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Single-Ion-Conducting Block Copolymer Electrolytes for Lithium Batteries: Morphology, Ion Transport, and Mechanical Properties

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Single-Ion-Conducting Block Copolymer Electrolytes for Lithium Batteries: Morphology, Ion Transport, and Mechanical Properties

By

Adriana Araceli Rojas

A dissertation submitted in partial satisfaction of the requirements for the degree of

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in

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in the Graduate Division

of the

University of California, Berkeley

Committee in Charge:

Professor Nitash P. Balsara, Chair
Professor Bryan McCloskey
Professor Andrew Minor

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by Adriana Araceli Rojas
Abstract

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Professor Nitash P. Balsara, Chair

Lithium metal batteries have high theoretical specific energies, which make it a favorable candidate to meet our need for energy storage applications for electric vehicles and grid storage. However, there are significant safety concerns that limit our use of lithium metal electrodes. For this reason, polymer electrolytes have been a favorable choice of electrolyte, as they are more thermally and electrochemically stable against lithium metal. Block copolymer electrolytes are a promising candidate for these battery systems because of their ability to microphase separate into unique nanostructures. Given a high molecular weight block copolymer, the ion transport and moduli can be significantly improved relative to its homopolymer counterpart. As a result, block copolymers have been effective at slowing the growth of lithium dendrites. However, the main problem with block copolymer electrolytes where a salt was physically integrated, is the problem of concentration gradients that form over the length of the electrolyte. Concentration gradients are a result of low transference numbers, that is, the lithium ion of interest will carry a low fraction of current relative to the anion. To eliminate concentration gradients, single-ion-conducting block copolymer electrolytes were synthesized and characterized: poly(ethylene oxide)-b-poly(styrenesulfonyl lithium)(trifluoromethylsulfonyl)imide) (PEO-b-PSLiTFSI). In this class of copolymers, the anion (TFSI) was covalently bonded to the polystyrene backbone, allowing only the lithium ion to move.

The work enclosed elucidates the relationship between the morphology, ion transport, and mechanical properties of this single-ion-conducting block copolymer electrolyte. In the first phase of this dissertation, the synthesis of the monomer, the PEO macroinitiator, and the subsequent nitroxide mediated polymerization procedure are detailed. Improvements to the polymerization are described, and the characterization steps for ion-exchange and polymer structure are discussed.

The subsequent work discusses the relationship between ion transport and morphology using small angle X-ray scattering (SAXS) and impedance spectroscopy. It was demonstrated that the placement of the charged group in the non-ion-conducting block (PS) rendered fundamentally different nanostructure morphology. Unlike uncharged block copolymers, it was found that PEO-b-PSLiTFSI completely disordered (homogenized). There was no presence of concentration fluctuations. When the copolymer underwent an order-to-disorder transition, the
ionic conductivity was found to increase three orders of magnitude. It was demonstrated that there are favorable interactions between the lithium ions and the ethyl ethers in PEO.

Next, the effect of ion concentration on morphology and ion transport were explored. It was found that copolymers of low ion concentration \( (r = [\text{Li}^+][\text{EO}]^{-1}) \) were microphase separated at room temperature. However, at high \( r \), the copolymers were found to be disordered (homogenous) at low temperature. This was due to the effects of ion-entropy and the favorable interactions between lithium ion and the PEO block. Copolymers exhibited higher ionic conductivities at low temperature when copolymers were disordered. At high temperatures, all copolymers were disordered, and ionic conductivity peaked for \( r = 0.111 \).

In the next segment, the molecular weight of the block copolymer electrolytes were increased to understand its effect on block copolymer morphology and ion transport. It was found that these copolymers also disordered in the similar manner that the lower molecular weight copolymers disordered. However, a qualitatively different trend of ionic conductivity with \( r \) was observed. We owe the effects of lower ionic conductivity to the increase in the glass transition temperature, \( T_g \). Preliminary studies in ion transport of lithium symmetric cells were shown. This was coupled with tomography studies.

Finally, a matched series of lithiated and magnesiated block copolymers were compared. It was found that the magnesiated block copolymers exhibited weak microphase separation for volume fractions of the ion-containing block, \( \phi_{\text{PSTFSI}} \), in the range \( 0.21 \leq \phi_{\text{PSTFSI}} \leq 0.36 \). Unlike uncharged block copolymers, the tendency for microphase separation decreased with increasing \( \phi_{\text{PSTFSI}} \). Moreover, the magnesiated block copolymer with \( \phi_{\text{PSTFSI}} = 0.38 \) was found to completely disorder in the similar manner as the lithiated copolymers. This loss of microstructure had significant influences on the resulting rheological and ion transport properties. The lithiated copolymers exhibited liquid-like rheological properties, characteristic of disordered copolymers. The magnesiated copolymers did not. Furthermore, the shear moduli of the magnesiated copolymers were several orders of magnitude higher than its lithiated pairs. The ionic conductivity of the lithiated copolymers was observed to be higher than its magnesiated pairs.
To mom and dad, who arrived in this country to allow me this opportunity
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Chapter 1. Introduction

1.1 Polymer Electrolytes for Lithium Metal Batteries

As intermittent alternative sources of renewable energy (wind and solar) become more economically abundant, there is a need for high energy dense rechargeable batteries to store the energy for later use. Promising candidates entail batteries where lithium metal is the anode, for they have a higher theoretical energy density than that of traditional lithium ion technology.[1-4] However, a more stable electrolyte will be necessary for safe use of lithium metal batteries.[3, 5] As a result, polymer electrolytes are attractive for use in lithium metal batteries because they are more electrochemically and thermally stable than traditional liquid organic electrolytes.[6, 7]

Polymer electrolyte systems have to meet certain criteria for effective ion transport. The polymers should be able to solvate ions, and those ions should effectively move through the system in the presence of an electric field. A well-studied polymer electrolyte system has been poly(ethylene oxide) (PEO) mixed with salt in the melt state.[8] PEO is an exceptional candidate because it has high segmental motion; this is owed to its low glass transition temperature.[6, 9] This often translates to high ionic conductivities. The polymer also needs to solvate lithium salts. Due to the presence of ether oxygens in PEO, it is also effective at solvating salts.[9, 10] The choice of salt is also important. Some considerations include the extent of polymer/salt complexation, the degree of salt dissociation, and the stabilities of the polymer/salt mixtures.[6] For these reasons, lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt with PEO has been a favorable choice.[11]

While the PEO/LiTFSI electrolyte system meets a lot of requirements necessary for lithium metal batteries, it also comes with several setbacks. When used regularly in a rechargeable lithium metal battery, the growth of lithium dendrites takes place.[12] That is, during the reduction reaction of lithium ions (Li\(^+ + e^{-} \rightarrow Li\)), lithium does not plate evenly on the lithium metal surface. As a result, needle-like, or moss-like dendritic growth of lithium metal will continue across the length of the electrolyte, leading to battery failure by short-circuit.[12, 13] Theoretical work has shown that failure takes places due to the low modulus that PEO/LiTFSI systems exhibit, and electrolyte systems with an elastic modulus greater than 7 GPa will be necessary to prevent the growth of lithium dendrites.[14]

To increase the modulus without significantly decreasing the ion transport properties has been the next feat in many studies. To attain this, block copolymers have been harnessed to covalently bond chemically distinct segments. For a simple A-B diblock copolymer, the A block can be an ion-conducting block, such as PEO, and the B block is chosen to be a mechanically rigid block, polystyrene (PS).[15] By itself, polystyrene-\(b\)-poly(ethylene oxide) (SEO) will microphase separate into diverse nanostructures (spherical, cylindrical, lamellar, and gyroidal), leading to unique implications in the modulus and the ion transport.[16-18] The parameter that governs the self-assembly of block copolymers is the Flory-Huggins interaction parameter, \(\chi\), the number of repeat units per polymer chain, \(N\), and the volume fraction of the block, \(f_A\).[19] When SEO is mixed with salt, it has been shown that the extent of microphase separation changes, rendering a unique relationship between ion-transport and modulus in the salt-doped block copolymer systems. [6, 20]
1.2 Ion Transport in an Electrolyte

However, like the PEO/LiTFSI system, SEO/salt systems still have disadvantages characteristic of binary electrolytes. (A binary electrolyte is defined as a system containing a solvent and a salt.)[21] To begin to describe these effects, the following ion transport relations are summarized from reference [21]. In a lithium battery, the driving force for the flow of reactions is an electric field $E$, which is given by equation 1.1:

$$E = -\nabla \Phi$$ (1.1)

where $\nabla \Phi$ is the gradient of potential, $\Phi$. Ohm’s law relates the current density, $i$, to $\nabla \Phi$ in equation 1.2, where $\sigma$ is the electronic conductivity.

$$i = -\sigma \nabla \Phi$$ (1.2)

The presence of an electric field across a solution of ions creates a driving force for ionic current. The current is simply the total flux of charged species (equation 1.3):

$$i = \sum_{i} z_i F N_i = 0$$ (1.3)

$N_i$ is the flux density of species $i$, $z_i$ is the charge of species $i$, and $F$ is Faraday’s constant. While electron flow occurs only in the presence of an electric field, ions in an electrolyte move under additional influences. Ions will move in the presence of an electric field; this is called migration. The migrational flux density of species $i$ is given by equation 1.4, where $u_i$ describes the intrinsic movement of an ion due to an electric field (mobility), and $c_i$ is the concentration of species $i$.

$$N_{i,migration} = -z_i u_i F c_i \nabla \Phi$$ (1.4)

Under the influence of migration, lithium cations are driven toward the cathode, and anions are driven toward the anode. The competition between the intrinsic mobility of the anion and the cation can be described by the transference number, $t_i$. It is defined as the fraction of current that an ion carries in a solution of uniform composition. Equivalently, this can be described by the ratio of mobility of species $i$ relative to the total mobility of all ions. This is represented by equation 1.5.

$$t_i = \frac{z_i F N_i}{i} = u_i \frac{u_i}{u}$$ (1.5)

While the anion and cation are driven to move opposite from one another under migration, the electroneutrality constraint requires that there be the same number of equivalent cations as anions. This is given by equation 1.6.

$$\sum_{i} z_i c_i = 0$$ (1.6)
The different extents to which the anions and cations move lead to changes in the ion concentration across the solution. Moreover, as one of the ions reacts at the cathode and if \( t_i \) of the reacting ion is less than one, a concentration gradient forms. Ions in an electrolyte will also move in response to a concentration gradient; this is termed diffusion. The flux due to diffusion is given by equation 1.7.

\[
N_{i,\text{diffusion}} = -D \nabla c_i
\] (1.7)

For an infinitely dilute solution, combining the effects of migration, diffusion, and the electroneutrality constraint, the current density in solution is given by equation 1.8.

\[
i = -F^2 \nabla \Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i + F \nu \sum_i z_i c_i
\] (1.8)

The effects of concentration gradients can be detrimental in a battery. It can lead to salt precipitation at the anode and salt depletion at the cathode.[22] Additionally, an overpotential due to the concentration gradient also manifests.[22, 23] These effects are depicted in Figure 1.1. Moreover, there is evidence to suggest that the effect of concentration gradients can accelerate dendrite growth across the electrolyte.[24, 25] Therefore, there is high motivation to eliminate the concentration gradients that are characteristic of binary electrolytes.

**Figure 1.1.** Schematic depicting the effects of a binary electrolyte in a battery during discharge.
1.3 Single-Ion-Conducting Electrolytes

An electrolyte that does not exhibit concentration gradients is called a single-ion-conducting electrolyte.[7, 26] In other words, the lithium ion transference number, $t^+$, is unity. Therefore, the lithium ion carries 100% of the current in a single-ion-conducting electrolyte. In contrast, $t^+$ varies between 0.2-0.4 for the PEO/LiTFSI binary electrolyte system.[27, 28] In other words, for $t^+ = 0.30$, the lithium ion carries approximately 30% of the total current, and the anion carries the remaining 70%.

Concentration gradients can be eliminated if the anion, which does not participate in the energy-producing reaction, has lower mobility than the cations. There have been several methods with chemistry by which to obtain this effect. One way is to trap the anion in a binary electrolyte with an anion acceptor.[29-31] Another way is to covalently tether the anion to an inorganic backbone.[32] Similarly, one can also covalently bond the anion to a polymer backbone.[33-35] In either of these strategies, the anion concentration across the electrolyte is kept constant by physical or chemical means; therefore, the electroneutrality constraint will ensure that the cation concentration is also uniform.[7, 21] Many architectures and chemical strategies have been employed, and the resulting effects on ion transport has been a subject of great study.

More recently, the single-ion-conducting characteristic has been employed in block copolymers by covalently bonding the anion to the polymer backbone.[36, 37] Ryu et. al. first employed this technique by comparing the ion transport properties of two block copolymers, wherein the anion was covalently bonded to the ion-conducting block in one, and the anion was attached to the mechanically-rigid block in the other.[36] They found that performance was improved in the latter case, and they owed this to the effects on the polymer glass transition temperature. After this study, Bouchet and coworkers proposed a triblock copolymer electrolyte, PSLiTFSI-B-PEO-B-PSLiTFSI, where the anion of the LiTFSI salt was covalently bonded to the PS backbone. While they exemplified that this polymer had good ion transport properties, studies on the morphology and its relation to ion transport were missing. This is a subject of great theoretical interest as well.[38-40] In the enclosed work, a simplified diblock copolymer based on Bouchet and coworkers’ polymer is studied, PEO-B-PSLiTFSI (Figure 1.1). The placement of the anion in the ion-insulating block is counter-intuitive; hence, its effect on block copolymer morphology, mechanical properties, and ion transport is studied.
1.4 Outline of Dissertation

In this work, single-ion-conducting block copolymer electrolytes were synthesized and characterized. The synthesis of the monomer, PEO macroinitiator, and the subsequent nitroxide mediated polymerization of the block copolymers are discussed in Chapter 2. The details for ion-exchange to obtain PEO-b-PSLiTFSI and PEO-b-PS[(STFSI)$_2$Mg] copolymers and the results to the characterization post-synthesis are also described in Chapter 2. In Chapter 3, X-ray scattering and ionic conductivity studies shed light on how ion migration takes place in PEO-b-PSLiTFSI of low ion concentration. In Chapter 4, the effect of ion concentration on morphology and ionic conductivity is studied. In this chapter, the PEO molecular weight was held constant at 5 kg·mol$^{-1}$ while the molecular weight of the PSLiTFSI block was varied. Chapter 5 discusses the effect of increasing the molecular weight of the PEO block on ion transport and morphology. Herein, details of lithium symmetric cell measurements are also discussed. Preliminary tomogram images of the lithium/polymer interfaces are shown. In Chapter 6, single-ion-conducting block copolymers of univalent (PEO-b-PSLiTFSI) and divalent (PEO-b-PS[(STFSI)$_2$Mg]) ions are studied through rheology and X-ray scattering. The enclosed work shows that block copolymer self-assembly of charged copolymers is fundamentally different than that of uncharged systems (binary block copolymer electrolytes). These effects on morphology are closely coupled to the ion transport properties and shear moduli.
Chapter 2. Synthesis and Characterization of Block Copolymer Electrolytes
PEO-b-PSLiTFSI and PEO-b-P[(STFSI)$_2$Mg]

Abstract

Single-ion-conducting block copolymer electrolytes were synthesized in four steps. First, the monomer was synthesized from trifluoromethanesulfonamide and 4-styrene sulfonyl chloride. Commercially available PEO methyl ether was functionalized with acryloyl chloride to yield PEO methyl ether acrylate. This was followed by the intermolecular radical addition of the commercially known Blocbuilder® to ultimately yield a PEO macroalkoxyamine, also called the PEO macroinitiator. This PEO macroinitiator was reacted in conjunction with the monomer to obtain the polymer using nitroxide mediated polymerization. Different ratios of each block were achieved by varying the ratio of the monomer and PEO macroinitiator in the reaction vessel. Finally, an ion-exchange from K$^+$ to Li$^+$ or to Mg$^{2+}$ was achieved with dialysis. Monodispersity was achieved when the starting monomer mole percent was at least 8% in solution. Block copolymers were analyzed with $^1$H-NMR, $^{19}$F-NMR, $^7$Li-NMR, GPC, ICP-OES, and DSC.

2.1 Materials

All anhydrous solvents and reagents were purchased from Sigma-Aldrich. PEO methyl ether was purchased from Polymer-Source and PEO methyl ether acrylate was purchased from Sigma-Aldrich. The precursor for the monomer, 4-styrene sulfonyl chloride, was acquired from Monomer-Polymer and Dajac Labs. Blocbuilder® was kindly provided by Arkema.

2.2 STFSIK Monomer Synthesis

The monomer, potassium 4-styrenesulphonyl(trifluoromethylsulphonyl) imide (STFSIK), was synthesized according to the reaction scheme in Figure 2.1. The synthesis for the monomer was adapted from previous work.[34, 37, 41] The reagents for the synthesis and purification are listed in Table 2.1.

Figure 2.1. Reaction scheme for STFSIK synthesis
Table 2.1 Reagents for STFSIK monomer synthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g mol(^{-1}))</th>
<th>Mass or Vol.</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-styrene sulfonyl chloride</td>
<td>202.7</td>
<td>25.0 g</td>
<td>0.126</td>
</tr>
<tr>
<td>Trifluoromethanesulfonamide</td>
<td>149.2</td>
<td>18.7 g</td>
<td>0.126</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>101.2</td>
<td>17.5 mL</td>
<td>0.126</td>
</tr>
<tr>
<td>Catalyst: 4-(Dimethylamino) pyridine (DMAP)</td>
<td>122.2</td>
<td>1.50 g</td>
<td>0.0123</td>
</tr>
<tr>
<td>Solvent: Acetonitrile</td>
<td>-</td>
<td>400 mL</td>
<td>-</td>
</tr>
<tr>
<td>Solvent: Dichloromethane</td>
<td>-</td>
<td>200 mL</td>
<td>-</td>
</tr>
<tr>
<td>NaHCO(_3) (aq)</td>
<td>-</td>
<td>100 mL</td>
<td>-</td>
</tr>
<tr>
<td>K(_2)CO(_3) (aq)</td>
<td>-</td>
<td>1200 mL</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 2.2.** Glassware schematic used for monomer synthesis.

**Synthesis**

All reaction glassware was cleansed in a base bath for one hour and thoroughly rinsed with deionized water followed by methanol. The glassware was allowed to dry in an oven at 110 °C. In a 1-liter 3-neck round bottom flask, the solid DMAP was added. The round bottom flask was assembled with an Allihn condenser at the center neck and an addition funnel at the right neck. The joints were lightly covered with vacuum grease and reinforced with keck clips. The left neck and the top of the addition funnel were equipped with rubber septums stable against organic solvents. They were also reinforced with a tight wire. The left neck and addition funnel were equipped with long inlet and short purge needles for argon gas flow. Figure 2.2 depicts a typical assembly.

The round bottom flask and addition funnel were flushed with argon gas using the inlet needles. The 250 mL of dry acetonitrile, the triethylamine, and the trifluoromethanesulfonamide were added via the left neck. The contents were thoroughly mixed via magnetic stirring, and the vessel was cooled in an ice bath. Argon was bubbled through the contents for a half hour. In the dropping funnel, 150 mL of dry acetonitrile and the liquid 4-styrene sulfonyl chloride were
added. The reaction commenced by slowly adding the contents of the addition funnel into the round bottom flask over the course of one hour. The contents were vigorously mixed under magnetic stirring. (Warning: This is an exothermic reaction. HCl (g) may form if there is significant water contamination. Cease the reaction and monitor the situation closely should this occur.) After 4 hours, the reflux column and addition funnel were removed, and glass stoppers were used to seal the vessel. Argon bubbling continued for another hour, and the vessel was covered with aluminum foil. Stirring continued for 11 more hours.

Purification

The acetonitrile was removed using a rotovap to reveal a viscous yellow/orange liquid. Dichloromethane (200 mL) was added to the resulting broth. A liquid-liquid extraction was performed in a 1-liter separatory flask to remove the salts. A saturated solution of NaHCO₃ (30 mL) was added slowly to the surface of the organic mixture and gently agitated. The vessel was vented after every inversion. After 15 minutes of rest, the organic phase was isolated and washed two more times with the NaHCO₃ (aq).

Dichloromethane was removed with a rotovap from the final organic phase. The acidic form of the monomer was neutralized with a saturated solution of K₂CO₃ (aq) under vigorous magnetic mixing overnight. The STFSIK monomer precipitated as a white/cream powder. The following day, the turbid mixture was allowed to sit undisturbed for two hours. The mixture was decanted and filtered with a vacuum Erlenmeyer flask equipped with a Büchner flask.

