrinsic conductivity differ in grain boundaries.

7.4 Conclusions

We have presented a method to relate local morphology to ionic conductivity in a block copolymer electrolyte based on simulating the electric potential distribution through 2D binarized STEM images of a sectioned bulk electrolyte. Two samples were imaged, an annealed electrolyte with large grain size and an unannealed electrolyte with small grain size. A morphology factor, $f$, was calculated based on the simulated electric potential distributions. The average value of $f$ for images from annealed samples is $0.45 \pm 0.04$, and the average value of $f$ for images from the unannealed samples is $0.37 \pm 0.03$. The value of $f$ for both sets of samples is surprisingly close to the ideal value predicted by effective medium theory, 0.5. The fact that ion transport through grains in regions with length scales
in the vicinity of 1 μm can be described by effective medium theory is an important conclusion of the present study.

However, the main objective of this study was to provide insight into the experimentally observed effect of annealing block copolymer electrolytes on bulk conductivity. The present simulations provide no basis for the experimental observations; in simulations, the ratio $f_{\text{Unannealed}}/f_{\text{Annealed}}$ is 0.82, and in experiments, it is 6.2. Further work is needed to understand the origin of this discrepancy. One possibility is that local ion transport is fundamentally different in 2D and 3D and thus one needs to image and simulate 3D morphologies. While considerable work will be required to examine this possibility, it can readily be done as 3D morphology can be determined by electron tomography.\textsuperscript{191,192} However, given the fact that our 2D results were in good agreement with effective medium theory, it is unlikely that the 3D results will differ significantly from that theory. It is more likely that annealing results in changes in the conducting pathways that are entirely not captured in the images that we have obtained thus far. For example, it is important to note that a single T-junction defect oriented perpendicular to the direction of ion transport located at any point along the conduction pathway will block ion transport along that pathway. It appears that understanding the relationship between local and bulk ion transport in randomly oriented block copolymer grains requires accurate determination of morphology over length scales much larger than 1 μm. These experiments will be considerably more challenging using conventional, well-developed tools used for block copolymer morphology characterization such as TEM, STEM, and SAXS. A third possible explanation for the discrepancy between theory and experiment is that the simulations do not capture changes in intrinsic conductivity that might occur with annealing. Further experimental work is needed to characterize segmental dynamics at grain boundaries in block copolymer electrolytes.

7.5 Supporting Information

7.5.1 Comparison between square and annular simulation domains

Figure 7.S1 shows electric potential distributions in two different geometries for STEM image Annealed 2. Figure 7.S1a, showing the annular geometry, is identical to Figure 7.3a, and Figure 7.S1b shows the square geometry. The horizontal edges of the square in Figure 7.S1b are held at constant potential, while the vertical edges are insulating. A number of conducting paths terminate on the insulating boundaries. The corresponding values of $f$ are 0.48 for the annular geometry and 0.24 for the square geometry. The low value of $f$ obtained for the square geometry is likely due to the influence of the insulating boundaries.
Figure 7.S1. Comparison of electric potential distribution in different simulation domains. Electric potential distribution is given for the same image in an annular geometry (a) and a square geometry (b). The color scale indicates electric potential. White regions are non-conducting.

7.5.2 Dependence of calculated morphology factor on inner electrode radius

Figure 7.S2 shows the dependence of morphology factor, $f$, on the radius of the inner boundary for an image. The variation in $f$ with $R_i$ is minimized at an intermediate radius around 100 nm. Hence, $R_i$ is fixed at around 100 nm for all of the analyses reported.

Figure 7.S2. Dependence of morphology factor, $f$, on inner electrode radius, $R_i$. 
8 Conclusion

Mixtures of block copolymers with salts are promising materials for multifunctional lithium battery electrolytes. Ion transport properties and structure-function relationships have been characterized in two polymer electrolyte systems, PFPE/LiTFSI and SEO/LiTFSI. The PFPE electrolytes are liquids that consist of short polymer chains with different endgroups. These have applications as nonflammable electrolytes for safer conventional lithium ion batteries. The SEO electrolytes are microphase-separated solid block copolymers in which the polystyrene block provides mechanical stiffness and the poly(ethylene oxide) block solvates and transports ions. These have applications as electrolyte-separators in high energy density lithium metal batteries.