The monomer was then dissolved in acetonitrile and filtered to remove any residual K₂CO₃ salts. The solvent was evaporated under reduced pressure, and the monomer was left to dry in a vacuum oven at 30 °C. The monomer was a white/cream solid.

Monomer characterization with NMR, elemental analysis, and mass spectrometry are shown in section 2.6.

2.3 PEO Macroinitiator Synthesis

2.3.1 Esterification of PEO methyl ether

PEO methyl ether was esterified according to the reaction in Figure 2.3. Similar esterification reactions have been previously conducted by others under different reaction conditions. In this reaction, PEO methyl ether is esterified with acryloyl chloride at 0 °C to yield PEO methyl ether acrylate.[41-46] The reagents necessary for the reaction are listed in Table 2.2. The synthesis and purification steps are described below.
Figure 2.3 Reaction scheme of hydroxyl end-group functionalization. Final product is PEO methyl ether acrylate.

Table 2.2 Reagents for PEO methyl ether acrylate synthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Mass or Vol.</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO methyl ether</td>
<td>9500</td>
<td>10.3 g</td>
<td>1.08 x 10⁻³</td>
</tr>
<tr>
<td>Acryloyl chloride</td>
<td>90.5</td>
<td>1.76 mL</td>
<td>2.16 x 10⁻²</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>101.2</td>
<td>3.00 mL</td>
<td>2.16 x 10⁻²</td>
</tr>
<tr>
<td>Catalyst: 4-(Dimethylamino) pyridine (DMAP)</td>
<td>122.2</td>
<td>0.05 g</td>
<td>-</td>
</tr>
<tr>
<td>Solvent: Tetrahydrofuran</td>
<td>-</td>
<td>500 mL</td>
<td>-</td>
</tr>
</tbody>
</table>

Synthesis

Glassware preparation and assembly were the same as previously described. Prior to use, PEO methyl ether was dried overnight in a vacuum oven at ambient temperature. The next day, PEO methyl ether and DMAP were added to the round bottom flask. The vessel was sealed, and 450 mL of dry THF and the anhydrous triethylamine were added under argon. The contents were well-mixed under stirring, and the vessel was immersed in an ice bath. In the dropping funnel, 50 mL THF and the acryloyl chloride were added. Over the course of one hour, the acryloyl chloride/THF solution was added drop-wise to the cold contents while argon was bubbled through the vessel. A color change from clear to pale yellow took place. The vessel was allowed to react for 2 hours before careful removal of the condenser and addition funnel. The vessel was sealed and bubbled with argon gas. The vessel was left to continue stirring vigorously overnight at room temperature while covered with aluminum foil. Warning: This is an exothermic reaction. Acryloyl chloride is extremely toxic, and it should not come in contact with skin.

Purification

The following day, the vessel was heated to 40 °C and continued to stir for a half hour. Afterward, the reaction broth was allowed to sit undisturbed for a half hour. The triethylamine salts that form over the course of the reaction are non-soluble in THF. These salts were removed through a qualitative filter over an Erlenmeyer vacuum flask and a Büchner funnel. The filtrate was then slowly added into cold diethyl ether to precipitate the PEO methyl ether acrylate. The polymer was collected through filtering and dried overnight in a vacuum oven at ambient temperature.
When PEO methyl ether acrylate became commercially available, this synthesis step was skipped. The inhibitor hydroquinone monomethyl ether (MEHQ) was removed from the commercially available polymer. The polymer was washed with acetone three times. It was filtered and dried, and $^1$H-NMR was used to verify the removal of MEHQ.

### 2.3.2 Intermolecular radical addition of Blocbuilder®

The next reaction scheme involves the functionalization of the acrylate end-group with $N$-(2-methylpropyl)-$N$-(1-diethylphosphono-2,2-dimethylpropyl)-$O$-(2-carboxylprop-2-yl)hydroxylamine (also known as MAMA-SG1 or Blocbuilder® by Arkema). This particular group has been used to obtain polymer structures of diverse architectures in a controlled manner.[47, 48] In Figure 2.4, Blocbuilder® breaks down into an initiator and the SG1. In Figure 2.5, the initiator reacts with the acrylate end-group in PEO methyl ether acrylate according to the reaction scheme. The remaining SG1 will combine to the polymer according to Figure 2.5. This yields the PEO macrorinitiator. Table 2.3 lists the reagents necessary for the reaction, and the synthesis and purification is described below.

![Reaction scheme of Blocbuilder® decomposition](image)

**Figure 2.4.** Reaction scheme of Blocbuilder® decomposition.
Figure 2.5. Reaction scheme of PEO macroinitiator.

Table 2.3. Reagents for synthesis of PEO macroalkoxyamine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>Mass or Vol.</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO methyl ether acrylate</td>
<td>5000</td>
<td>3 g</td>
<td>0.7 g</td>
</tr>
<tr>
<td>Blocbuilder®</td>
<td>381.45</td>
<td>2 g</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Solvent: anhydrous 1,4-dioxane or ethanol</td>
<td>Ethanol</td>
<td>15 mL</td>
<td>500 mL</td>
</tr>
</tbody>
</table>

Synthesis

Glassware cleansing was the same as previously described. Dry PEO methyl ether and Blocbuilder were added into a round bottom flask and sealed with an Allihn condenser at the center neck. Anhydrous solvent was added under argon. After a half hour of argon bubbling, the reaction was allowed to proceed at 100 °C under vigorous stirring. A color change occurred from clear to yellow. The reaction time in ethanol was 3 hours, and the reaction time in dioxane was 1.5 hours. The reaction was quenched and the reaction broth was dropped into cold diethyl ether. The polymer was washed two more times in diethyl ether. The polymer was left to dry under vacuum at room temperature.

2.4 Nitroxide Mediated Polymerization (NMP)
Nitroxide mediated polymerization (NMP) was used to obtained PEO-\(b\)-PSKTFSI diblock copolymers. Details about NMP can be found in the literature.[48-51] In Figure 2.6, the reaction scheme for NMP is shown, and the synthesis is described below.

![Reaction scheme for PEO-\(b\)-PSKTFSI](image)

**Figure 2.6.** Reaction scheme for PEO-\(b\)-PSKTFSI

It was determined that the concentration of the monomer in solution was important to minimize the polydispersity of the block copolymers. In Figure 2.7a, the dispersity is high for polymers containing low quantities of the PSLiTFSI block. The reason for this is clear in Figure 2.7b. When the concentration of the monomer in the DMF and PEO macrorinitiator solution was less than 8 mol\%, the dispersity was high. It is evident that the monodispersity approaches 1.1 when the concentration of the monomer approached 8 mol\%. Therefore, subsequent polymerization reactions were modified such that the concentration of the monomer in the reaction vessel started out at 8 mol\%.
**Figure 2.7.** Dispersity of the block copolymers plotted against the (a) the molecular weight of PSLiTFSI and (b) the concentration of the reactants in solution.

**Synthesis**

In a 10-mL roundbottom flask, the dry PEO macroinitiator was added along with anhydrous dimethylformamide (DMF). The monomer was then added, such that the monomer concentration in solution was 8 mol%. The vessel was sealed, and the contents were vigorously mixed under magnetic stirring and bubbled with argon gas for 30 minutes. The vessel was immersed in an oil bath at 115 °C and left to react for three days. In the case of AAR10Li (PEO-PSLiTFSI(5-1.6), see Appendix B), the reaction proceeded for 16 hours. \(^1\)H-NMR of the reaction broth revealed the complete consumption of the monomer, at which point the reaction was quenched in an ice bath. The reaction broth was left on a hotplate at 55 °C for 3 days to evaporate the majority of the DMF.

**2.5 Ion-Exchange**

Dialysis was used to perform an ion-exchange from the potassium version of the polymer to the lithiated version or to the magnesiated version of the polymer. Dialysis is also useful to remove any trace ionic species and residual DMF solvent from the previous reaction step. The reaction schemes are shown in Figures 2.8 and 2.9 to attain the lithiated and magnesiated copolymers, respectively.
**Figure 2.8.** Scheme for ion-exchange from PEO-\(b\)-PSKTFSI to PEO-\(b\)-PSLiTFSI

**Figure 2.9.** Scheme for ion-exchange from PEO-\(b\)-PSKTFSI to PEO-\(b\)-\(P[(STFSI)_{2}Mg]\)

**Table 2.4.** Components for dialysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g mol(^{-1}))</th>
<th>Mass or Vol.</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-(b)-PSKTFSI</td>
<td>5000-100,000</td>
<td>&lt;10 g/L polymer concentration in water</td>
<td>-</td>
</tr>
<tr>
<td>LiCl(s)</td>
<td>42.4</td>
<td>20 g</td>
<td>0.47</td>
</tr>
<tr>
<td>MgCl(_2)(s)</td>
<td>95.2</td>
<td>20 g</td>
<td>0.21</td>
</tr>
<tr>
<td>Solvent: DI water</td>
<td>-</td>
<td>1.6 L</td>
<td>-</td>
</tr>
</tbody>
</table>
Procedure

PEO-$b$-PSKTFSI was solvated in DI water, and the solution was carefully sealed in a dialysis membrane having a molecular cut-off weight of 3500 Da. The sealed dialysis membrane was placed in a salt bath for three days. A fresh salt bath was replenished every 24 hours. Afterward, the polymer was dialyzed with DI water for three additional days to remove any trace salt species. Fresh DI water was replenished every 24 hours too. The lithiated copolymers remained soluble in water. In the dialysis of PEO-$b$-PSKTFSI to PEO-$b$-P[(STFSI)$_2$Mg] however, the magnesiated polymers precipitated out of solution. The copolymers were then freeze-dried under reduced pressure at 0 °C.
2.6 STFSIK Monomer Characterization

Figure 2.10. $^1$H-NMR of STFSIK

Figure 2.11. $^{19}$F-NMR of STFSIK. A singlet is observed at -78.80 ppm.
Elemental analysis was performed at the Microanalytical Facility in the College of Chemistry on a Perkin Elmer 2400 Series II combustion analyzer. The results are shown in table 2.5. The data shows that the mass of the monomer is within 2% of the expected mass.

**Table 2.5. Elemental analysis results**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass % Estimated</th>
<th>Mass % Found</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>30.60</td>
<td>30.99</td>
<td>1.27</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.00</td>
<td>2.03</td>
<td>1.50</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.96</td>
<td>3.92</td>
<td>1.01</td>
</tr>
<tr>
<td>Sulfur</td>
<td>18.20</td>
<td>18.39</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Mass spectrometry was performed at the QB3 facility in Stanley Hall. The expected molecular weight of the monomer (without the potassium) is 314. Mass spectrometry showed that the monomer had minimal contamination with higher molecular weight species (Figure 2.12).

**Figure 2.12.** Mass spectrometry of the STFSIK monomer
2.7 Polymer Characterization

2.7.1 Characterization using $^1$H-NMR

Figure 2.13. $^1$H-NMR of Blocbuilder® collected at 5 °C in CDCl$_3$. 
Figure 2.14. $^1$H-NMR of PEO methyl ether in CDCl$_3$ at room temperature
Figure 2.15. $^1$H-NMR of PEO methyl ether acrylate at room temperature
Figure 2.16. $^1$H-NMR of PEO-macroinitiator
Determination of Molecular Weight via $^1$H-NMR

The area from the aromatic ring (6.3-8 ppm) was compared to the area from the -CH$_2$-CH$_2$- (3.4-3.8 ppm) bonds. Both the aromatic ring and the oxyethylene proton signals correspond to 4 hydrogens. The molecular weight of the PEO was predetermined as reported by the manufacturer; therefore, the molecular weight of the PSLiTFSI was determined through the following equation:

$$M_{n,PSLiTFSI} = A_{PSTFSI} \times N_{PEO} \times m_{STFSILi}$$  \hspace{1cm} (1.1)$$

where $A_{PSTFSI}$ is the area corresponding to the aromatic ring relative to a PEO area of 1. $N_{PEO}$ is the degree of polymerization, or the number of repeat units of the PEO polymer, and $m_{STFSILi}$ is the molecular weight of each monomer segment in PSLiTFSI ($m_{STFSILi} = 322$ kg·mol$^{-1}$).

Figure 2.17. $^1$H-NMR of the PEO-$b$-PSLiTFSI 9.5 kg mol$^{-1}$ series in d-DMSO at room temperature.
2.7.2 Characterization using $^{19}$F-NMR

Figure 2.18. $^{19}$F-NMR of PEO-$b$-PSLiTFSI in d-DMSO showing a broad singlet at -78.75 ppm
2.7.3 Characterization using $^7$Li-NMR

Figure 2.19. $^7$Li-NMR of PEO-\textit{b}-PSLiTFSI in d-DMSO showing a singlet at 1.14 ppm.
2.7.4 Characterization using GPC

The single-ion-conducting block copolymers were characterized by a Malvern Viscotek TDA 305 gel permeation chromatography (GPC) system consisting of two 8 x 300 mm MCX (1000 and 100000 Å) columns from Polymer Standards Service-USA Inc. The mobile phase flow rate was 0.5 mL·min⁻¹, and it was composed of 30 wt% acetonitrile and 70 wt% water containing a 0.05 wt% of Na₂HPO₄. The dispersity, \( D \), was determined based on a calibration of PEO homopolymers.

Representative GPC chromatographs are given in Figure 2.12 for PEO-\( b \)-PSLiTFSI (blue) and the PEO macroinitiator (grey). GPC traces of the PEO-macroinitiator (5 kg mol⁻¹) and the PEO-\( b \)-PSLiTFSI block copolymer confirm polymerization of the PSLiTFSI block.

![Figure 2.20. Representative GPC traces of PEO-\( b \)-PSLiTFSI(9.5-3.5) (blue) and the PEO macroinitiator (black).](image)

2.7.5 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

ICP-OES is a type of mass spectrometry that uses plasma to excite atoms.\[^{52, 53}\] A polymer sample (5-10 mg) was digested using dilute nitric acid (2%). The solution is atomized through an argon plasma, and the atoms become excited, emitting radiation specific to the elemental component. Based on the intensity of these emissions from a sample, one can compare this to a set of standards to determine the absolute quantity of metal in the starting compound within 5-10% error. In this study, ICP-OES was used to determine the efficacy from the ion-exchange reactions. In Figure 2.13, the ICP-OES results are shown for the 9.5 kg·mol⁻¹
series of the PEO-\textit{b}-PSLiTFSI diblock copolymers, where the molecular weight of the PEO block is held constant at 9.5 kg·mol\textsuperscript{-1}. The molecular weight of the PSLiTFSI block was varied from 3.5 to 8.3 kg·mol\textsuperscript{-1}. From Figure 2.13, it is evident that some K\textsuperscript{+} remains in the block copolymers after dialysis. This quantity remaining is equivalent to 3 mol\%; therefore, 97 mol\% is Li\textsuperscript{+}. We take the small quantity of K\textsuperscript{+} to be negligible.

![Figure 2.21.](image)

**Figure 2.21.** Representative ICP-OES results of the 9.5 kg·mol\textsuperscript{-1} series.

### 2.7.6 Differential Scanning Calorimetry (DSC)

Polymer samples were hermetically sealed in aluminum pans inside an argon glovebox. Glovebox integrity was maintained during sample preparation. Experiments were carried out on a Thermal Advantage Q200 calorimeter at the Molecular Foundry (LBNL) in the following sequence: heating, cooling, heating. Each heating run was at a 20 °C min\textsuperscript{-1} rate, and the cooling run was conducted with a 2 °C min\textsuperscript{-1}. The temperature range was from -90 to 120 °C. The melting temperature and glass transition temperature was obtained from the second heating run.

In Figure 2.14, a representative DSC thermogram for one of the PEO-\textit{b}-PSLiTFSI block copolymers is shown. From the thermogram, one can determine the glass transition temperature, \( T_g \), the melting temperature, \( T_m \), and a crystallization temperature, \( T_c \). PEO-\textit{b}-PSLiTFSI(9.5-3.5) in Figure 2.14 is characteristic of exemplifying all three thermal parameters.
Figure 2.22. Representative DSC thermogram of PEO-\textit{b}-PSLiTFSI(9.5-3.5).
Chapter 3. Morphology- Conductivity Relationship of Single-Ion Conducting Block Copolymer Electrolytes for Lithium Batteries†

ABSTRACT

A significant limitation of rechargeable lithium-ion batteries arises because most of the ionic current is carried by the anion; the ion that does not participate in energy-producing reactions. Single-ion-conducting block copolymer electrolytes, wherein all of the current is carried by the lithium cations, have the potential to dramatically improve battery performance. The relationship between ionic conductivity and morphology of single-ion-conducting poly(ethylene oxide)-b-polystyrenesulfonyl-lithium(trifluoromethylsulfonyl)imide (PEO-PSLiTFSI) diblock copolymers was studied by small angle X-ray scattering and AC impedance spectroscopy. At low temperatures, an ordered lamellar phase is obtained, and the “mobile” lithium ions are trapped in the form of ionic clusters in the glassy polystyrene-rich microphase. An increase in temperature results in a thermodynamic transition to a disordered phase. Above this transition temperature, the lithium ions are released from the clusters and ionic conductivity increases by several orders of magnitude. This morphology-conductivity relationship is very different from all previously published data on electrolytes. The ability to design electrolytes wherein most of the current is carried by the lithium ions, to sequester them in non-conducting domains, and release them when necessary, has the potential to enable new strategies for controlling the charge-discharge characteristics of rechargeable lithium batteries.

3.1 Introduction

Single-ion-conducting polymer electrolytes, with ionic groups covalently bonded to the polymer and free counterions, are fundamentally different from conventional electrolytes wherein salts comprising positive and negative ions are dissolved in either liquid or polymeric solvents.[7, 21, 23] A popular example of a single-ion-conducting electrolyte is hydrated Nafion wherein negatively charged sulfonate groups are fixed onto a fluorinated polymer backbone while the associated hydronium counterions are mobile.[54, 55] Transport of counterions in such systems occurs in the absence of concentration gradients provided that the bound ion concentration is uniform. This follows from the electroneutrality constraint. The performance of batteries and fuel cells with single-ion-conducting electrolytes are predicted to be superior to that obtained using conventional electrolytes, due to the absence of concentration polarization effects.[23] Commercial lithium-ion batteries contain electrolytes where a majority of the current is carried by the ion that does not participate in energy-producing reactions. It has long been recognized that dramatic improvements in batteries can be realized if single-ion conductors with high ionic conductivity can be designed.

† This chapter was reported in ACS Macro Letters 3, 510-514 (2014), and is adapted with permission from coauthors S. Inceoglu, D. Devaux, X. Chelsea Chen, G.M. Stone, and N.P. Balsara
In this paper, we focus on single-ion-conductors containing “mobile” lithium ions. Most of the studies on such materials are limited to single-phase systems wherein ionic groups are covalently attached to homopolymers.[56, 57] Dramatically different single-ion-conductors based on block copolymers were first proposed by Ryu et al.[36] and more recently by Bouchet et al.[37] The work in ref. [37] is based on polystyrene-b-poly(ethylene oxide)-b-polystyrene triblock copolymers, wherein lithium bis(trifluoromethane)sulfonamide (LiTFSI) was covalently linked to styrene units in the polystyrene blocks. Polystyrene (PS) and poly(ethylene oxide) (PEO) chains are highly incompatible.[58] Extensive works on the thermodynamics of polystyrene-b-poly(ethylene oxide) (SEO) copolymers with added lithium salts, particularly LiTFSI, indicate that the tendency for microphase separation is enhanced by the presence of ions.[6, 20] One thus expects microphase separation in the triblock copolymers, but no evidence for the presence or absence of such effects were reported in ref. [37]. The ionic conductivities of these single-ion-conducting triblock copolymers[37] were similar to that of mixtures of SEO and LiTFSI.[59] In contrast, the cation transference number of these triblock copolymer was in the vicinity of unity, well above typical values obtained in electrolytes containing lithium salts (between 0.1 and 0.5).[60-64]

In Figure 3.1, we show a schematic of lithium ion migration in a microphase separated poly(ethylene oxide)-b-polystyrenesulfonyllithium(trifluoromethylsulfonyl)imide diblock copolymer (PEO-PSLiTFSI) electrolytes. The most interesting aspect of these electrolytes is that “mobile” lithium counterions are ionically bound to the immobile and glassy polystyrene blocks. Transport of lithium ions can only occur if they migrate from the PS-rich microphase into a PEO-rich environment. The expected scenario is illustrated in Figure 3.1. The main purpose of this study is to describe the effect of lithium ion migration on morphology in single-ion-conducting block copolymer electrolytes.

Figure 3.1. Schematic of lithium ion migration in single-ion conducting block copolymer electrolyte.
3.2 Experimental

3.2.1 Synthesis and Characterization

Poly(ethylene oxide)-b-polystyrenesulfonyllithium(trifluoromethylsulfonylimide) diblock copolymers (PEO-PStLiTFSI) were synthesized as described in Chapter 2 following previous reports.[37, 41] Polymerization was confirmed with GPC (Figure 3.S1).

3.2.2 Electrolyte preparation and symmetrical cells assembly

The PEO-PStLiTFSI copolymer electrolytes (10 wt% solution of polymer in nanopure water obtained from a Barnstead NANOpure Diamond instrument, resistivity of 18.2 MΩ cm) were drop-casted on electrochemical grade aluminum foil and were then allowed to dry in the fume hood overnight. The samples were then dried at 45 °C under vacuum for 24 hours in an oven, and then brought into a glove box antechamber to dry under vacuum at 45 °C for at least 24 hours. Finally, samples were brought into an argon glove box for all sample preparation. Glove box integrity was maintained throughout subsequent sample preparation. The samples were prepared by hot pressing the drop-casted material into insulating spacers made of Kapton to obtain sample thicknesses ranging from 200-400 μm for SAXS. For conductivity measurements, samples were hot-pressed into 30 μm thick Kapton spacers (area = 0.0792 cm²) and assembled with electrochemical grade aluminum foil on both sides of the spacer containing the electrolyte. Aluminum tabs were taped to the outside of the foils, and the entire cell was vacuum sealed inside of air-tight pouches. The sealed cells were loaded into a custom heating stage and the tabs were connected to a Bio-Logic VMP3 (Variable Multichannel Potentiostat). Lithium symmetrical cells were prepared in the same way as conductivity cells with the exception of Nickel tabs placed in contact with the lithium metal electrodes.

3.2.3 Conductivity measurements

A Biologic-VMP3 was used to measure the complex impedance of the samples from 1 MHz to 1 Hz frequency (ω) range with an applied AC potential of 50 mV. The sample resistance was determined from the plateau value in the Bode plot of the modulus of the complex impedance, $|Z' + iZ''| vs \omega$. This value was identical to the resistance determined from the low frequency minimum on a Nyquist impedance plot. Samples were placed in a custom-made heating stage, and they were studied at selected temperatures: from 25 to 60 °C in 5 degree increments and from 60 to 90 °C in 10 degree increments. Samples were then cooled down using the same temperature steps and subjected to a second heating cycle. The samples had an equilibration time of 15 min at each temperature. The reported conductivity values are from the second heating run. After the conductivity measurements were completed, the samples were carefully disassembled, and the thicknesses were measured with a micrometer. We report average ionic conductivities and standard deviations obtained using three independent samples.

3.2.5 Transference Number Measurement

The lithium/polymer/lithium symmetric cells used in the transference number measurements were similar to those described in the preceding paragraph, except that lithium
electrodes were used instead of aluminum electrodes. Nickel tabs and nickel current-collectors were used to complete the symmetric cell construction. These cells were also vacuum-sealed in pouch material. The steady-state current method was utilized, where chronoamperometry experiments were carried out on these cells at 90 °C using the VMP3 potentiostat.[65, 66] A constant 20. mV potential was applied, and the current was measured as a function of time. Impedance spectra were collected at every hour increment to probe the bulk and interfacial resistances. A sequence of measurements for the experiment is represented in Figure 3.2. The transference number is calculated with equation 4.1. The initial and steady-state interfacial resistances, $R_{int}^0$ and $R_{int}^\infty$, respectively, were determined by fitting an equivalent circuit (Figure 3.2) to the Nyquist plot of the impedance data using EC-Lab. The steady-state current, $I^\infty$, and the initial current, $I^0$, were determined from a current response to a 20. mV bias over a period of one hour. L1 and R1 are the instrument cables’ inductance and resistance, respectively. This is followed in series by a resistor and a constant phase element (CPE) in parallel, and this is followed by another similar construction in series.

\[
t^+ = \frac{I^\infty (\Delta V - I^0 R_{int}^0)}{I^0 (\Delta V - I^\infty R_{int}^\infty)}
\]  

(3.1)

**Figure 3.2.** Schematic of steady-state current method used to determine the transference number.

**Figure 3.3.** Equivalent circuit used to fit the Nyquist impedance data.
### 3.2.6 Small-Angle X-ray Scattering (SAXS) Experiments

Small-angle X-ray scattering experiments (SAXS) experiments under quiescent conditions were performed on samples contained within sealed cells with Kapton windows. Sample thicknesses ranged from 200-400 μm. Samples were placed in a custom-made heating stage, and they were studied using the same thermal history described in the conductivity section. The measurements were performed at beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory.\[67\] The azimuthally averaged scattering intensity, $I$, is reported as a function of the magnitude of the scattering vector, $q$. Silver behenate was used as a standard and scattering patterns were reduced using the Nika program for IGOR Pro available from Jan Ilavsky at Argonne National Laboratories.\[68\] The background scattering from Kapton was subtracted from the reduced SAXS data. We report data obtained during the second heating cycle.

### 3.2.7 Scanning Transmission Electron Microscopy measurements

Bulk samples containing PEO-PSLiTFSI(5.0-3.2), $r=0.088$, copolymer were prepared by the drop-casting method for electrolyte preparation. Thin sections with thickness of approximately 100 nm were obtained by cryo-microtoming using a Leica EM FC6 at −120 °C and transferred onto a lacy carbon coated copper grid (Electron Microscopy Sciences). Samples were stained in RuO$_4$ vapor for 10 min. Scanning Transmission Electron Microscopy (STEM) experiments were performed on a Tecnai F20 UT FEG, equipped with a high angle annular dark field (HAADF) detector, using 200 keV acceleration voltages.

### 3.3 Results and Discussion

In this study, we focus on a particular copolymer, PEO-PSLiTFSI(5.0-3.2) where 5.0 and 3.2 are the molecular weights in kg·mol$^{-1}$ of the PEO and PSLiTFSI blocks. The ratio of lithium ions to ethylene oxide monomers, $r$, is 0.088. We also present results obtained from a PEO-PSLiTFSI(5.0-2.0) diblock copolymer with $r=0.056$.

Small angle X-ray scattering (SAXS) intensities, $I$, as a function of the magnitude of the scattering vector, $q$, of PEO-PSLiTFSI(5.0-3.2), obtained during a heating run, are shown in Figure 3.4a. At room temperature, the scattering profile indicates the presence of a lamellar morphology, with a primary scattering peak at $q=q^*=0.228$ nm$^{-1}$, and higher order scattering peaks in the vicinity of $2q^*$, $3q^*$ and $4q^*$. The location of the higher order peak in the vicinity of $2q^*$ differs substantially from the calculated value. Observed SAXS peak locations may be affected by the low-$q$ up-turn (Figure 3.4). Similar up-turns have been observed in other charged block copolymers.\[69\] The domain spacing, $d$, defined as the center-to-center distance between adjacent PEO-rich lamellae is 28 nm ($d=2\pi q^*$). SEO copolymers with comparable molecular weights exhibit $d$ spacing in the vicinity of 15 nm.\[70\] While the addition of charges on the chain is expected to increase $d$ spacing, the observed magnitude of this increase is surprising.

An additional SAXS peak is observed at $q=q_c=1.33$ nm$^{-1}$ (Figure 3.4a). Similar peaks have been observed in a wide variety of ionomers including polystyrene sulfonate, Nafion, and sulfonated polyesters.\[54, 55, 71-73\] We thus conclude that the TFSI$^-$ and Li$^+$ ions are clustered
at room temperature in PEO-PSliTFSI(5.0-3.2). The average distance between clusters, \( d_{\text{cluster}} \), is approximately 4.7 nm \( (d_{\text{cluster}}=2\pi q_c^{-1}) \). Heating the sample results in a decrease of peak intensities as shown in Figure 3.4a. Scattering peaks indicative of the lamellar structure are absent at temperatures above 50 °C. The intensity of the ion cluster peak also decreases substantially above 50 °C (Figure 3.4b). Changes in the scattering intensity are reversible. The lamellar peaks are obtained during the cooling run at temperatures below 45 °C as shown in Figure 3.4c. The intensity of the ion cluster peak also increases as the sample is cooled (Figure 3.4d and Figure 3.S4 in section 3.5, the Supplementary Information). The hysteresis seen in Figure 3.4 is commonly observed when both semicrystalline and amorphous diblock copolymers are heated and cooled across the order-disorder transition.[74, 75]

The data in Figure 3.4 indicates that the PEO-PSliTFSI(5.0-3.2) diblock copolymer exhibits a reversible order-to-disorder transition (ODT) between 50 and 55 °C. The ODT in block copolymers with or without salt has been studied extensively.[19, 70, 76] In all cases, the transition is accompanied by an abrupt increase in the width of the primary SAXS peak. The broad peak obtained from the disordered phase is a signature of large amplitude concentration fluctuations. In contrast, the primary peak is absent in disordered PEO-PSliTFSI(5.0-3.2) indicating the remarkable absence of concentration fluctuations. Note that the higher order scattering peaks are detected at 50 °C while neither primary nor higher order peaks are evident at 55 °C.

**Figure 3.4.** Temperature dependence of SAXS for the PEO-PSliTFSI electrolyte. (a) SAXS intensity versus scattering vector, \( q \), during a heating scan, (b) Scattering in the vicinity of the ion cluster peak during a heating scan, (c) SAXS intensity versus scattering vector, \( q \), during a cooling scan, and (d) Scattering in the vicinity of the ion cluster peak during the cooling scan of PEO-PSliTFSI(5.0-3.2), \( r=0.088 \).

Differential scanning calorimetry (DSC) experiments on PEO-PSliTFSI copolymers indicate the presence of a melting peak at 55 °C. The DSC data are shown in section 3.5 of the Supplementary Information, Figure 3.S2. The observed melting peaks in PEO-PSliTFSI are
qualitatively similar to those seen in PEO homopolymer. This observation, in combination with data presented in Figure 3.4, suggests that microphase separation in PEO-PSLiTFSI is driven by the crystallization of the PEO block.

The lamellar morphology of PEO-PSLiTFSI(5.0-3.2) at room temperature was confirmed by scanning transmission electron microscopy (STEM) as shown in Figure 3.5. The $d$ spacing determined by STEM is 23 nm, which is in reasonable agreement with SAXS measurements. It is evident that PEO crystallization is confined within the microphase separated structure.[77]

![Figure 3.5](image)

**Figure 3.5.** Scanning transmission electron micrograph of PEO-PSLiTFSI(5.0-3.2), $r =0.088$. The PEO phase is brightened by RuO$_4$ staining.

The temperature dependence of the ionic conductivity of PEO-PSLiTFSI(5.0-3.2) is shown in Figure 3.6. At room temperature, the conductivity is $3.0 \times 10^{-8}$ S·cm$^{-1}$. The conductivity increases from $7.4 \times 10^{-8}$ S·cm$^{-1}$ at 45 °C to $2.7 \times 10^{-5}$ S·cm$^{-1}$ at 60 °C. A further increase in the temperature results in a slower increase in conductivity, reaching a value of $3.8 \times 10^{-4}$ S·cm$^{-1}$ at 90 °C. Also shown in Figure 3.6 is the temperature dependence of the SAXS intensity at $q=0.228$ nm$^{-1}$ in the vicinity of the primary peak. There is a correlation between morphology and conductivity: high conductivity values are obtained when the sample is disordered, and normalized $I (q=0.228$ nm$^{-1})$ is nearly zero. This suggests that the migration of the lithium ions into a PEO-rich environment coincides with homogenization of the block copolymer microstructure. Further work is needed to establish the quantitative relationship between SAXS profiles and conductivity. In order to verify the morphology-conductivity relationship described above, we performed *in situ* SAXS experiments wherein the conductivity was measured concurrently with the SAXS experiment during a heating run. The conductivity data obtained during this run are included along with three separate *ex situ* conductivity measurements to obtain the values and error bars shown in Figure 3.6. The SAXS experiments were also repeated several times.
Figure 3.6. Conductivity and SAXS results of the PEO-PSLiTFSI(5.0-3.2) electrolyte. The temperature dependence of the ionic conductivity (blue circles) and normalized SAXS intensity at $q=0.228$ nm$^{-1}$ (red circles) for PEO-PSLiTFSI(5.0-3.2), $r=0.088$.

The PEO-PSLiTFSI(5.0-3.2) electrolyte was placed between two lithium foils and the current needed to sustain a potential drop of 80 mV ($\Delta V$) across the electrodes was measured as a function of time at 90 °C.[65, 66, 78] The results of this experiment are shown in Figure 3.7. The current density values obtained when the experiment was started and after one hour were $I^0=6.99\times10^{-2}$ and $I^\infty=6.90\times10^{-2}$ mA·cm$^{-2}$, respectively. The results of ac impedance measurements before starting the experiment and after its completion are shown in the inset in Figure 3.7. The Nyquist plot of the impedance data contains two semi-circles, a small semi-circle representing electrolyte resistance ($R_{\text{elect}}$) and a large semi-circle representing interfacial resistances, $R_{\text{int}}$.[79] The resistance values obtained before and after the cell polarization are $R_{\text{elect}}^0=127$ $\Omega$ cm$^2$, $R_{\text{elect}}^\infty=119$ $\Omega$ cm$^2$, $R_{\text{int}}^0=1018$ $\Omega$ cm$^2$ and $R_{\text{int}}^\infty=1028$ $\Omega$ cm$^2$, respectively.

The ionic conductivity values obtained from symmetrical cells using either lithium or aluminum electrodes are similar. In principle, determination of cation transference number, $t^+$, requires knowledge of salt activity coefficients.[76] In typical lithium battery electrolytes, the ratio $I^\infty/I^0$ obtained during the polarization experiment described in the preceding paragraph is about 0.3. In contrast, the value of $I^\infty/I^0$ obtained from PEO-PSLiTFSI(5.0-3.2) is 0.99. This implies that most of the current in our electrolyte is carried by the cation. In this case, the cation transference number, $t^+$, is approximately given by equation 3.1. This gives $t^+=0.95$. To a very good approximation, our PEO-PSLiTFSI(5.0-3.2) electrolyte is a single-ion-conductor.
Figure 3.7. Transference number determination of the PEO-PSLiTFSI electrolyte. Current density as a function of time for PEO-PSLiTFSI(5.0-3.2) during an 80 mV polarization experiment at 90 °C. The inset shows the ac impedance of the cell (◊) before and (Δ) after polarization.

The DSC, conductivity, and transference number results presented here are qualitatively consistent with those reported in ref. [37]. To assess the generality of our conclusions, we also studied the morphology-conductivity relationship in PEO-PSLiTFSI(5.0-2.0) diblock copolymer with \( r=0.056 \). The data obtained from this sample are very similar to those obtained from PEO-PSLiTFSI(5.0-3.2) and thus presented in 3.5 Supplementary Information, Figure 3.S3.

The morphology-conductivity relationship derived from the results is pictured in Figure 3.8. At low temperatures, below 50 °C, we have an ordered microphase separated structure with crystalline PEO-rich domains and glassy PSLiTFSI-rich domains \( (T_g=160 \, ^\circ C) \). The \( \text{Li}^+ \) and TFSI ions form clusters in the glassy domains. The concentration of lithium ions in the PEO-rich domains is negligible, and this results in very low conductivity values (below \( 10^{-7} \, \text{S cm}^{-1} \)). At high temperatures, above 50 °C, we have a disordered morphology wherein amorphous PEO and PSLiTFSI blocks are intimately mixed and most of the ions are no longer in clusters. A majority of the lithium ions in this state are “mobile” and conductivity values as high as \( 3.8 \times 10^{-4} \, \text{S cm}^{-1} \) are obtained at 90 °C.
Figure 3.8. Schematics of the single-ion conducting block copolymer electrolyte at low and high temperatures. At low temperatures, the PEO (red) and PSLiTFSI (blue) blocks are microphase separated and the ions are clustered (green circles). At high temperatures, the PEO and PSLiTFSI blocks are mixed (purple), the clusters (gray circles) are nearly dissolved and the lithium ions are mobile.

3.4 Conclusion

In conclusion, we have shown that the transfer of lithium ions from the glassy PSLiTFSI-rich domains into a PEO-rich environment results in disordered and highly conductive single-ion-conducting block copolymer electrolytes. The ability to design electrolytes wherein most of the current is carried by the lithium ions, to sequester them in non-conducting domains, and release them when necessary has the potential to enable new strategies for controlling the charge-discharge characteristics of rechargeable lithium batteries.
3.5 Supplementary Information

3.5.1 GPC

Parameters for GPC is described in 2.7.4. GPC traces of the PEO macroinitiator and the diblock copolymer confirm polymerization in Figure 3.S1. As expected, the larger diblock (red) elutes first, before the PEO macroinitiator.

![GPC traces](image)

**Figure 3.S1.** GPC traces of PEO macroinitiator (5.0 kg·mol⁻¹, blue curve) and its block copolymer, PEO-PSLiTFSI(5.0-3.2) (red curve).

3.5.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimeter (DSC) experiments were performed as described in Chapter 2.7.6 with the exception that cycles were conducted over the range -90 to 150 °C. DSC curves of the PEO-macroinitiator (5 kg·mol⁻¹), PEO-PSLiTFSI(5.0-3.2), and PEO-PSLiTFSI(5.0-2.0) from the second heating scan are shown in Figure 3.S2. Endothermic peaks, corresponding to the melting of PEO crystallites, are obtained in all samples. The observed reduction in melting enthalpy with increasing Li⁺ content is consistent with published results.[37, 41] The DSC curves of the PEO-PSLiTFSI block copolymers show no evidence of the glass transition of the PSLiTFSI block. This is because the block copolymers are disordered above the melting transition of the PEO block. Above this temperature, the $T_g$ of the mixed phase can be estimated using the Fox equation to be 32 °C (based on the assumption that $T_g$ of PEO is -17 °C).
for PEO-PSLiTFSI(5.0-3.2) diblock copolymer.\[80\] The $T_g$ values of PEO reported in the literature vary considerably, and values as low as -62 °C can be found.\[81\] Regardless of the assumed values of $T_g$ of PEO, it is obvious that the homogeneous disordered phase of PEO-PSLiTFSI(5.0-3.2) is rubbery.

![DSC thermograms of PEO-macroinitiator (5.0 kg mol\(^{-1}\), black line), PEO-PSLiTFSI(5.0-3.2) (red line), and PEO-PSLiTFSI(5.0-2.0) (orange line).](image)

**Figure 3.S2.** DSC thermograms of PEO-macroinitiator (5.0 kg mol\(^{-1}\), black line), PEO-PSLiTFSI(5.0-3.2) (red line), and PEO-PSLiTFSI(5.0-2.0) (orange line).

### 3.5.3 SAXS and Conductivity of PEO-PSLiTFSI(5.0-2.0)

The temperature dependence of the conductivity of PEO-PSLiTFSI(5.0-2.0), $r=0.056$, is shown in Figure 3.S3. At low temperatures the conductivity is about $8\times10^{-10}$ S cm\(^{-1}\), and the conductivity increases rapidly between 50 and 60 °C reaching values of $4.7\times10^{-4}$ S cm\(^{-1}\) at 90 °C. The cation transference number for PEO-PSLiTFSI(5.0-2.0) at 90 °C is $t^+ = 0.87$. Also shown in Figure 3.S3 is the temperature dependence of the SAXS intensity at $q = 0.282$ nm\(^{-1}\) in the vicinity of primary peak. All of these results for the PEO-PSLiTFSI(5.0-2.0) are in good agreement with PEO-PSLiTFSI(5.0-3.2).
3.5.4 SAXS results of PEO-PSLiTFSI(5.0-3.2) for the cluster peak

The temperature dependence of the normalized peak intensity in the heating and cooling scans for the cluster peak of PEO-PSLiTFSI(5.0-3.2), \( r=0.088 \), is shown in Figure 3.54. The cluster peak intensity as a function of temperature is different than the behavior of the peaks indicative of lamellar morphology. The intensity remains relatively constant from 25 °C to 50 °C. A sudden drop in the peak intensity is observed between 50 °C and 55 °C. An increase in the intensity is observed at 60 °C, but the cluster peak intensity drops again at 90 °C. We attribute the latter discrepancy to changes in the sloping baseline at high \( q \)-values. It is important to note however that the cluster peak does not disappear at temperatures greater than 50 °C as the \( q^* \), \( 2q^* \), \( 3q^* \), and \( 4q^* \) peaks do. Finally, the cluster peak exhibits reversible behavior as well.
Figure 3.S4. The temperature dependence of the normalized SAXS intensity for the cluster peak at $q=1.33$ nm$^{-1}$ in the heating (black diamonds) and cooling (gray diamonds) scans for PEO-PSLiTFSI (5.0-3.2), $r=0.088$. 
Chapter 4. Effect of Lithium-Ion Concentration on Morphology and Ion Transport in Single-Ion-Conducting Block Copolymer Electrolytes‡

ABSTRACT

Single-ion-conducting polymers are ideal electrolytes for rechargeable lithium batteries as they eliminate salt concentration gradients and concomitant concentration overpotentials during battery cycling. Here we study the ionic conductivity and morphology of poly(ethylene oxide)-b-poly(styrenesulfonyllithium(trifluoromethylsulfonyl)imide) (PEO-b-PSLiTFSI) block copolymers with no added salt using AC impedance spectroscopy and small angle X-ray scattering. The PEO molecular weight was held fixed at 5.0 kg·mol⁻¹ and that of PSLiTFSI was varied from 2.0 to 7.5 kg·mol⁻¹. The lithium ion concentration and block copolymer composition are intimately coupled in this system. At low temperatures, copolymers with PSLiTFSI block molecular weights ≤ 4.0 kg·mol⁻¹ exhibited microphase separation with crystalline PEO-rich microphases and lithium ions trapped in the form of ionic clusters in the glassy PSLiTFSI-rich microphases. At temperatures above the melting temperature of the PEO microphase, the lithium ions were released from the clusters, and a homogenous disordered morphology was obtained. The ionic conductivity increased abruptly by several orders of magnitude at this transition. Block copolymers with PSLiTFSI block molecular weights ≥ 5.4 kg·mol⁻¹ were disordered at all temperatures, and the ionic conductivity was a smooth function of temperature. The transference numbers of these copolymers varied from 0.87 to 0.99. The relationship between ion transport and molecular structure in single-ion-conducting block copolymer electrolytes is qualitatively different from the well-studied case of block copolymers with added salt.