In chapter 2, ion transport properties were characterized for PFPE electrolytes with different endgroup segments. Electrolytes consisting of only PFPE segments with dihydroxyl or dimethylcarbonate endgroups exhibit high cation transference numbers and moderate ionic conductivities. In these electrolytes, measurements of ion transport properties by NMR and electrochemical methods give qualitatively different results, indicating that the electrolytes behave non-ideally. In PFPE electrolytes with PEO segments, ionic conductivity increases at the expense of cation transference number. In these electrolytes, measurements of ion transport properties by NMR and electrochemical methods give similar results indicating that the electrolytes behave ideally. The addition of PEO segments has significant effect on the ion transport properties of PFPE electrolytes. Specifically, PEO segments promote anion mobility.

In chapter 3, the structures of neat, short chain PFPE-PEO block copolymers were characterized. Scattering due to concentration fluctuations between PEO and PFPE segments was detected in the wide angle scattering regime. Due to high electron density contrast and high immiscibility between the fluorinated and non-fluorinated segments, scattering intensity could be detected despite the low degree of polymerization of the polymers. The length scale of the incipient microphase separation was found to be on the order of 1 nm.

In chapter 4, the structure of PFPE/LiTFSI homopolymer electrolytes and PFPE-PEO/LiTFSI block copolymer electrolytes were characterized as a function of salt concentration and temperature. The scattering of homopolymer PFPE/LiTFSI electrolytes does not change significantly with salt concentration. In PFPE-PEO/LiTFSI block copolymer electrolytes, the scattering peak due to concentration fluctuations between non-fluorinated and fluorinated segments changes with increasing salt concentration. The peak shifts to lower values of scattering vector, indicating an increase in the radius of gyration.
of the polymer electrolyte; the peak decreases in full width at half maximum, indicating an increase in immiscibility between the blocks; and lastly, the peak decreases in intensity, indicating a decrease in electron density contrast between the PEO- and PFPE-rich fluctuations. Taken together, these changes in peak shape with salt concentration suggest that the salt preferentially associates with the PEO segments. This finding is consistent with the observation in chapter 2 that PEO segments have a large impact on the ion transport of PFPE/LiTFSI electrolytes.

In chapters 2-3, structure and ion transport properties were reported for a polymer electrolyte with order on the length scale of 1 nm. In chapters 5-6, structure-property relationships were examined for a polymer electrolyte system with order on the length scale of 1 nm – 1 μm. In chapter 5, the relationship between grain size and ionic conductivity was presented for microphase-separated, lamellar SEO/LiTFSI. Grain growth was induced by annealing a freeze-dried electrolyte, and grain size and ionic conductivity were simultaneously characterized by SAXS and ac impedance spectroscopy. In the limit where the grain size is much smaller than the sample thickness, increasing grain size correlates with decreasing ionic conductivity.

In chapter 6, the effect of salt concentration on the structure and ionic conductivity of SEO/LiTFSI block copolymer electrolytes was presented. In homopolymer PEO/LiTFSI electrolytes, ionic conductivity exhibits a simple maximum. In block copolymer electrolytes, the dependence of ionic conductivity on grain size is more complex; two local maxima are observed. Based on SAXS and ac impedance measurements, it was found that salt alters the structure of the electrolyte as well as the intrinsic conductivity of the PEO/LiTFSI microphase. Decreasing grain size correlates with increasing salt concentration. Isolating the effect of grain size on ionic conductivity, increasing grain size was found to correlate with decreasing ionic conductivity, a similar result to that in chapter 5.

In chapter 7, ionic conductivity was simulated in 2D TEM micrographs of microtomed SEO/LiTFSI electrolytes with small and large grains. The simulated ionic conductivity corresponded well to predictions by effective medium theory; however, ionic conductivity was not found to decrease with increasing grain size. The conclusion from this chapter is that the experimental observation that ionic conductivity decreases with increasing grain size is due to phenomena not captured by the 2D simulations. Reasons for the discrepancy between experiments and simulation could include relatively rare grain boundary defects that occur outside the 1 μm length scale of the TEM images, changes in the intrinsic conductivity of the conductive phase at grain boundaries, or effects only evident in a 3D network of grains.
Block copolymer electrolytes, whether disordered or microphase-separated, have complex structural features over a range of length scales. Studies on the two electrolyte materials, PFPE/LiTFSI and SEO/LiTFSI, reveal complex interrelationships among structure, salt content, and ion transport. The work in this dissertation underscores the importance of fully characterizing these interrelationships in multifunctional electrolytes.
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