4.1 Introduction

There is continuing interest in electrolytes that are stable against lithium metal anodes. [6, 14, 15] Dry polymer electrolytes are more electrochemically and thermally stable when compared to conventional liquid electrolytes for lithium batteries. Most battery electrolytes are mixtures comprising a salt dissolved in a solvent. The salt dissociates into two (or more) ionic species, and the concentration gradients obtained during battery operation depend on the relative mobilities of the dissociated species. The resulting concentration overpotential is one of the factors that limit the rate at which batteries can be cycled.[21] Large salt concentration gradients can result in precipitation of the salt. Lithium dendrite growth rates are also dependent on the magnitude of the concentration gradients.[24] Polymer electrolytes wherein the anion is covalently bonded to the polymer backbone are of considerable interest because lithium ion transport in these systems occurs in the absence of concentration gradients.[82]

‡This chapter was reported in Macromolecules 48, 6589-6595 (2015), and is adapted with permission from coauthors S. Inceoglu, N.G. Mackay, J.L. Thelen, D.Devaux, G.M. Stone, and N.P. Balsara
Bouchet and co-workers have synthesized and characterized a novel single-ion-conducting BAB triblock copolymer, polystyrene-\(b\)-poly(ethylene oxide)-\(b\)-polystyrene (SEOS), wherein lithium bis(trifluoromethane)sulfonylimide (LiTFSI) was covalently bonded to the styrene moieties in the polystyrene blocks.[37] Only the Li\(^+\) is mobile because the TFSI\(^-\) anion is covalently bonded to the glassy polystyrene (PS) backbone. However, PS is an ionic insulator while PEO is an ionic conductor. Thus, the Li\(^+\) must be located in the PEO-rich microphase for efficacious ion transport.[6, 83] There is practical interest in these electrolytes because ionic conductivities as high as \(3.4 \times 10^{-5}\) S cm\(^{-1}\) have been reported at 90 °C.[37] Little is known about the morphology of this class of block copolymers. In contrast, extensive studies have been conducted on the relationship between conductivity and morphology in block copolymer binary electrolytes, i.e. block copolymers with added salt. An example of such a system is polystyrene-\(b\)-poly(ethylene oxide) (SEO)/LiTFSI wherein the salt is preferentially located in the PEO-rich microphase. These systems are known to microphase separate into ordered morphologies that enable independent control over mechanical and electrical properties, and increasing salt concentration generally enhances the propensity for microphase separation.[6, 17, 36, 84-88]

The objective of our study is to explore the dependence of ionic conductivity and cation transference number on morphology in a series of single-ion-conducting poly(ethylene oxide)-\(b\)-poly(styrenesulfonyllithium(trifluoromethyl sulfonyl)imide) (PEO-\(b\)-PSLiTFSI) diblock copolymers (Figure 1). The molecular weight of the PEO block was held fixed at 5.0 kg mol\(^{-1}\) while the PSLiTFSI block molecular weight was varied from 2.0 to 7.5 kg mol\(^{-1}\). The present paper builds upon work published in a letter wherein results of a particular molecular weight of PEO-\(b\)-PSLiTFSI copolymer were described.[89]

![Figure 4.1. Chemical structure of PEO-\(b\)-PSLiTFSI. End groups are not shown.](image)

4.2 Experimental

4.2.1 Diblock Copolymers

PEO-\(b\)-PSLiTFSI diblock copolymers were synthesized and characterized as described in Chapter 2. Table 4.1 shows the samples that were used in this study. Polymers are labeled PEO-PSLiTFSI(x-y) where x and y are the nominal molecular weights of the PEO and PSLiTFSI blocks, respectively, in kg mol\(^{-1}\). The GPC traces of the polymers, shown in Figure 4.S1 (in the Supplementary Information section 4.6.1), confirm polymerization of the PSLiTFSI block. The
PEO precursor sample contained a small high molecular weight shoulder. All of the block copolymer samples were approximately unimodal except for PEO-PSLiTFSI(5-2), which exhibited 3 GPC peaks: a main high-molecular weight peak corresponding to the block copolymer and two additional peaks due to the unreacted PEO. We attribute this to the low concentration of the TFSI-containing monomer during polymerization.

The concentration of lithium ions increases with increasing molecular weight of the PSLiTFSI block. We quantify this concentration by \( r \), defined as the molar ratio of lithium ions to ethylene oxide moieties, \( r = [\text{Li}^+] / [\text{EO}]^{-1} \), without accounting for the end groups on either side of the chain. The volume fraction of the PEO block (\( \phi_{\text{PEO}} \)) is listed in Table 4.1, and it was estimated from the densities of PSLiTFSI homopolymer (1.57 g cm\(^{-3}\)) and PEO homopolymer (1.20 g cm\(^{-3}\)). The density of the PSLiTFSI homopolymer was estimated using Van Krevelen’s group contribution method, and the details of this calculation are shown in Table 4.1 of the Supplementary Information. In addition to the polymers listed in Table 4.1, we also synthesized PEO-b-PSLiTFSI with PSLiTFSI molecular weights 10.2 and 10.6 kg mol\(^{-1}\). These samples were brittle, and we were unable to make films necessary for conductivity measurements. We do not discuss these samples in this study.

Table 4.1. Characteristics of the single-ion-conducting block copolymers used in this study.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>( M_{\text{PEO}} ) (kg mol(^{-1}))</th>
<th>( M_{\text{PSLiTFSI}} ) (kg mol(^{-1}))</th>
<th>( D )</th>
<th>( r = [\text{Li}^+] / [\text{EO}]^{-1} )</th>
<th>( \phi_{\text{PEO}} )</th>
<th>( t^+ )</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO(5)</td>
<td>5.0</td>
<td>0</td>
<td>1.05</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>17.1</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-2)</td>
<td>5.0</td>
<td>2.0</td>
<td>1.53</td>
<td>0.056</td>
<td>0.77</td>
<td>0.87</td>
<td>20.4</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-3)</td>
<td>5.0</td>
<td>3.2</td>
<td>1.29</td>
<td>0.088</td>
<td>0.69</td>
<td>0.95</td>
<td>27.6</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-4)</td>
<td>5.0</td>
<td>4.0</td>
<td>1.26</td>
<td>0.111</td>
<td>0.64</td>
<td>0.97</td>
<td>27.8</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-5)</td>
<td>5.0</td>
<td>5.4</td>
<td>1.21</td>
<td>0.150</td>
<td>0.53</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-7)</td>
<td>5.0</td>
<td>7.2</td>
<td>1.25</td>
<td>0.199</td>
<td>0.49</td>
<td>0.99</td>
<td>-</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-8)</td>
<td>5.0</td>
<td>7.5</td>
<td>1.18</td>
<td>0.207</td>
<td>0.48</td>
<td>0.98</td>
<td>-</td>
</tr>
</tbody>
</table>

\( M_{\text{PEO}} \), molecular weight of the PEO block; \( M_{\text{PSLiTFSI}} \), molecular weight of the PSLiTFSI block; \( D \), the dispersity; \( \phi_{\text{PEO}} \), volume fraction of the PEO block; \( t^+ \), the lithium ion transference number; \( d \), the domain spacing.

Polymer films for conductivity, transference number, and X-ray scattering, were prepared using the drop-casting method as described in Chapter 3.2.2. Improvements were made to the conductivity sample construction. Each polymer film for electrochemical testing was placed in a Kapton spacer and melt-pressed in a custom-made hand-press at about 55 °C. Typical sample thicknesses ranged from 50-100 μm. Aluminum electrodes (18 μm in thickness) and aluminum tabs were used in the conductivity sample construction, and Kapton tape was used to seal the gap between the spacer and the electrode. (See Supplementary Information Figure 4.S2 for a
schematic of the cell). The conductivity samples were vacuum sealed in pouch material (Showa-Denka), which allowed us to conduct electrochemical tests outside of the glove box using a BioLogic VMP3 (Variable Multichannel Potentiostat). Ionic conductivity was determined as described in Chapter 3.2.4, and the transference number measurements were performed as described in Chapter 3.2.5. DSC measurements were conducted according to Chapter 2.7.6. SAXS and WAXS experiments were performed as described in Chapter 3.2.6. We also conducted in situ experiments wherein SAXS and conductivity measurements were made simultaneously for the same samples for PEO-PSLiTFSI(5-2), (5-3), (5-4), and (5-5). The data obtained from these measurements were consistent with the conductivity values reported herein.

4.2.2 PEO(5)/LiTFSI Sample Preparation

Poly(ethylene oxide) with molecular weight 5.0 kg·mol⁻¹ was obtained from Polymer Source, and LiTFSI was obtained from Novolyte. Both were dried under vacuum at 90 °C for 3 days in the glove box antechamber. The polymer and salt were dissolved in THF and stirred at 45 °C for 1-2 hours at the r values of interest. Following complete dissolution, the mixture was poured into a Teflon dish and allowed to dry on a hot plate at 45 °C overnight in the glove box. Upon evaporating off the THF, the sample was then dried under vacuum at 90 °C overnight in a glove box antechamber. Samples for electrochemical impedance testing were constructed as described in the corresponding section above, with the exception of the use of fiberglass fabric-reinforced silicone rubber spacers. These samples were approximately 800 μm in thickness.

4.3 Results and Discussion

The SAXS profiles obtained at 25 °C after the heating and cooling cycle are shown in Figure 4.2, where the SAXS intensity, I, is plotted as a function of the magnitude of the scattering vector, q. For PEO-PSLiTFSI(5-2) a weak scattering maximum is observed at q=q*=0.307 nm⁻¹. For PEO-PSLiTFSI(5-3) and (5-4), well-defined primary scattering peaks are observed at q*= 0.228 and 0.226 nm⁻¹, respectively. These values correspond to domain spacings, d, the center-to-center distance between adjacent PEO-rich lamellae, of 20.4, 27.6, and 27.8 nm (d = 2π/q*) for PEO-PSLiTFSI(5-2), (5-3), and (5-4), respectively. Higher order peaks in the vicinity of 2q*, 3q*, and 4q* are observed for these three polymers as well. SAXS profiles of polymers with a higher content of PSLiTFSI, PEO-PSLiTFSI(5-5), (5-7), and (5-8), do not contain any peaks as shown in Figure 4.2a. It is evident that increasing the PSLiTFSI molecular weight from 4.0 to 5.4 kg·mol⁻¹ results in a change in the room temperature morphology from ordered to disordered. Also shown in Figure 4.2a, are data obtained from PEO-PSLiTFSI(5-5) in the unannealed state before commencing the heating and cooling cycle, labeled (5-5)u in Figure 4.2a. A weak scattering shoulder and a broad higher-order scattering peak is evident in this sample. We thus conclude that PEO-PSLiTFSI(5-5) is at the border between order and disorder. The unannealed sample was held at room temperature for 9 days before the SAXS measurements were made. It is evident that weak order is obtained in the sample after extensive annealing at room temperature. In contrast, the cycled PEO-PSLiTFSI(5-5) sample shows no evidence of order (Figure 4.2a). In all other cases, the unannealed and cycled SAXS profiles obtained at room temperature were qualitatively similar. We conclude that order formation in PEO-b-PSLiTFSI is relatively rapid when the molecular weight of the PSLiTFSI block is ≤ 4.0 kg·mol⁻¹. On the other hand, when the molecular weight of the
PSLiTFSI block is $\geq 7.2$ kg·mol$^{-1}$, ordered phases are absent regardless of annealing time at room temperature.

Figure 4.2. The scattering data shown are vertically offset for clarity. (a) SAXS intensity versus the magnitude of the scattering vector, $q$, at 25 °C of PEO-$b$-PSLiTFSI copolymers and PEO homopolymer. The markers shown, grey stars, blue rectangles, green triangles, and yellow diamonds, designate $q^*$, $2q^*$, $3q^*$, and $4q^*$ for ordered samples. Most of the data shown were obtained during the second heating run except for (5-5)u where the data were obtained from an unannealed sample during the first heating run. (b) WAXS intensity versus the magnitude scattering vector, $q$, at 25 °C of PEO-$b$-PSLiTFSI copolymers. (c) SAXS intensity versus magnitude of the scattering vector, $q$, at 90 °C of PEO-$b$-PSLiTFSI copolymers. The SAXS profile of homopolymer PEO(5) is also shown in Figure 4.2a. This profile is qualitatively similar to that obtained from the ordered block copolymers with a primary scattering peak at $q^*$=0.368 nm$^{-1}$ and higher order scattering peaks at $2q^*$, $3q^*$, and $4q^*$. Similar SAXS profiles of PEO have been reported in the literature.[72] The SAXS signal in semicrystalline polymers is due to contrast between crystalline and amorphous domains. The
domain spacing of PEO(5), which represents the distance between adjacent PEO lamellar crystals is 17.1 nm. Comparing the data obtained from PEO(5) to that obtained of PEO-b-PSLiTFSI (Figure 4.2), we conclude that order formation in the block copolymers is driven by the crystallization of PEO. It appears as if the PSLiTFSI block is accommodated within the amorphous phase. Increasing the length of the PSLiTFSI block results in an increase in $d$ up to a maximum of 27.8 nm when the PSLiTFSI block molecular weight is 4.0 kg·mol$^{-1}$. Further increase of the PSLiTFSI block molecular weight results in a disordered morphology.

Wide angle X-ray scattering profiles shown in Figure 4.2b confirm the crystalline nature of the block copolymers with PSLiTFSI block molecular weights $\leq$ 4.0 kg·mol$^{-1}$. The scattering profile of PEO(5) is shown in grey for comparison. (The intensity of this profile was divided by a factor of ten to facilitate comparison with the block copolymers.) Differential scanning calorimetry experiments reveal a melting temperature of $52 \pm 4^\circ C$ for PEO-PSLiTFSI(5-2), (5-3) and (5-4), consistent with the scattering data (Supplementary Information Figure 4.S3.)

The SAXS profiles of PEO-PSLiTFSI and the PEO homopolymer all have a low $q$-upturn (Figure 4.2a). We attribute this to the lack of perfect periodic order and the presence of large lengthscale structures (e.g. spherulites) in both the homopolymer and the block copolymers. The locations of the observed higher order peaks in Figure 4.2a are not in perfect agreement with the expected locations for a lamellar phase. We attribute this to the complexity of order formation in the presence of crystallization.[75, 77]

In Figure 4.2c, we show data obtained from the block copolymers at 90 °C, which is above the crystalline melting temperature of PEO(5). All of the samples are disordered at this temperature. The SAXS and WAXS profiles for samples PEO-PSLiTFSI(5-5), (5-7), and (5-8) are essentially independent of temperature. (See similarity of SAXS profiles obtained from these samples at 25 and 90 °C in Figures 4.2a and 4.2c.)

Samples PEO-PSLiTFSI(5-2), (5-3), and (5-4) exhibit a peak at $q \approx 1.3$ nm$^{-1}$, which we attribute to the presence of ionic clusters. SAXS in the vicinity of this peak for selected samples is shown in Figure 4.3. This peak is often referred to as the ionomer peak, and it is found in numerous charged polymers.[54, 55, 71] This peak indicates that the ionic clusters are separated by a distance of about 5 nm ($2\pi / 1.3$). The peak intensity is a non-monotonic function of charge concentration. At 25 °C, PEO-PSLiTFSI(5-3) exhibits the highest cluster peak intensity (Figure 4.3a). Peaks with significantly lower intensity are seen in PEO-PSLiTFSI(5-2) and (5-4) at 25 °C. The cluster peak is absent in PEO-PSLiTFSI(5-5) (Figure 4.3a) and in samples with higher PSLiTFSI volume fraction. It is evident that at 25 °C, the cluster peak is only seen in samples that are ordered. In all cases, the cluster peak intensity decreases with increasing temperature. At 90 °C, only the cluster peak in PEO-PSLiTFSI(5-3) is significantly above the background.
Figure 4.3 SAXS intensity versus the magnitude of the scattering vector, $q$, for PEO-PSLiTFSI(5-2), (5-3), (5-4), and (5-5) in the vicinity of the ion cluster peak at (a) 25 °C and (b) 90 °C.

The temperature dependence of the ionic conductivity of the samples listed in Table 4.1 is shown in Figure 4.4. Samples that are disordered over the entire temperature range, e.g. PEO-PSLiTFSI(5-8), exhibit relatively simple behavior that is consistent with the Vogel-Fulcher-Tammann-Hesse relationship that is often used to describe the ionic conductivity of homopolymer electrolytes.[6] In contrast, dramatic changes in the conductivity are observed in samples that exhibit an order-to-disorder transition, e.g. PEO-PSLiTFSI(5-3).
Figure 4.4 Ionic conductivity, $\sigma$, versus temperature of PEO-\textit{b}-PSLiTFSI copolymers.

The dependence of conductivity on temperature and molecular structure (Figure 4.4) can be explained by using the morphological characterization described above. At low temperatures, the ionic groups in PEO-PSLiTFSI(5-2), (5-3), and (5-4) are sequestered in clusters in the PSLiTFSI microphase, and the crystalline PEO microphases are devoid of ions. Both factors contribute to conductivities between $10^{-9}$ and $10^{-8}$ S cm$^{-1}$ in the ordered state at temperatures below the PEO microphase melting temperature. These same polymers exhibit high conductivities in the disordered state above 60 °C. The conductivities of the ordered samples increase abruptly, by as much as five orders of magnitude, across the order-to-disorder transition. No abrupt changes in conductivity are seen in samples that are fully disordered – PEO-PSLiTFSI(5-5), (5-7), and (5-8); see Figure 4.4.

Increasing the molecular weight of the PSLiTFSI block increases ion concentration. This however has a non-trivial effect on ionic conductivity because the volume fraction of the ion-conducting PEO domains decreases with increasing ion concentration (see Table 4.1). This interplay is clarified in Figure 4.5 where conductivity is plotted as a function of Li$^+$ concentration, $r$, at selected temperatures. At 45 °C, conductivity generally increases with increasing salt concentration up to $r=0.199$ before decreasing abruptly in the $r=0.207$ sample. It is perhaps interesting to note that this abrupt decrease in conductivity of PEO-PSLiTFSI(5-8), the polymer with the highest ion concentration, is seen at all temperatures (Figure 4.5). At 55 °C, ionic conductivity is a weak decreasing function of $r$ over most of the experimental window from $r=0.088$ to 0.207. At 90 °C, conductivity increases with increasing ion concentration up to $r=0.111$, and then it decreases at higher ion concentration. The ratio $\sigma/r$ at 90 °C is nearly constant in the low concentration regime; at $r=0.056$, 0.088, and 0.111, $\sigma/r = 1.32 (\pm 0.17) \times 10^{-3}$ S cm$^{-1}$. We thus attribute the conductivity increase at low $r$ values (90 °C) to an increase
in ion concentration. Effects other than ion concentration dominate the behavior of these block copolymer electrolytes at other temperatures and $r$ values.

![Figure 4.5](image.png)

**Figure 4.5.** Ionic conductivity, $\sigma$, versus $r$ value for temperatures 45, 55, and 90 °C. The top axis identifies the molecular weight of the PSLiTFSI block.

Returning to Figure 4.2, we can now address the underlying reason for disappearance of crystallinity at room temperature when the molecular weight of the PSLiTFSI exceeds 4.0 kg·mol$^{-1}$ while the PEO molecular weight is constant at 5.0 kg·mol$^{-1}$. The fact that both crystallinity and microphase separation disappear at the same ion concentration indicates that the two phenomena are coupled. In other words, PEO crystallinity is lost when Li$^+$ ions are not confined to the PSLiTFSI domains. We propose that this is due to two effects: favorable interactions between Li$^+$ and PEO and the entropy of Li$^+$ counterions. Complexation of Li$^+$ by PEO chains is well-established,[91] and disordering enables contact between Li$^+$, that are nominally located on the PSLiTFSI block, and PEO segments. Figure 4.5 shows a dramatic increase in low-temperature conductivity when $r$ is increased from 0.111 to 0.150, which is a clear indication of the presence of free Li$^+$ counter-ions. As the molecular weight of the PSLiTFSI block increases, the concentration of ions increases as well, increasing the importance of Li$^+$ counterion entropy.[92] Beyond a critical charge concentration, $r > 0.111$, in the present set of samples, favorable energetic interactions between the Li$^+$ and PEO segments and contributions to the free energy of the block copolymer due to counterion entropy increase and overwhelm the forces that drive PEO crystallization at room temperature.
To shed light on the complex interplay between conductivity and molecular structure, we define a normalized conductivity, \( \sigma_n \),

\[
\sigma_n(T) = \frac{\sigma(T)}{\sigma_{PEO}(T) \phi_{PEO}}
\]

where \( \sigma_{PEO} \) is the conductivity of PEO(5)/LiTFSI mixtures (5.0 kg·mol\(^{-1}\) PEO homopolymer) at the \( r \) value of interest. We restrict our attention to temperatures between 60 and 90 °C where all the polymers are disordered. In Figure 4.6a, we plot \( \sigma_{PEO} \) versus \( r \) for temperatures 60-90 °C. We used this dataset to calculate normalized conductivities, and the results are shown in Figure 4.6b, where \( \sigma_n \) is plotted as a function of \( r \). The data at the different temperatures collapse on one another, with an average difference of about 15% between values at each temperature. The relatively large error bars in Figure 4.6b are due to the limited number of samples that we could examine and the fact that the samples were difficult to handle. The normalized conductivity, \( \sigma_n \), is peaked at \( r=0.111 \). The conductivity maximum in PEO(5)/LiTFSI is also obtained at \( r=0.111 \) (Figure 4.6a). This value is similar to that reported for PEO/LiTFSI mixtures.\(^{[11]}\)

**Figure 4.6.** (a) Ionic conductivity of PEO(5)/LiTFSI, \( \sigma_{PEO} \), versus \( r \) value for temperatures 60-90 °C. (b) Normalized ionic conductivity of PEO-\( b \)-PSLiTFSI copolymers, \( \sigma_n \), as defined by equation (1), versus Li\(^+\) concentration, \( r \), for temperatures 60-90 °C. The data at these different temperatures roughly collapse on one another. (c) Normalized ionic conductivity of PEO-\( b \)-PSLiTFSI copolymers corrected for transference number, \( \sigma_N \), as defined by equation (2), versus Li\(^+\) concentration, \( r \), for temperatures 60-90 °C. The data at these different temperatures are within close proximity to one another.
Equation 4.1 does not account for the fact that the $\text{Li}^+$ transference number, $t^+$, in PEO homopolymer and PEO-$b$-PSLiTFSI block copolymers are very different. The steady-state-current method was used to estimate $t^+$ of the PEO-$b$-PSLiTFSI samples, and the results are tabulated in Table 4.1. This method is only accurate when $t^+$ is close to unity as effects due to the friction between oppositely charged ions and non-ideality of mixing are not accounted.[21, 66, 93] The values of $t^+$ obtained for PEO-$b$-PSLiTFSI samples ranged from 0.87 to 0.99. In our analysis, we assume $t_{PEO}^+=0.30$, for the PEO(5)/LiTFSI mixtures, independent of salt concentration.[27] Literature values for $t_{PEO}^+$ range between 0.10-0.50.[60-62] It is conceivable that $t^+$ in polymer/salt mixtures decreases with increasing salt concentration due to ion complexation,[22] but this effect has not yet been quantified for PEO/LiTFSI. We also assume that the transference number in both these systems is independent of temperature. We define a transference-number-corrected normalized conductivity, $\sigma_N$:

$$\sigma_N(T) = \frac{\sigma(T)}{t^+} \frac{t_{PEO}^+}{\phi_{PEO} t_{PEO}}$$

(4.2)

where $t^+$ is the lithium ion transference number reported in Table 4.1. In Figure 4.6c, we plot $\sigma_N$ versus $r$. The normalized conductivity, $\sigma_N$, approaches unity at $r=0.111$. It is evident that PEO-PSLiTFSI(5-4) is the most effective single-ion-conducting block copolymer electrolyte that we have studied thus far. The maximum conductivity of this copolymer is $1.65 \times 10^{-4}$ S cm$^{-1}$ at 90 °C.

Our analysis suggests that in the highly conducting electrolytes, $\sigma/r = 1.32 \times 10^{-3}$ S cm$^{-1}$ at 90 °C. Using this relationship, we estimate a conductivity of $3.70 \times 10^{-5}$ S cm$^{-1}$ at $r=0.028$. In their study of PSLiTFSI-$b$-PEO-$b$-PSLiTFSI, Bouchet et al. determined that the most conductive electrolyte in their sample set had $r=0.028$, and their reported conductivity of $3.4 \times 10^{-5}$ S cm$^{-1}$ at 90 °C is in agreement with the proposed relationship.

### 4.4 Conclusion

We have synthesized and characterized a series of single-ion-conducting block copolymer electrolytes, PEO-$b$-PSLiTFSI, where the PEO molecular weight was held fixed at 5.0 kg·mol$^{-1}$, and the ion-containing block, PSLiTFSI, was varied from 2.0-7.5 kg·mol$^{-1}$. Below the PEO melting temperature (52 ± 4 °C), a lamellar morphology with ion clusters were found for PEO-PSLiTFSI(5-2), (5-3), and (5-4). These polymers exhibited an order-to-disorder transition coincident with the melting of the PEO crystals, and the conductivity increased abruptly by as much as five orders of magnitude. Polymers with higher Li$^+$ content, PEO-PSLiTFSI(5-7) and (5-8), were disordered at all temperatures, and their conductivities were a smooth function of temperature. PEO-PSLiTFSI(5-5) was shown to lie at the border between partially ordered and fully disordered systems. Samples that exhibited conductivities above $10^{-5}$ S·cm$^{-1}$ were all disordered. However, samples that exhibited the highest conductivities at high temperatures were ordered at low temperatures (see Figures 4.4 and 4.5). In contrast, samples that exhibited low conductivities in the high-temperature disordered state were also disordered at low temperatures. Ion transport in PEO-$b$-PSLiTFSI copolymers depends on a complex
interplay between the volume fraction of the PEO block that provides avenues for ion transport and that of the PS\textit{LiTFSI} block where the ions are stored.
4.5 Nomenclature

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTFSI</td>
<td>lithium bis(trifluoromethane sulfonyl) imide</td>
</tr>
<tr>
<td>PEO</td>
<td>poly(ethylene oxide)</td>
</tr>
<tr>
<td>PEO-(b)-PSLiTFSI</td>
<td>poly(ethylene oxide)-(b)-polystyrenesulfonyllithium (trifluoromethyl sulfonyl) imide</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>SAXS</td>
<td>small angle X-ray scattering</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>WAXS</td>
<td>wide angle X-ray scattering</td>
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</table>

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d)</td>
<td>the domain spacing</td>
</tr>
<tr>
<td>(D)</td>
<td>the dispersity</td>
</tr>
<tr>
<td>(M_{\text{PEO}})</td>
<td>molecular weight of the PEO block</td>
</tr>
<tr>
<td>(M_{\text{PSLiTFSI}})</td>
<td>molecular weight of the PSLiTFSI block</td>
</tr>
<tr>
<td>(t^+)</td>
<td>the lithium ion transference number</td>
</tr>
<tr>
<td>(t_{\text{PEO}}^+)</td>
<td>transference number of PEO/LiTFSI system</td>
</tr>
</tbody>
</table>

Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_{\text{PEO}}(T))</td>
<td>ionic conductivity of PEO/LiTFSI system</td>
</tr>
<tr>
<td>(\sigma_n(T))</td>
<td>normalized conductivity</td>
</tr>
<tr>
<td>(\sigma_N(T))</td>
<td>transference number corrected normalized conductivity</td>
</tr>
<tr>
<td>(\sigma(T))</td>
<td>ionic conductivity</td>
</tr>
<tr>
<td>(\phi_{\text{PEO}})</td>
<td>volume fraction of the PEO block</td>
</tr>
</tbody>
</table>
4.6 Supplementary Information

4.6.1 GPC

GPC traces of the PEO-macroinitiator (5.0 kg·mol⁻¹) and the PEO-PSLiTFSI block copolymers confirm polymerization of the PSLiTFSI block (Figure 4.S1). Due to the complex molecular structure of PEO-\textit{b}-PSLiTFSI copolymer and potential interactions between the ionic group and the columns, we only use the GPC data to confirm addition of PSLiTFSI segments onto the PEO chain. Quantification of the relations between elution volume and molecular weight is not possible based on our current understanding.

![Figure 4.S1. GPC traces of PEO-macroinitiator (5.0 kg mol⁻¹, dotted curve) and the block copolymers PEO-\textit{b}-PSLiTFSI.](image-url)
4.6.2 Density Estimation via the Van Krevelen Method

We used the group contribution approach of Van Krevelen to estimate the density of PSLiTFSI. The density of the polymer is determined by the quotient of the molecular weight and the total molar volume. The table below illustrates the calculation for the PSLiTFSI density. In the absence of explicit contributions for $\text{N}^-\text{Li}^+$, we have used an NH group.

<table>
<thead>
<tr>
<th>PSLiTFSI Van Krevelen method</th>
<th>number of groups</th>
<th>molar volume (cm$^3$ mol$^{-1}$)</th>
<th>total molar volume (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-CH2-)</td>
<td>1</td>
<td>16.37</td>
<td>16.37</td>
</tr>
<tr>
<td>(-CH&lt;)</td>
<td>1</td>
<td>10.8</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>65.5</td>
<td>65.5</td>
</tr>
<tr>
<td>(-NH-)</td>
<td>1</td>
<td>12.8</td>
<td>12.8</td>
</tr>
<tr>
<td>(-SO2-)</td>
<td>2</td>
<td>32.5</td>
<td>65</td>
</tr>
<tr>
<td>(-CF3)</td>
<td>1</td>
<td>34.75</td>
<td>34.75</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>-</td>
<td>205.22</td>
</tr>
</tbody>
</table>

Table 4.S1. Calculation of PSLiTFSI density using the Van Krevelen method.

4.6.3 Conductivity Sample Construction

Aluminum electrodes (18 μm in thickness) and aluminum tabs were used in the conductivity sample construction, and Kapton tape was used to seal the gap between the spacer and the electrode. This additional seal prevented the polymer from leaking out of the spacer when the polymer was in the melt. Figure 4.S2 outlines the conductivity construction before it was vacuum sealed in pouch material.
Figure 4.S2 Conductivity sample assembly for PEO-$b$-PSLiTFSI samples. The Kapton spacer (yellow circle) is shown containing polymer. The aluminum tabs and aluminum electrodes are shown in grey. The Kapton tape, shown in orange, has a concentric hole.

4.6.4 Differential Scanning Calorimetry (DSC).

Figure 4.S3 DSC thermograms for (a) PEO-PSLiTFSI(5-2), (5-3), and (5-4) (b) PEO-PSLiTFSI(5-5), (5-7), and (5-8). The inset in (a) shows a magnification of the low-temperature data.
Table 4.1 Thermodynamic data for PEO-PSLiTFSI.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PEO weight fraction</th>
<th>T_{m,PEO} (°C)</th>
<th>ΔH_{m,PEO} (J/g)</th>
<th>X_{c,PEO} (%)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-PSLiTFSI(5-2)</td>
<td>0.71</td>
<td>55</td>
<td>187</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-3)</td>
<td>0.61</td>
<td>53</td>
<td>148</td>
<td>72</td>
<td>-</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-4)</td>
<td>0.56</td>
<td>48</td>
<td>185</td>
<td>90</td>
<td>-10</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-5)</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-19</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-7)</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-10</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(5-8)</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-11</td>
</tr>
</tbody>
</table>

The (onset) melting temperature (T_m), melting enthalpy normalized by PEO weight fraction (ΔH_{m,PEO}), degree of crystallinity (X_{c,PEO}), and the glass transition temperature (T_g) are listed. The reference melting enthalpy of 100% crystalline PEO (5.0 kg mol\(^{-1}\)) was measured, 206 J/g, which is in close accordance with literature.\cite{R.H. Beaumont, 1966 #48}

Signatures of the glass transition were not evident in the DSC scans of the crystalline samples and in the PEO5 homopolymer. It is likely that this is due to the dominance of the crystalline phase. Similar difficulties were first noted by Beaumont et al. in 1966.\cite{94}
Chapter 5. Molecular Weight Increase of a Single-Ion- Conducting Block Copolymer Electrolyte: Ion Transport & Performance

ABSTRACT

Due to favorable interactions between lithium ions and the ether oxygens in PEO, single-ion-conducting block copolymer electrolyte, PEO-PSLiTFSI became homogenous at elevated temperatures. There is interest in understanding the effect of molecular weight increase in these systems. PEO-PSLiTFSI electrolytes were synthesized where the molecular weight of the PEO block was increased to a new constant of 9.5 kg·mol\(^{-1}\) and the molecular weight of the PSLiTFSI block was allowed to vary. The results from SAXS, ionic conductivity, and lithium symmetric cells are discussed. We also present preliminary tomography images of cells with PEO-PSLiTFSI.

5.1 Introduction

Block copolymer self-assembly is governed by the Flory-Huggins interaction parameter \(\chi\), the volume fraction of a block, \(f\), and the number of repeat units per polymer chain, \(N\). While the 5 kg·mol\(^{-1}\) series of Chapter 4 were all homogenous at elevated temperatures, one way by which to induce self-assembly is to increase \(N\), or the molecular weight. There is interest in understanding the effect of molecular weight increase on the morphology and ion transport properties in block copolymer electrolytes.[59, 70, 95] For instance, it was shown that the binary block copolymer electrolyte, polystyrene-\(b\)-poly(ethylene oxide) (SEO) with LiTFSI salt, exhibited higher ionic conductivities relative to the PEO homopolymer of comparable molecular weight.[15] This was owed to enhanced lithium ion diffusion away from the interfacial zone between blocks.[15, 96] More recently, it was shown that low molecular weight SEO exhibited a new maximum in ion conductivity at high salt concentration due to changes in grain structure.[95]

In this study, a higher molecular weight series of the single-ion-conducting block copolymer electrolyte, PEO-PSLiTFSI, was synthesized where the molecular weight of the PEO block was held constant at 9.5 kg·mol\(^{-1}\). The molecular weight of the PSLiTFSI block was allowed to vary from 3.5 to 8.3 kg·mol\(^{-1}\). Herein, we discuss the SAXS profiles of these block copolymers and its relationship to ionic conductivity. The resulting conductivity as a function of temperature is analyzed with Vogel-Tamman-Fulcher-Hesse fits to elucidate the mechanisms that influence the ionic conductivity. Finally, the ion-transport properties of lithium symmetric cells are discussed. We also show preliminary tomography studies of cells with PEO-PSLiTFSI.

5.2 Experimental

5.2.1 Electrolyte Preparation

The polymers were synthesized and characterized as discussed in Chapter 2, and they are listed in Table 5.1. GPC confirmed polymerization (Figure 5.S1). Samples for ionic conductivity, SAXS, and transference number measurement were not drop-casted as previously
discussed in Chapter 3.2.2. Following ion-exchange and sublimation of water under reduced pressure (Chapter 2.5), polymers were dried in the glove box antechamber under vacuum at 90 °C for at least 12 hours. Polymers were then brought into the glovebox for sample preparation.

Table 5.1. Single-ion-conducting diblock copolymers in this study.

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>(M_n) PEO</th>
<th>(M_n) PSLiTFSI</th>
<th>(D)</th>
<th>(r)</th>
<th>(\phi_{PEO})</th>
<th>(d) (nm)</th>
<th>(T_{m, PEO}) (°C)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-PSLiTFSI(9.5-3.5)</td>
<td>9.5</td>
<td>3.5</td>
<td>1.15</td>
<td>0.05</td>
<td>0.97</td>
<td>0.79</td>
<td>33.5</td>
<td>48.9</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(9.5-4.9)</td>
<td>9.5</td>
<td>4.9</td>
<td>1.15</td>
<td>0.07</td>
<td>1.0</td>
<td>0.73</td>
<td>-</td>
<td>50.6</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(9.5-7.6)</td>
<td>9.5</td>
<td>7.6</td>
<td>1.14</td>
<td>0.11</td>
<td>0.99</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEO-PSLiTFSI(9.5-8.3)</td>
<td>9.5</td>
<td>8.3</td>
<td>1.15</td>
<td>0.12</td>
<td>0.98</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.1. \(M_n\) PEO = number average molecular weight of the PEO block; \(M_n\) PSLiTFSI = number average molecular weight of the PSLiTFSI block; \(D\) = dispersity; \(r = [Li^+] [EO]^{-1}\) for the PEO-PSLiTFSI copolymers; \(t^+\) = the \(Li^+\) transference number; \(\phi_{PEO}\) = volume fraction of PEO block; \(d\) = the domain spacing of the block copolymers; \(T_m\) = the onset melting temperature determined from DSC; \(T_g\) = the glass transition temperature determined from DSC.

5.2.2 Electrochemical Measurements

Samples for ionic conductivity were constructed as indicated in Chapter 4.2.1 following the measurement method outlined in 3.2.3. Samples for transference number were constructed using the similar construction for conductivity (Chapter 4.2.1), except with the use of lithium electrodes. Nickel tabs and nickel current-collectors were used to complete the symmetric cell construction. These cells were vacuum-sealed in pouch material. The steady-state current method was utilized, where chronoamperometry experiments were carried out on the cells at 60 °C using the VMP3 potentiostat.[65, 66] Three separate experiments were carried out where a different constant \(\Delta V\) potential was applied, and the current was measured as a function of time. Impedance spectra were collected every 10 minutes to probe the bulk and interfacial resistances. (One experiment length occurred for a total of 40 minutes.) The bulk and interfacial resistances were determined by fitting an equivalent circuit (Figure 3.3) to the data using EC-Lab and using equation 3.1. The experiments were performed for values of \(\Delta V = 20, 40,\) and \(60\) mV. The data was consistent regardless of the value of \(\Delta V\). The data reported herein correspond to the experiment using \(\Delta V = 20\) mV.

Lithium symmetric cells were cycled at 60 °C. First, the samples were pre-conditioned at 0.02 mA·cm\(^{-2}\) for 15 cycles, where each cycle consisted of a 4 hour charge, 10 minute rest, and a 4 hour discharge. Then, samples were cycled at a higher current density of 0.17 mA·cm\(^{-2}\).

5.2.3 Hard X-ray Microtomography
After cycling, samples were taken back to the glovebox and carefully opened up to remove the Nickel current collectors. The samples were carefully marked to keep track of which electrode was connected to the working and counter electrode at the potentiostat. The samples were placed on a polystyrene platform for rigidity, and then samples were vacuum sealed. Radiograph images were collected at the Advanced Light Source beamline 8.3.2 at 20 keV energy using a 5x magnification lens about a single axis of rotation. The radiographs were then processed to construct a three-dimensional map of the sample.[97] Images were analyzed using a commercial image processing software, Avizo. Images shown herein apply a median filter for image smoothing.[98]

5.3 Results and Discussion

The SAXS profiles for PEO-PSLiTFSI(9.5-3.5) obtained at three different temperatures are shown in Figure 5.1. At 30 °C, there is a broad peak at \( q = q^* = 0.187 \text{ nm}^{-1} \) (Figure 5.1a). This corresponds to a domain spacing, the center-to-center distance between adjacent PEO-rich lamellae \( (d = 2\pi \cdot q^*) \), of 33.5 nm. As the sample is heated to 50 °C, the primary peak at \( q^* \) decreases in intensity (Figure 5.1b). At 60 °C, no peaks are observed (Figure 5.1c). It is evident that PEO-PSLiTFSI(9.5-3.6) undergoes an order-to-disorder transition. As previously demonstrated, the observed microphase separation is due to the crystallization of the PEO domain.[89, 99] When the crystalline PEO lamellae are melted, PEO-PSLiTFSI(9.5-3.5) becomes completely disordered (homogenous). This is due to the favorable interactions between the Li\(^+\) and the ether oxygens of PEO.[89, 99]

![Graph 5.1](image)

**Figure 5.1.** SAXS scattering intensity versus the magnitude of the scattering vector, \( q \), of PEO-PSLiTFSI(9.5-3.5) at (a) 30 °C, (b) 50 °C, and (c) 60 °C.

In Figure 5.2, the characteristic domain spacing for PEO-PSLiTFSI(9.5-3.5) is plotted against temperature. The data in Figure 5.2 are derived from SAXS profiles obtained at 30-50 °C. The increase in \( d \) is smooth over the course of the experiment. This was also observed in PEO-PSLiTFSI(5.0-3.2).[89]
Figure 5.2. The domain spacing, $d$, plotted against temperature for PEO-PSLiTFSI(9.5-3.5).

SAXS profiles for PEO-PSLiTFSI(9.5-4.9), (9.5-7.6), and (9.5-8.5) at 30 °C are shown in Figure 5.3. These copolymer electrolytes are homogenous at 30 °C, and they remain homogenous at elevated temperatures. The data is truncated in Figure 5.2b and Figure 5.2c because the measured scattering from the sample fell below that of the empty cell at $q > 0.32$.

Figure 5.3. SAXS scattering intensity versus the magnitude of the scattering vector, $q$ at 30 °C for (a) PEO-PSLiTFSI(9.5-4.9), (b) PEO-PSLiTFSI(9.5-7.6) and (c) PEO-PSLiTFSI(9.5-8.3).

The temperature dependence of the ionic conductivities of the samples listed in Table 5.1 are shown in Figure 5.4. Samples that were disordered at all temperatures (Figure 5.2), PEO-
PSLiTFSI(9.5-4.9), (9.5-7.6), and (9.5-8.3), did not exhibit a sharp increase in the ionic conductivity (Figure 5.4b, c, and d). PEO-PSLiTFSI(9.5-3.5) with $r = 0.05$ exhibits a significant change in the ionic conductivity across temperature. This is due the observed order-to-disorder transition previously described. At low temperatures ($T = 30$ °C) the copolymer is microphase separated (Figure 5.1a); therefore, Li$^+$ are trapped in the ion-insulating PS domain. As a result, the ionic conductivity is low, 6.5 x $10^{-10}$ S·cm$^{-1}$. As microphase separation is lost in the range 35 °C < $T$ < 60 °C (Figure 5.1b), the ionic conductivity increases five orders of magnitude (Figure 5.4a) to 1.5 x $10^{-5}$ S·cm$^{-1}$ at 60 °C.

![Figure 5.4](image)

Figure 5.4. Ionic conductivity plotted against temperature (a) PEO-PSLiTFSI(9.5-3.5), (b) PEO-PSLiTFSI(9.5-4.9), (c) PEO-PSLiTFSI(9.5-7.6), and (d) PEO-PSLiTFSI(9.5-8.3).

In Figure 5.5, the ionic conductivity is plotted against $r$. There are two temperature regions in which we can observe different conductivity trends with increasing Li$^+$ concentration.
At $T > T_m$, the ionic conductivity decreases with increasing $r$. We show this in Figure 5.5a at 60 °C. However, at $T < T_m$, there is a peak in ionic conductivity at $r = 0.07$ (PEO-PSLiTFSI(9.5-4.9)). Increasing $r$ beyond 0.07 however, results in a decrease in the ionic conductivity (Figure 5.5b). In order to understand the parameters that govern these trends, we attempt to normalize the data in the following discussion.

**Figure 5.5.** Ionic conductivity plotted against $r$ (a) 60 °C and (b) 45 °C.

We normalize the data in Figure 5.5a with equation 4.2 in order to understand the underlying factors that influence the ionic conductivity, where $\sigma_{PEO}$ is the intrinsic ionic conductivity of PEO 5 kg·mol$^{-1}$ homopolymer at the corresponding $r$ value. (While the molecular weight of the PEO homopolymer by which we normalize is not the same as the PEO molecular weight in this study, we do not expect significant changes as the ionic conductivity of PEO homopolymer plateaus at 5 kg·mol$^{-1}$.)[7, 100] We find that the qualitative trend seen in Figure 5.5a is similar despite this normalization step in equation 4.2. (See Figure S5.1)

Another method by which to understand the parameters that influence the ionic conductivity can be by using the Vogel-Fulcher-Tammann-Hesse relationship (equation 5.1). It is typically used to describe the ionic conductivity of homopolymer electrolytes. [6] This relationship is outlined by equation 5.1, where $A$ is a prefactor, $E_a$ is a pseudoactivation energy, $R$ is the gas constant, and $T_0$ is the Vogel temperature. This reference temperature is taken to be 50 °C below the $T_g$.[6, 95, 101] The fits were performed on conductivity data in the homogenous melt state (60-90 °C) on three independent samples for each electrolyte. The error bars reported are an average of the results to the three samples. In Figure 5.5, we show the results to the VTF fit as a function of $r$. $E_a$, is relatively constant versus $r$ with the exception at $r = 0.11$ (Figure 5.5a). $E_a$ is thought to relate the activation energy associated with ion hopping.[102] The prefactor, $A$, increases with increasing $r$, until it peaks at $r = 0.11$. The prefactor then sharply decreases at $r = 0.12$. $A$ is associated to the effective charge carrier concentration.[103] Therefore, the charge carrier concentration expectedly increases with increasing ion
concentration. However, the sharp decrease beyond the threshold value of \( r = 0.11 \) may be owed to trapped ions in the ion-insulating polystyrene backbone.

\[
\sigma(T) = A(T)^{-1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right)
\]  

(5.1)

With the determined \( E_a \) and \( A \) from equation 5.1, we can determine a reduced conductivity, \( \sigma_r \). Previous studies have calculated \( \sigma_r \) in a similar manner in order to decouple the effects of solvation-site density and segmental motion (equation 5.2). [104-106] The temperature is taken to be 75 K above the measured \( T_g \) of the copolymer electrolyte.

\[
\sigma_r = A(T_g + 75 K)^{-1/2} \exp\left(\frac{-E_a}{R(125K)}\right)
\]  

(5.2)

Using this relationship and the determined \( E_a \) and \( A \), we determine that \( \sigma_r \) is relatively constant across the entire sample set (Figure 5.6c). This indicates that the conductivity measured in PEO-PSLiTFSI is strongly related to the segmental motion of the copolymers. Based on the result in Figure 5.6c, we deduce that there is no significant effect from solvation-site density. Therefore, the differences we observe in \( E_a \) and \( A \) (Figures 5.6a and b) are owed to the increasing effects of \( T_g \) across the sample set.

**Figure 5.6.** (a) Pseudo activation energy, \( E_a \), (b) prefactor, \( A \), and (c) \( \sigma_r \), reduced conductivity plotted against ion-concentration, \( r \).

Comparing the ionic conductivity of the 9.5 kg·mol\(^{-1}\) series to the previously studied 5 kg·mol\(^{-1}\) series (Chapter 4), it is evident that this series exhibits lower ionic conductivities. For \( r = 0.11 \), there is an order of magnitude difference in the ionic conductivity. It is worth noting that the glass transition temperatures of the 5 kg·mol\(^{-1}\) series are lower than those of the 9.5 kg·mol\(^{-1}\)
series. We limit our analysis with equations 5.1 and 5.2 to the 9.5 kg·mol\(^{-1}\) due to the differences in \(D\) of the 5 kg·mol\(^{-1}\).

In Figure 5.7, we compare the ion-transport results from lithium symmetric cells to that of aluminum symmetric cells. Qualitatively, the trend observed in ionic conductivity from the aluminum symmetric cells is preserved in lithium symmetric cells (Figure 5.7a). The interfacial resistance, \(R_{\text{interfacial}}\), is relatively constant at low \(r\) (\(r = 0.05\) and 0.07). However, \(R_{\text{interfacial}}\) increases gradually to about an order of magnitude higher at \(r = 0.12\). This indicates that there is a significant kinetic barrier in the reaction at the polymer and Li anode at these high \(r\) values.[66] This may be related to the low effective charge concentration, \(A\), observed for this sample, PEO-PSLiTFSI(9.5-8.3).

![Figure 5.7](image_url)

**Figure 5.7.** (a) Ionic conductivity from aluminum symmetric cells (yellow squares) and lithium symmetric cells (purple circles) plotted against \(r\) at 60 °C, and (b) the interfacial resistance from lithium symmetric cells plotted against \(r\) at 60 °C.

To gain more insight of behavior at the polymer/lithium interface, X-ray microtomography was conducted on cycled samples. Preliminary cycling and examination of these electrolyte/lithium surfaces shows qualitatively different features than that of samples cycled with binary block copolymer electrolytes (SEO + LiTFSI).[98, 107] In Figure 5.8, we show cross sections of a lithium symmetric cell with PEO-PSLiTFSI(9.5-3.5) before cycling. The dark regions are lithium metal, and the light grey across the center is the polymer electrolyte.
Figure 5.8. X-ray tomogram of a lithium symmetric cell before cycling. The dark regions are lithium, and the brighter horizontal strip through the center is the polymer electrolyte. Interfacial surfaces between the lithium electrodes and the polymer electrolyte appear smooth.

In Figure 5.9, tomograms corresponding to different cross-sections of a sample are shown, where the sample was cycled 13 times at 0.17 mA·cm⁻² before imaging. This sample shorted. (The cycling profile for this sample is shown in Figure 5.53.) This corresponds to 63 C·cm⁻² of charge passed. Surfaces appear to be less smooth, and the appearance of globular-like dendrite growth is absent. Instead, sharp protrusions appear from the electrolyte into the lithium metal. In some regions, the electrolyte becomes as thin as 10 μm between the lithium electrodes (Figure 5.9e). It is hypothesized that this may be due to the weak structural integrity of the copolymer in the melt phase.
5.4 Conclusion

A series of PEO-PSLiTFSI were synthesized, where the PEO block was held constant at 9.5 kg·mol\(^{-1}\) and the PSLiTFSI was allowed to vary. These copolymers exhibited transference numbers approaching unit. Only PEO-PSLiTFSI(9.5-3.5) exhibited an order-to-disorder transition. All other polymers with a higher volume fraction of the ion-containing block were found to be homogenous at all temperatures. Qualitatively, the ionic conductivity trends were similar to those reported in Chapter 4. However, the ionic conductivity was found to decrease with increasing ion concentration, \(r\). There was no peak in ionic conductivity in this series as previously reported in the 5 kg·mol\(^{-1}\) series. The conductivity trend with \(r\) was shown to be strongly correlated to the effect of increasing \(T_g\). Preliminary cycling and tomography studies with PEO-PSLiTFSI(9.5-3.5) shows that the polymer/electrolyte interface is fundamentally different than what was previously observed in high molecular weight binary block copolymer electrolytes.
5.5 Supplementary Information

**Figure 5.S1.** GPC of the PEO-PSLiTFSI copolymers and the PEO macroinitiator.

The low current (0.02 mA·cm\(^{-2}\)) cycling profile of PEO-PSLiTFSI(9.5-3.5) at 60 °C is shown in Figure 5.S2. At the beginning of the experiment, the potential is high. It then decreases and equilibrates to approximately 25 mV (-25 mV in the opposite direction). This can be attributed to the changing interfacial impedance, the second semi-circle in a Nyquist plot (Figure 5.S3). Before cycling, the interfacial impedance is large (distance of the second semi-circle), approximately 2000 Ω·cm\(^2\). After 30 hours of cycling, it reaches a minimum of approximately 700 Ω·cm\(^2\). After all 15 cycles are completed, the final interfacial impedance increased to 900 Ω·cm\(^2\). The final impedance spectroscopy is represented by the yellow triangles in Figure 5.S3. The arrow shows the decrease in the length of the second semi-circle from the start of the low-current cycling to the final cycle.
Figure 5.S2. Chronopotentiometry cycling profile of PEO-PSLiTFSI(9.5-3.5) upon application of constant current density of 0.02 mA·cm\(^{-2}\). The red lines represent the positive application of current, and the blue lines are the negative application of current. The black lines are the rest periods.

Figure 5.S3. The impedance spectroscopy of PEO-PSLiTFSI(9.5-3.5) during the low current cycling. The yellow triangles demonstrate the impedance spectroscopy during the final cycle.

Figure 5.S4. Chronopotentiometry cycling profile of PEO-PSLiTFSI(9.5-3.5) upon application of a constant current density of 0.17 mA·cm\(^{-2}\). The red lines represent the positive application of current, and the blue lines are the negative application of current. The black lines are the rest periods. The sample shorted after 13 cycles (63 C·cm\(^{-2}\) charge passed).
Figure 5.S5. The impedance spectroscopy of PEO-PSLiTFSI(9.5-3.5) during the high current cycling.

In Figure 5.S6, tomogram images are shown in the plane of the lithium symmetric cell with electrolyte PEO-PSLiTFSI(9.5-3.5). The grain structure of the lithium metal can be observed. In Figure 5.S6a the bottom lithium electrode is shown. In Figure 5.S6b, the electrolyte (lighter grey) emerges in a distinct pattern in the top-right corner. In Figure 5.S4c-g both the electrolyte (lighter grey) and lithium (darker grey) can be observed. In the final image (Figure 5.S6h) the top lithium electrode is observed. The goal with this image is to demonstrate that the polymer electrolyte conforms to the surrounding grain structure of the lithium metal.
Figure 5.6. Tomogram images taken in plane of the lithium symmetric cell with electrolyte PEO-PSLiTFSI(9.5-3.5). (a) the bottom lithium electrode (b) electrolyte (lighter grey) emerges in a distinct pattern in the top-right corner. (c-g) electrolyte (lighter grey) and lithium (darker grey) (h) top lithium electrode
Chapter 6. Dependence of Conductivity, Morphology, and Modulus on the Composition of Lithiated and Magnesiated Single-Ion-Conducting Block Copolymer Electrolytes

ABSTRACT

Single-ion-conducting block copolymers are of considerable interest as electrolytes for battery systems, as they eliminate overpotentials due to concentration gradients. In this study, we characterize a library of poly(ethylene oxide) (PEO) based diblock copolymers where the second block is poly(styrene-4-sulfonyltrimfluoromethylsulfonylimide with either cation: univalent lithium or divalent magnesium counterions (PEO-b-PSLiTFSI or PEO-P[(STFSI)2Mg]). The PEO chain length is held fixed in this study. Polymers were synthesized in matched pairs that were identical in all aspects except for the identity of the counter ion. Using rheology, SAXS, and DSC, we show that the dependence of morphology and modulus on composition in these charged copolymer systems are fundamentally different from uncharged block copolymers. At a given frequency and temperature, the shear moduli of the magnesiated copolymer systems were approximately three to four orders of magnitude higher than those of the matched lithiated pair. The shear moduli of all of the lithiated copolymers showed liquid-like rheological features while the magnesiated copolymers did not. All of the lithiated copolymers were completely disordered (homogenous), consistent with the observed rheological properties. As expected, the moduli of the lithiated copolymers increased with increasing volume fraction of the ion-containing block (\( \phi_{PSTFSI} \)). However, the magnesiated copolymers followed a distinct trend. We show that this was due to the presence of microphase separation in the regime \( 0.21 < \phi_{PSTFSI} < 0.36 \), and the tendency for microphase separation becomes weaker with increasing \( \phi_{PSTFSI} \). The magnesiated copolymer with \( \phi_{PSTFSI} = 0.38 \) was homogenous. The morphological and rheological properties of these systems are governed by the affinity of the cations for PEO chains; homogenous systems are obtained when the cations migrate from the ion-containing block to PEO.

6.1 Introduction

The phase behavior of uncharged A-B diblock copolymer melts is well-established.[16, 19, 108-110] We consider a hypothetical experiment wherein the length (or molecular weight) of the A block is held fixed while the molecular weight of the B block is systematically increased such that the volume fraction of B, \( \phi_B \), increases from about 0.2 to 0.4. (B is the minor component.) We expect to see an increasing tendency to form ordered phases with increasing \( \phi_B \). The total chain length increases with increasing \( \phi_B \) in our hypothetical experiment, and this is known to promote ordering.[19] The block copolymer becomes more symmetric with increasing \( \phi_B \), and this is also known to promote ordering.[19] One could use this information to predict changes in rheological properties in our hypothetical experiment. If the B block is more rigid than the A block, one would predict that the shear moduli at a given frequency and temperature would increase with \( \phi_B \). It is worth noting that increasing chain length and promoting order also
results in an increase in the shear moduli; in fact, an increase in the moduli is often used to detect a disorder-to-order transition.[111-115]

This study deals with single-ion-conducting block copolymers comprising a nonionic block (A) and an ion-containing block (B). These systems are of interest for their potential application in rechargeable batteries, as they eliminate overpotentials due to concentration gradients.[36, 37, 89, 99, 101, 116-118] Ion-containing block copolymers have been the subject of numerous recent theoretical studies. [38, 40, 119-122] It has been shown that coulombic effects can fundamentally alter the thermodynamics of block copolymers. In our work, the ion-containing block comprises poly(styrene-4-sulfonylitrifluoromethylsulfonyl)imide repeat units with either lithium (univalent) or magnesium (divalent) counterions PSLiTFSI or P[(STFSI)₂Mg]. The non-ionic block is poly(ethylene oxide) (PEO). The chemical structures of the block copolymers are shown in Figure 1. Our work on this class of materials is motivated by the pioneering work of Bouchet et. al. who first proposed the possibility of using these systems for battery applications.[37]

![Chemical structures of (a) PEO-b-PSLiTFSI copolymer, and (b) PEO-b-P[(STFSI)₂Mg]](image)

**Figure 6.1** Chemical structures of (a) PEO-b-PSLiTFSI copolymer, and (b) PEO-b-P[(STFSI)₂Mg]

Here we fix the molecular weight of the PEO block (9.5 kg·mol⁻¹) and study the properties of the block copolymers as a function of increasing molecular weight of the ion-containing block. The volume fraction of the ion-containing block, 𝜙_{PSTFSI}, is thus increased from 0.21 to 0.38. We focus our attention to temperatures above the melting temperature of the PEO block. We show that the lithiated systems are disordered at all temperatures and all compositions, consistent with our previous studies on low molecular weight samples.[89, 99] In contrast, the magnesiated samples show signatures of microphase separation in the regime 0.21 < 𝜙_{PSTFSI} < 0.36, and the tendency for microphase separation becomes weaker with increasing 𝜙_{PSTFSI}. These signatures disappear when 𝜙_{PSTFSI} is increased from 0.36 to 0.38. The consequence of these morphological characteristics on rheology is described below. For reasons that we will clarify, the dependence of morphology and mechanical properties of single-ion-
conducting block copolymers on composition is qualitatively different from that of uncharged block copolymers outlined in the first paragraph of the introduction.

6.2 Experimental

6.2.1 Block Copolymer Electrolytes

The synthesis of PEO-b-PSLiTFSI and PEO-b-P[(STFSI),Mg] block copolymers are described in Chapter 2.[89, 99, 101] Briefly, a 9.5 kg·mol⁻¹ PEO macroinitiator was used to synthesize a series of PEO-b-PSKTFSI copolymer precursors. The potassium ion in each precursor was exchanged in separate reactions to yield a matched pair of PEO-b-PSLiTFSI and PEO-b-P[(STFSI),Mg] block copolymers. Polymerization was verified with ¹H-NMR (Figure 6.1S1) and GPC (Figure 6.1S2), and ion-exchange was verified via ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) (Figure 2.13 and Figure 6.1S3). Polymer samples for DSC were prepared according to Chapter 2.7.6. Polymers are labeled PEO-PLiTFSI(x-y) or PEO-[(STFSI),Mg](x-y), where x and y are the molecular weights of the PEO and PSLiTFSI (P[(STFSI),Mg]) blocks, respectively, in kg·mol⁻¹. The resulting molecular weights (Mₙ), dispersities (D), ion concentrations (r), and volume fractions (ϕ) for the copolymers in this study are listed in Table 6.1. The volume fractions were estimated using the densities of PEO, PSLiTFSI, and P[(STFSI),Mg] homopolymers.[99, 101] The ion-concentration is quantified by r, where r = [Li⁺][EO]⁻¹ for the PEO-PLiTFSI copolymers, and r=[Mg²⁺][EO]⁻¹ for the magnesiumated copolymers.

Table 6.1. Characteristics of lithiumated and magnesiated copolymers

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Mₙ PEO</th>
<th>Mₙ PSLiTFSI or P[(STFSI),Mg]</th>
<th>D</th>
<th>r</th>
<th>ϕₚEO</th>
<th>ϕₚSTFSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO 9.5</td>
<td>9.5</td>
<td>0</td>
<td>1.09</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>PEO-PLiTFSI(9.5-3.5)</td>
<td>9.5</td>
<td>3.5</td>
<td>1.15</td>
<td>0.05</td>
<td>0.79</td>
<td>0.21</td>
</tr>
<tr>
<td>PEO-PLiTFSI(9.5-4.9)</td>
<td>9.5</td>
<td>4.9</td>
<td>1.15</td>
<td>0.07</td>
<td>0.73</td>
<td>0.27</td>
</tr>
<tr>
<td>PEO-PLiTFSI(9.5-7.6)</td>
<td>9.5</td>
<td>7.6</td>
<td>1.14</td>
<td>0.11</td>
<td>0.64</td>
<td>0.36</td>
</tr>
<tr>
<td>PEO-PLiTFSI(9.5-8.3)</td>
<td>9.5</td>
<td>8.3</td>
<td>1.15</td>
<td>0.12</td>
<td>0.62</td>
<td>0.38</td>
</tr>
<tr>
<td>PEO-P<a href="9.5-3.6">(STFSI),Mg</a></td>
<td>9.5</td>
<td>3.6</td>
<td>1.15</td>
<td>0.025</td>
<td>0.79</td>
<td>0.21</td>
</tr>
<tr>
<td>PEO-P<a href="9.5-5.0">(STFSI),Mg</a></td>
<td>9.5</td>
<td>5.0</td>
<td>1.15</td>
<td>0.035</td>
<td>0.73</td>
<td>0.27</td>
</tr>
<tr>
<td>PEO-P<a href="9.5-7.7">(STFSI),Mg</a></td>
<td>9.5</td>
<td>7.7</td>
<td>1.14</td>
<td>0.055</td>
<td>0.64</td>
<td>0.36</td>
</tr>
<tr>
<td>PEO-P<a href="9.5-8.5">(STFSI),Mg</a></td>
<td>9.5</td>
<td>8.5</td>
<td>1.15</td>
<td>0.06</td>
<td>0.62</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Mₙ PEO = number average molecular weight of the PEO block; Mₙ PSLiTFSI = number average molecular weight of the PSLiTFSI block, Mₙ P[(STFSI),Mg] = number average molecular weight of the P[(STFSI),Mg] block; D = dispersity; r
\[ \text{[Li}^+\text{]}\text{[EO]}^{-1} \] for the PEO-PSLiTFSI copolymers, and \[ \text{r}=[\text{Mg}^{2+}\text{][EO]}^{-1} \] for the magnesiated copolymers; \( \phi_{\text{PEO}} \) = volume fraction of PEO block; \( \phi_{\text{PSTFSI}} \) = volume fraction of the ion-containing block

6.2.3 Small-Angle X-ray Scattering

In an argon glovebox, samples were melt-pressed (60-90 °C) into AFLAS rubber spacers (800 μm thick) until translucent pucks were obtained. Samples were hermetically sealed in custom-made sample holders with Kapton windows. Samples were annealed overnight at 90 °C, and they were slowly cooled for 12 hours to room temperature. Acquisitions of the magnesiated copolymers were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL), and acquisitions of the lithiated copolymers were obtained at the Advanced Light Source (LBNL).[67] Glassy carbon (Sample M13 provided by Jan Ilavsky) was used as the standard for absolute scattering.[123] The beam center and sample-to-detector distance were calibrated using silver behenate in Ilavsky’s Nika module for Igor Pro.[68] The scattering profile of an empty sample holder was obtained as \( I_{\text{air}} \). An empty sample holder with two Kapton films was used to acquire \( I_{\text{Kapton}} \). \( I_{\text{Sample}} \), \( I_{\text{Kapton}} \), and \( I_{\text{air}} \) were all acquired with the same exposure time. The final scattering profiles were obtained by the following equation:

\[
I_{\text{corrected}} = c \ast \frac{I_{\text{Sample}} - I_{\text{air}} - \frac{T_{\text{Sample}}}{T_{\text{Kapton}}} (I_{\text{Kapton}} - I_{\text{air}})}{\text{Sample thickness} \ast \text{time}}
\]

(6.1)

The scaling constant \( c \) for absolute intensity was obtained with the aid of Jan Ilavsky’s Irena module in Igor Pro.[124] \( T_{\text{Sample}} \) and \( T_{\text{Kapton}} \) are the transmission coefficients of the polymer sample and Kapton sample, respectively.

6.2.4 Rheometry Experiments

A parallel-plate geometry was used on a Rheometric Scientific ARES (Advanced Rheometric Expansion System) rheometer. Rheometry measurements were conducted starting with 90 °C and cooled in 10 °C intervals until 50 °C. Thermal expansion of the plattens at each temperature was taken into account using a thermal expansion factor of 2.2 μm·°C⁻¹. Samples were first subjected to a dynamic strain sweep test at 1 rad·s⁻¹ to determine a linear regime in which the storage (\( G' \)) and loss (\( G'' \)) moduli were constant as a function of strain. A strain in this linear regime was chosen such that the torque in the subsequent dynamic frequency sweep test was greater than 0.2 g·cm of force. The gap distance was adjusted for every temperature, as the polymer sample would contract with decreasing temperature. Final sample gap distances were between 0.5 and 1.5 mm.

All lithiated polymers were measured with 25 mm diameter plates, and the magnesiated copolymers were measured with 8 mm plates. A larger geometry was necessary for the lithiated copolymers because a higher strain was necessary to obtain strain-independent moduli. The PEO 9.5 kg·mol⁻¹ homopolymer was measured using a 50 mm plate geometry.
A 7.9 and 15.9 mm mold made of fabric-reinforced silicone rubber sheet with an adhesive back (purchased from McMaster-Carr) was adhered onto a clean Teflon sheet. The magnesiated samples were melt-pressed into the 7.9 mm molds, and the lithiated copolymers were melt into the 15.9 mm molds. (The PEO 9.5 kg·mol\(^{-1}\) homopolymer was prepared in a 25.4 mm mold.) The PEO homopolymer and lithiated samples were degassed under vacuum for 12 hours at 90 °C to remove air bubbles. The magnesiated samples were pressed under 73 PSI overnight at 90 °C for effective removal of air bubbles. The samples were then subjected to a slow cooling for 12 hours under an inert atmosphere of nitrogen gas, and they were left at room temperature overnight for 12 hours in an inert environment. The samples were then brought back into the glovebox for sample removal from the mold. The free-standing samples were removed from the glovebox in an air-tight container for sample loading.

The plattens were rubbed clean with isopropanol before fixing them into the rheometer. An oven providing an inert atmosphere surrounded the plattens for the experiment. The plattens were heated up to 65 °C, at which point the gap was zeroed. The samples were quickly loaded concentrically to the plates at this temperature. The lithiated samples melted and thermally expanded, upon which the sample was pressed by the top plate until the sample filled up approximately 50% of the gap volume. Samples were then heated to 90 °C upon which samples thermally expanded to fill the gap volume. The samples were pressed with the top platten until the sample filled the void space and a slight polymer bulge was observed at the edges. Any residual polymer drip was removed, being careful not to damage the integrity of the polymer loaded in the plates. The robust magnesiated samples were pressed in the plattens until they filled the sample space. Samples equilibrated in the plattens for an hour before the start of the experiment. Samples were equilibrated for 20 minutes at every subsequent temperature before measurement.

6.3 Results and Discussion

The frequency (\(\omega\)) dependence of \(G'\) and \(G''\) were measured for all polymers between 60 and 90 °C. These data are shown in Figures S5-S12. Time-temperature superposition was used to generate master curves, and the results are shown in Figure 6.2. Figures 6.2a and 6.2b show \(G'\) and \(G''\) against reduced frequency for the matched pair: PEO-P[(STFSI)\(_2\)Mg](9.5-3.6) and PEO-PSLiTFSI(9.5-3.5). For the lithiated copolymer, \(G'' > G'\) and \(G'' \approx \omega\) over the entire frequency range. These are characteristics of viscoelastic liquids. In the range 1 < log(\(\omega\alpha_T\)) < 2, \(G' \sim \omega^2\); \(\alpha_T\) is the shift factor used at temperature, \(T\). The \(G'\) versus \(\omega\) scaling observed in this frequency window is also characteristic of viscoelastic liquids. The liquid-like rheological properties of PEO-PSLiTFSI(9.5-3.5) are consistent with our previous studies indicating that these copolymers are disordered.[89, 99] However, in the low frequency regime, log(\(\omega\alpha_T\)) < 0, we observe deviations from rheological liquid-like behavior in PEO-PSLiTFSI(9.5-3.5); \(G'\) approaches a frequency independent plateau. This plateau may arise from physical cross-links due to the presence of widely spaced ionic clusters.[55, 125, 126] Uncharged block copolymers in the disordered state do not exhibit such a plateau.[111] The rheological properties of PEO-P[(STFSI)\(_2\)Mg](9.5-3.6) differ qualitatively from those of the lithiated matched pair (Figure 6.2a and 2b). Over the accessible reduced frequency range, \(G'\) of the magnesiated sample at a given reduced frequency is three to four orders of magnitude higher than its lithiated counterpart. Similarly, \(G''\) is two to three orders of magnitude higher than its lithiated counterpart. In addition, both \(G'\) and \(G''\) of the magnesiated sample are similar in magnitude and scale with \(\omega^{0.5}\) across
much of the accessible reduced frequency window. These characteristics are often seen in microphase-separated block copolymers.[17, 111]

The rheological properties of the matched pair PEO-P[(STFSI)$_2$Mg](9.5-5.0) and PEO-PSLiTFSI(9.5-4.9) (Figures 6.2c and 6.2d) are similar to those described in the preceding paragraph. Further increase of the molecular weight of the ion-containing block to 7.7 kg·mol$^{-1}$ results in qualitative differences (Figures 6.2e and 6.2f). Low frequency deviations from liquid-like rheological behavior in PEO-PSLiTFSI(9.5-7.6) are no longer evident. In addition, high frequency plateaus are evident in both $G'$ and $G''$ of PEO-P[(STFSI)$_2$Mg](9.5-7.7). The rheological properties of the PEO-P[(STFSI)$_2$Mg](9.5-8.5) and PEO-PSLiTFSI(9.5-8.3) matched pair (Figure 6.2g and 6.2h) are similar to those of the PEO-P[(STFSI)$_2$Mg](9.5-7.7) and the PEO-PSLiTFSI(9.5-7.6) pair (Figures 6.2e and 6.2f), except for the absence of the high-frequency plateaus.
**Figure 6.2.** Master curves of $G'$ and $G''$ of the matched copolymer pairs, where $\alpha_T$ is the shift factor as a function of reduced frequency. PEO-PStLiTFSI(9.5-3.5) and P[(STFSI)$_2$Mg](9.5-3.6): (a) $G'$ (b) $G''$; PEO-PStLiTFSI(9.5-4.9) and P[(STFSI)$_2$Mg](9.5-5.0): (c) $G'$ (d) $G''$; PEO-PStLiTFSI(9.5-7.6) and P[(STFSI)$_2$Mg](9.5-7.7): (e) $G'$ (f) $G''$; PEO-PStLiTFSI(9.5-8.3) and P[(STFSI)$_2$Mg](9.5-8.5): (g) $G'$ (h) $G''$. The expected scalings for simple liquids ($G' \sim \omega^2$ and $G'' \sim \omega$) and ordered block copolymers ($G' \sim \omega^{0.5}$ and $G'' \sim \omega^{0.5}$) are shown in each figure.

The temperature-dependence of shift factors for each matched pair is shown in Figure 6.3, where $\log(\alpha_T)$ is plotted versus temperature. The surprising observation is that the shift factors for the lithiated and magnesiated matched pairs at a given temperature are very similar in spite of the fact that their rheological properties are very different. For example, at $\log(\omega\alpha_T) = -1$, the $G'$
of PEO-P[(STFSI)₂Mg](9.5-7.7) is six orders of magnitude larger than its lithiated matched pair (Figures 6.2e and 6.2f). In comparison, the differences in the shift factors of these two systems are unremarkable (Figure 3c). The same can be said of all of the data in Figures 6.2 and 6.3.

Figure 6.3. Shift factors for the matched copolymer pairs as a function of temperature.

In Figure 6.4a, we plot $G'$ and $G''$ (as measured, unshifted) of each of the magnesiated copolymers at fixed temperature and frequency (80 °C and $\omega=1$ rad·s⁻¹) versus $\phi_{\text{PSTFSI}}$. Both $G'$ and $G''$ increase steadily with increasing $\phi_{\text{PSTFSI}}$ (or equivalently with increasing molecular weight of the ion-containing block), until $\phi_{\text{PSTFSI}}$ reaches a threshold of 0.36. Beyond this threshold, both $G'$ and $G''$ decrease. In Figure 6.4b, we plot $G'$ and $G''$ of each of the lithiated copolymers at fixed temperature and frequency (80 °C and $\omega=1$ rad·s⁻¹) versus $\phi_{\text{PSTFSI}}$ of that sample. In this set, both $G'$ and $G''$ increase steadily with increasing $\phi_{\text{PSTFSI}}$ across the entire experimental window. (While we have shown rheology data at a particular temperature and frequency in Figure 6.4, the same conclusion is obtained for data at all temperatures and frequencies.) To explain the distinct trends in the rheological features of the lithiated and magnesiated copolymer systems, we conducted SAXS experiments.
Figure 6.4. $G'$ and $G''$ at 80 °C and $\omega=1$ rad·s$^{-1}$ plotted against the volume fraction of the ion-containing block, $\phi_{\text{PSTFSI}}$ of (a) $G'$ (orange squares) and $G''$ (peach pentagons) of the magnesiated copolymers (b) $G'$ (grey diamonds) and $G''$ (navy circles) of the lithiated copolymers.

The SAXS profiles obtained at 80 °C for each of the copolymers are shown in Figure 6.5, where the scattering intensity, $I$, is plotted against the magnitude of the scattering vector, $q$. The scattering profiles of the lithiated copolymers are shown in Figure 6.5a. The scattering from these samples was comparable to the scattering from the empty cell. In one of the samples (PEO-P[(STFSI)$_2$Mg](9.5-7.6)) the data are truncated because the measured scattering from the sample fell below that of the empty cell at $q > 0.32$. We conclude that all of the PEO-PSLiTFSI are completely disordered (homogenous). This is consistent with our previous work wherein we concluded that the effective Flory-Huggins interaction parameter, $\chi$, between PEO and PSLiTFSI is negative.[101]

The scattering profiles of the magnesiated copolymers are shown in Figure 6.5b. Sample PEO-P[(STFSI)$_2$Mg](9.5-3.6) with $\phi_{\text{PSTFSI}} = 0.21$, exhibits a broad well-defined peak at $q=q^* = 0.330$ nm$^{-1}$. In addition, we see an upturn at low $q$. We take the presence of scattering peaks to be a signatures of microphase separation. As we increase $\phi_{\text{PSTFSI}}$ to 0.27 (PEO-P[(STFSI)$_2$Mg](9.5-5.0)), a broad peak is also observed at $q^* = 0.227$ nm$^{-1}$. This peak is not as well-defined as the sample with $\phi_{\text{PSTFSI}} = 0.21$. Further increase of $\phi_{\text{PSTFSI}}$ to 0.36, results in a very weak scattering maximum at $q^* = 0.221$ nm$^{-1}$. Finally, increasing $\phi_{\text{PSTFSI}}$ to 0.38 results in a monotonic scattering profile with no evidence of a scattering maximum. As mentioned in the introduction, the tendency for ordering in uncharged block copolymers is expected to increase with increasing molecular weight of the minor component when the chain length of the major component is held fixed. The data in Figure 6.5b are not in accordance with this expectation. The data presented here do not allow for distinction between weak microphase separation and disordered concentration fluctuations; we use the term weak microphase separation in the discussion below.
The low-angle SAXS scattering seen in Figure 6.5b at \( q < 0.2 \text{ nm}^{-1} \) is inconsistent with the expected scattering from both disordered and microphase separated uncharged block copolymers. In Figure 6.6 we show the temperature dependence of \( I(q) \) of PEO-P[(STFSI)\( _2 \)Mg](9.5-3.6). It is evident that the low \( q \) scattering decreases considerably when the sample is cooled to 62 °C. The changes in low \( q \) scattering are reversible.

**Figure 6.5.** SAXS scattering intensity versus the magnitude of the scattering vector, \( q \) (a) The SAXS profiles of the lithiated block copolymers. The top profile in yellow is PEO-PSLiTFSI(9.5-3.5). The second profile from the top in purple is PEO-PSLiTFSI(9.5-4.9). The third profile in blue is PEO-PSLiTFSI(9.5-7.6). The bottom-most profile is PEO-PSLiTFSI(9.5-8.3) in green. The profiles are vertically offset by factors of 600, 25, 15, and 1. (b) SAXS profiles of the matched magnesiated block copolymers in the same order and color coordination. The scattering profiles are vertically offset for clarity by factors of 150, 20, 15, and 0.2, respectively.
The scattering profiles from weakly microphase separated magnesiated block copolymers are qualitatively different from those of uncharged block copolymers. Features like low-angle upturns have previously been observed in charged block copolymers. Such features may be related to the fact that our samples are not perfectly monodisperse; small differences in the length of the charged block may lead to the formation of large length-scale structures with low-angle scattering signatures. The SAXS profiles of the weakly microphase separated magnesiated block copolymers (Figure 6.5b) are qualitatively consistent with a model proposed by Teubner and Strey. This model (T-S model) was originally developed to describe scattering from oil/water/surfactant microemulsions. It assumes a sinusoidal correlation function with a characteristic period $d$ that is exponentially damped with characteristic correlation length, $\xi$. Our objective is to describe the morphology of the weakly microphase separated magnesiated block copolymers using these parameters.

The T-S equation for the scattering intensity is described by equation (6.2), where the additional term, $I_{bgd}$, accounts for the connectivity of polymer chains.

$$I(q) = \frac{1}{a + bq^2 + cq^4} + I_{bgd}(q)$$  \hspace{1cm} (6.2)

$$I_{bgd}(q) = \frac{1}{eq^2 + g}$$  \hspace{1cm} (6.3)

From the fitting coefficients ($a$, $b$, and $c$), one can determine the correlation length ($\xi$) and the domain spacing ($d$), given by equations (4) and (5).
\[
\xi = \left[ \frac{1}{2} \left( \frac{a}{c} \right)^{1/2} + \frac{b}{4c} \right]^{-1/2}
\]
\[
d = 2\pi \left[ \frac{1}{2} \left( \frac{a}{c} \right)^{1/2} - \frac{b}{4c} \right]^{-1/2}
\] (6.4) (6.5)

In Figure 6.7, we show a least-squares fit to the T-S equation for the microphase separated magnesiated copolymers at 80 °C. It is evident that the shape of the main scattering peak in our samples is consistent with the T-S equation. (Analyzing features like the low-angle upturn require more sophisticated models.) In Figure 6.8, we show \(d\) and \(\xi\), obtained from the T-S fits as a function of \(\phi_{\text{PSTFSI}}\). We find that \(d\) increases with increasing \(\phi_{\text{PSTFSI}}\) (Figure 6.8a). This is attributed to the increase in chain length with increasing \(\phi_{\text{PSTFSI}}\). In contrast, \(\xi\) decreases with increasing \(\phi_{\text{PSTFSI}}\) (Figure 6.8b), reflecting the decreasing tendency for microphase separation. Note that at \(\phi_{\text{PSTFSI}} = 0.38\), no microphase separation is observed in the magnesiated sample. The decrease in \(\xi\) and homogenization with increasing \(\phi_{\text{PSTFSI}}\) is qualitatively different from the behavior of uncharged block copolymers. We posit that this observation is due to the favorable interactions between \(\text{Mg}^{2+}\) and PEO. Above a critical value of \(\phi_{\text{PSTFSI}} = 0.36\), the \(\text{Mg}^{2+}\) ions prefer to be solvated in the PEO microphase. The analogous critical value of the \(\phi_{\text{PSTFSI}}\) of the lithiated chains is much smaller. We attribute this to two factors: (1) the interactions between ether oxygens and \(\text{Li}^+\) are more favorable than those between the ether oxygens and \(\text{Mg}^{2+}\), and (2) the divalent nature of \(\text{Mg}^{2+}\) increases the tendency for these ions to be localized in the PSTFSI block. It should be noted that this is the first report of homogenization in magnesiated single-ion-conducting block copolymers.

Figure 6.7. The SAXS intensity graphed against the magnitude of the scattering vector, \(q\) for the three microphase separated magnesiated copolymers at 80 °C. For clarity, every 10\(^{\text{th}}\) data point is shown by a shape. The solid black lines are the T-S model fits to the data.
Figure 6.8. Results of T-S fits at 80 °C for the magnesiated samples (a) $d$, in blue circles, (b) $\xi$, in yellow triangles versus $\phi_{\text{PSTFSI}}$.

The main objective of this study is to discuss the properties of our copolymers above the melting point of the PEO block; all of the data in Figures 6.2-6.8 are in this regime. The melting point of PEO homopolymers is in the vicinity of 60 °C.[133] In many cases this crystallization drives microphase separation in our single-ion-conducting block copolymers.[89, 99, 101] This is shown in Figure 6.9, where DSC data from our polymers are shown. PEO-PSLiTFSI(9.5-3.5) and (9.5-4.9) exhibit a readily identifiable melting temperature, $T_m$, while PEO-PSLiTFSI(9.5-7.6) and (9.5-8.3) did not show signatures of crystallinity. (PEO-PSLiTFSI(9.5-3.5) exhibits a crystallization peak prior to melting, as is often seen in semicrystalline polymers.[134, 135] )

The absence of crystallinity is due to the migration of the Li$^+$ ions from the PSTFSI block to the PEO block.[89, 99] Similarly, the magnesiated copolymers, PEO-P[(STFSI)$_2$Mg](9.5-3.6), (9.5-5.0), and (9.5-7.7) exhibited melting behavior (Figure 6.9b) while PEO-P[(STFSI)$_2$Mg](9.5-8.5) did not. As argued above, the absence of crystallinity in this case is due to the migration of Mg$^{2+}$ ions from the PSTFSI block to the PEO block. The melting behavior of our samples summarized in Table 2, where we list $T_m$, the melting enthalpy, $\Delta H_m$, and degree of crystallinity, $X_c$. We calculate the degree of crystallinity ($X_c$) from equation 6.6, where $\Delta H_m^0$ is the melting enthalpy of a fully crystalline PEO sample (206 J.g$^{-1}$), and $w_{\text{PEO}}$ is the PEO weight fraction of the copolymer.[94, 135]

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 w_{\text{PEO}}} \quad (6.6)$$

It is evident that $X_c$ is highly dependent on $\phi_{\text{PSTFSI}}$ (Table 6.2).
Figure 6.9. DSC thermograms of (a) the lithiated copolymers, the (b) magnesiated copolymers, and (c) the PEO 9.5 kg·mol⁻¹ homopolymer.
### Table 6.2. Summary of DSC Experiments

<table>
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<tr>
<th></th>
<th>( w_{PEO} )</th>
<th>( T_{m,PEO} ) (°C)</th>
<th>( \Delta H_{m,PEO} ) (J/g)</th>
<th>( X_{c,PEO} )</th>
<th>( T_g ) (°C)</th>
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<td>PEO-PSLiTFSI(9.5-3.5)</td>
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<td>0.42</td>
<td>0.002</td>
<td>-15.3</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-7.98</td>
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<td>-</td>
<td>-</td>
<td>14.1</td>
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<td>12</td>
<td>0.056</td>
<td>16.2</td>
</tr>
<tr>
<td>PEO-P[(STFSI)(_2)Mg(9.5-8.5)]</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59.5</td>
</tr>
</tbody>
</table>

The weight fraction of PEO \( w_{PEO} \), the (onset) melting temperature \( T_m \), melting enthalpy normalized by PEO weight fraction \( \Delta H_{m,PEO} \), degree of crystallinity \( X_c,PEO \), and the glass transition temperature \( T_g \) are listed.

The DSC scans also contain signatures of a glass transition temperature, \( T_g \), and these values are also listed in Table 2 and plotted in Figure 6.10. Increasing the molecular weight of the ion-containing block results in an increase in \( T_g \). This is not surprising because the ion-containing blocks are known to be glassy.\[^{[37]}\] Within each matched pair, the \( T_g \) of the magnesiated copolymer is higher. Comparing data obtained from the matched pair with the highest \( \phi_{STFSI} =0.38 \), we conclude that the presence of divalent Mg\(^{2+} \) ions retards segmental motion to a greater extent than univalent Li\(^+ \) ions (Figure 6.10). While the same qualitative conclusion may be drawn from other matched pairs, the difference in morphology precludes quantitative comparisons. The difference in \( T_g \) increases with increasing volume fraction of the ion-containing block from 7 to 46 °C.
Figure 6.10. Graph of the glass transition temperature, \( T_g \), plotted against the volume fraction, \( \phi_{PSTFSI} \), of the PSLiTFSI or P[(STFSI)\_2Mg] block. The blue circles represent data for the lithiated copolymers, and the orange triangles correspond to the magnesiated copolymers.

In Figure 6.11a, we plot \( G' \) and \( G'' \) (as measured, unshifted) of each of the magnesiated copolymers at fixed temperature and frequency (80 °C and \( \omega = 1 \text{ rad} \cdot \text{s}^{-1} \)) versus \( T_g \) of that sample. Both \( G' \) and \( G'' \) increase steadily with increasing \( T_g \) (or equivalently with increasing molecular weight of the ion-containing block, see Figure 6.10), until \( T_g \) reaches a threshold of 16 °C. Beyond this threshold, both \( G' \) and \( G'' \) decrease in spite of the fact that \( T_g \) increases. The reason for this is now obvious: PEO-P[(STFSI)\_2Mg]9.5-8.5 is homogenous while the other magnesiated copolymers are weakly microphase separated.

In Figure 6.11b, we plot \( G' \) and \( G'' \) of each of the lithiated copolymers at fixed temperature and frequency (80 °C and \( \omega = 1 \text{ rad} \cdot \text{s}^{-1} \)) versus \( T_g \) of that sample. In this set, both \( G' \) and \( G'' \) increase steadily with increasing \( T_g \) across the entire experimental window. The reason for this is also obvious; all of the lithiated samples are homogenous. Also shown in Figure 10b, is the data for PEO-P[(STFSI)\_2Mg](9.5-8.5). Surprisingly, data from the lithiated copolymers and PEO-P[(STFSI)\_2Mg](9.5-8.5) fall on the same line (see dashed lines in Figure 6.10b). (While we have shown rheology data at a particular temperature and frequency in Figure 6.11, the same conclusion is obtained for data at all temperatures and frequencies.) It is thus evident that the sheer moduli of both lithiated and magnesiated block copolymers that are homogenous are mainly governed by \( T_g \).
Figure 6.11. $G'$ and $G''$ at 80 °C and $\omega=1$ rad·s$^{-1}$ plotted against $T_g$ of each sample (a) $G'$ (orange squares) and $G''$ (peach pentagons) of the magnesiated copolymers (b) $G'$ (grey diamonds) and $G''$ (navy circles) of the lithiated copolymers with PEO-P[(STFSI)$_2$Mg](9.5-8.5) data.

In Figure 6.12, we compare the ionic conductivity of the block copolymer electrolytes at 80 °C. Within each matched pair, the ionic conductivity of the magnesiated block copolymer is 3 to 4 order of magnitude lower than that of its lithiated pair. Another notable feature is the trend in ionic conductivity of the magnesiated copolymers. The conductivity decreases steadily with increasing $\phi_{PSTFSI}$ until there is an unexpected increase in the conductivity for $\phi_{PSTFSI} = 0.38$. We now understand that this increase is due to the loss of microphase separation. This deviation in the ionic conductivity trend is not observed in the lithiated copolymer electrolytes.
6.4 Conclusion

We synthesized and characterized a series of matched pairs of lithiated and magnesiated single-ion-conducting block copolymer electrolytes. We used rheology, SAXS, and DSC to characterize our samples. We obtained master curves from the rheology measurements. At a given frequency and temperature, $G'$ and $G''$ of the magnesiated copolymers were approximately three to four orders of magnitude higher than its lithiated matched pair. Furthermore, the lithiated copolymers showed liquid-like rheological signatures while the magnesiated samples did not. In spite of these differences, the shift factor for the matched copolymer pairs at a given temperature was similar. While $G'$ and $G''$ of the lithiated copolymers monotonically increased with $\phi_{PSTFSI}$. This is expected due to the glassy nature of the ion-containing block. The magnesiated copolymers however followed a slightly different trend. While $G'$ and $G''$ values increased with increasing $\phi_{PSTFSI}$ in the range $0.21 \leq \phi_{PSTFSI} \leq 0.36$, the moduli of the sample with $\phi_{PSTFSI} = 0.38$ was lower than that of the sample with $\phi_{PSTFSI} = 0.36$.

SAXS data showed that all of the lithiated samples were homogenous. In contrast, the magnesiated samples with $0.21 \leq \phi_{PSTFSI} \leq 0.36$ were weakly microphase separated while the sample with $\phi_{PSTFSI} = 0.38$ was homogenous. Microphase separation is suppressed by increasing $\phi_{PSTFSI}$, a trend that is qualitatively different than that seen in uncharged block copolymers. Homogenization is driven by favorable interactions between the ions and ether oxygens in the PEO block. The extent to which these interactions are captured by current models of microphase separation in charged polymers is unclear.[38, 119-121] These favorable interactions are more dominant in the lithiated samples. DSC data enabled determination of the crystallinity of the samples, and $T_g$. Crystallinity is also dominated by interactions between ions and ether oxygens. Both $T_g$ and the morphology affect $G'$ and $G''$ of the lithiated and magnesiated copolymers. When the copolymers are completely disordered (Figure 6.10b) the moduli of both lithiated and magnesiated copolymers steadily increase with $T_g$. When the copolymers are weakly microphase separated, they follow a separate trend with $T_g$ (Figure 6.11a).

6.5 Nomenclature

PEO  
poly(ethylene oxide)

PEO-$b$-PSLiTFSI or PEO-PSLiTFSI  
poly(ethylene oxide)-$b$-polystyrenesulfonyllithium (trifluoromethyl sulfonyl) imide

PEO-$b$-P[STFSI]$_2$Mg or PEO-P[STFSI]$_2$Mg  
poly(ethylene oxide)-$b$-polystyrenesulfonyl magnesium (trifluoromethyl sulfonyl) imide

SAXS  
small angle x-ray scattering

Symbols

Figure 6.12. Ionic conductivity plotted against $\phi_{PSTFSI}$ at 80 °C of the lithiated copolymers (blue squares) and the magnesiated copolymers (orange triangles).
\( \text{the domain spacing} \)
\( \text{the dispersity} \)
\( \text{storage modulus} \)
\( \text{loss modulus} \)
\( \text{the melting enthalpy} \)
\( \text{the reference melting enthalpy} \)
\( \text{magnitude of the scattering vector} \)
\( \text{the scattering intensity} \)
\( \text{molecular weight of the PEO block} \)
\( \text{molecular weight of the PSLiTFSI block} \)
\( \text{transmission coefficient of the sample} \)
\( \text{the crystallization temperature} \)
\( \text{the glass transition temperature} \)
\( \text{the onset melting temperature} \)
\( \text{the weight fraction of PEO} \)

**Greek**

\( \alpha_T \) \hspace{1cm} \text{shift factor} \\
\( \xi \) \hspace{1cm} \text{correlation length} \\
\( \pi \) \hspace{1cm} \text{pi} \\
\( \phi_{\text{PEO}} \) \hspace{1cm} \text{volume fraction of the PEO block} \\
\( \phi_{\text{PSTFSI}} \) \hspace{1cm} \text{volume fraction of the ion-containing block} \\
\( \omega \) \hspace{1cm} \text{frequency}
6.5 Supplementary Information

6.5.1 Nuclear Magnetic Resonance $^1$H-NMR

![NMR Spectrum](image)

Figure 6.S1 $^1$H-NMR of the PEO-$b$-PSLiTFSI 9.5 kg·mol$^{-1}$ series in d-DMSO at 25 °C. Blocbuilder® end-group (0.75-1.8 ppm), PEO ethyl ether groups (3.4-3.8 ppm), methyl end-group (3.36 ppm), PSLiTFSI aromatic ring (6.3-7.8 ppm).
6.5.2 Gel Permeation Chromatography (GPC)

The conditions for GPC were previously discuss in Chapter 2. GPC traces of the PEO-macroinitiator (9.5 kg mol\(^{-1}\)) and the PEO-PSLiTFSI block copolymers confirm polymerization of the PSLiTFSI block (Figure 6.S2). The small peaks in the vicinity of 17.8 and 18.7 mL correspond to precursor polymer: PEO methyl ether acrylate. We take this quantity to be negligible.

![GPC traces of the copolymers in the 9.5 kg·mol\(^{-1}\) series of PEO-\(b\)-PSLiTFSI.](image)

**Figure 6.S2.** GPC traces of the copolymers in the 9.5 kg·mol\(^{-1}\) series of PEO-\(b\)-PSLiTFSI.
6.5.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The ICP-OES results for the lithiated block copolymers are shown in Figure 2.13 of Chapter 2. The ICP-OES results for the magnesiated block copolymers are shown in Figure 6.S3. Three different wavelengths of light were used to detect the presence of Mg$^{2+}$ (280, 294, and 383 nm). While three wavelengths of light were used to detect the presence of K$^+$ (345, 404, and 770 nm), only one wavelength of light could detect the small quantities of K$^+$ remaining in the magnesiated block copolymers. The other two wavelengths of light reported values that were below the range of the calibration standards.

![ICP-OES results for the magnesiated block copolymers.](image)

**Figure 6.S3.** ICP-OES results for the magnesiated block copolymers. There is a negligible quantity of K$^+$ left behind in the block copolymers.
6.5.4 Teubner-Strey Fitting Parameters for PEO-P[(STFSI)$_2$Mg]

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<th>$\xi$ (nm)</th>
<th>d (nm)</th>
<th>a</th>
<th>b</th>
<th>c</th>
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6.5.5 Frequency Dependent Moduli for the PEO-PSTFSILi Copolymers

Figure 6.54. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-PSLiTFSI(9.5-3.5)

Figure 6.55. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-PSLiTFSI(9.5-4.9).
Figure 6.S6. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-PSLiTFSI(9.5-7.6)

Figure 6.S7. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-PSLiTFSI(9.5-8.3)
6.5.6 Frequency Dependent Moduli for the PEO-P[(STFSI)$_2$Mg] Copolymers

Figure 6.S8. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-3.6)

Figure 6.S9. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-5.0)
**Figure 6.S10.** Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-7.7)

**Figure 6.S11.** Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-8.5)
Figure 6.12. Frequency dependent (a) $G'$ and (b) $G''$ at several temperatures for PEO 9.5 kg·mol$^{-1}$. 
Chapter 7. Summary

The purpose of this work was to demonstrate the relationship between the morphology, ion transport, and shear modulus of a single-ion-conducting block copolymer electrolyte, PEO-b-PSLiTFSI. First, the synthesis and characterization of these block copolymers were outlined in Chapter 2. Then, it was shown in Chapter 3 that the placement of the charged group on the PS-rich backbone had significant repercussions in the self-assembly of the block copolymer. For a low molecular weight PEO-b-PSLiTFSI with a low ion-concentration (r = 0.085), the morphology and ionic conductivity relationship was shown through SAXS and impedance spectroscopy measurements. When the PEO phase was semicrystalline at temperatures below $T_m$, the block copolymer was microphase separated, trapping the lithium ions in the PS-rich domain. This led to poor ionic conductivity. When the PEO lamellae melted, the block copolymer completely disordered (homogenized), releasing the trapped lithium ions for ion conduction. PEO has a high dielectric constant; therefore, there are favorable interactions between the ether oxygens in PEO and lithium ions in the PS-rich domain. It was demonstrated that these interactions were necessary for efficacious ion conduction to take place.

In the next study (Chapter 4), the effect of ion concentration was studied. Keeping the molecular weight of the PEO block constant at 5 kg·mol$^{-1}$, the molecular weight of the PSLiTFSI block was allowed to vary from 2.0 to 7.5 kg·mol$^{-1}$ corresponding to ion concentrations between $r = 0.056$ and 0.207. At low temperatures, copolymers with $r \leq 0.111$ were microphase separated, and copolymers with $r > 0.111$ were homogenous at low temperatures. Copolymers that were homogenous at low temperatures exhibited higher ionic conductivities. This was due to the loss of PEO crystallinity impeding ion conduction. All copolymers were homogenous at elevated temperatures, and the sample with $r = 0.111$ exhibited a maxima in ionic conductivity.

Next, the effect of molecular weight increase was employed to study the resulting morphology and ion transport relationship. The molecular weight of the PEO block was increased to a constant of 9.5 kg·mol$^{-1}$. At elevated temperatures ($T > 55^\circ C$), the conductivity of PEO-PSLiTFSI(9.5-3.5) ($r = 0.05$) was comparable to the ionic conductivity of PEO-PSLiTFSI(5.0-2.0) ($r = 0.056$). However, the ionic conductivity steadily decreased with increasing $r$. For example, the ionic conductivity of PEO-PSLiTFSI(9.5-7.5) ($r = 0.11$) was about an order of magnitude lower than that of the PEO-PSLiTFSI(5.0-4.0) ($r = 0.111$). This decrease in ionic conductivity can be attributed to the increase of the glass transition temperature for PEO-PSLiTFSI(9.5-7.5). Through a normalization of the ionic conductivity of the 9.5 kg·mol$^{-1}$ series copolymers with respect to its glass transition temperature, the ionic conductivity was found to be independent of $r$. The ion transport properties of the copolymers in lithium symmetric cells were also discussed. The interfacial impedance was found to increase with increasing $r$. Finally, preliminary tomography studies of a copolymer showed the presence of fundamentally different morphologies.

Finally, the presences of univalent and divalent ions in single-ion-conducting block copolymers were studied. Within a matched pair of lithiated and magnesiated block copolymers, DSC studies revealed that $T_g$ was higher for the magnesiated copolymer. Rheology studies demonstrated that the magnesiated block copolymers had shear moduli that were three orders of magnitude higher than its lithiated pair. The shear moduli of the lithiated copolymers exemplified liquid-like rheological features, characteristic of disordered copolymers. The shear
moduli of the lithiated copolymers increased with increasing volume fraction of the ion-containing block, $\phi_{PSTFSI}$. Similarly, the shear moduli of the magnesiated copolymers were found to increase with $\phi_{PSTFSI}$ until a critical $\phi_{PSTFSI} = 0.38$. Through SAXS acquisitions, this work showed that the magnesiated block copolymers also became homogenous beyond a critical $\phi_{PSTFSI}$. This loss in microstructure led to the observed increase in the ion conductivity and a decrease in the shear moduli.
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Appendix A. PEO-PSLiTFSI(5.0-1.6), \( r = 0.04 \)

Synthesis was a challenge for block copolymers of low ion concentration. In this appendix, the characteristics of a cleaner diblock are discussed. PEO-PSLiTFSI(5.0-1.6) was synthesized and characterized according to Chapter 2, where the precursor PEO methyl ether acrylate was obtained from Sigma Aldrich. The results of the GPC are shown in Figure A.1. PEO-\( b \)-PSLiTFSI(5.0-1.6) was analyzed in an Agilent 1260 Infinity Series GPC with an RI detector. The columns were a Waters Styragel HR 3 and HR 4. The solvent in this system was N-Methyl-2-pyrrolidone (NMP) with 0.05M LiBr operating at 0.75ml/min and 70 °C. The dispersity, \( D \), was determined based on a calibration of PEO homopolymers.

The grey is PEO macroinitiator, and the block copolymer is shown in blue. The dispersity of the copolymer peak at 14.9 mL is 1.05. There are other small speaks due to the remaining PEO macroinitiator. The other peaks in the region of 16.5-18.5 may be due to residual monomer. These small quantities are taken to be negligible relative to the primary copolymer peak.

![Figure A.1. GPC of PEO-PSLiTFSI(5.0-1.6) in blue and the PEO macroinitiator in grey.](image)

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>( M_n ) PEO</th>
<th>( M_n ) PSLiTFSI</th>
<th>( D )</th>
<th>( r = [\text{Li}^+] [\text{EO}]^{-1} )</th>
<th>( \phi_{\text{PEO}} )</th>
<th>( \phi_{\text{PSLiTFSI}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-PSLiTFSI(5.0-1.6)</td>
<td>5.0</td>
<td>1.6</td>
<td>1.05</td>
<td>0.044</td>
<td>0.30</td>
<td>0.70</td>
</tr>
</tbody>
</table>

\( M_n \) PEO = number average molecular weight of the PEO block; \( M_n \) PSLiTFSI = number average molecular weight of the PSLiTFSI block; \( D \) = dispersity; \( r = \)
\[ [\text{Li}^+][\text{EO}]^1; \phi_{\text{PEO}} = \text{volume fraction of PEO block}; \phi_{\text{PSTFSI}} = \text{volume fraction of the ion-containing block} \]

Electrolyte preparation was the same as that described in Chapter 5.2.1. Sample preparation and measurements for transference number and SAXS were the same as described in Chapter 5.2.2. Samples for conductivity were prepared with silicone spacers and stainless steel shims as electrodes. Samples were approximately 300 μm thick.

The DSC of the copolymer electrolyte had a very small melting peak. Because of the low levels of crystallinity, this block copolymer was disordered at all temperatures. (SAXS not shown.)

**Table A.2.** DSC results of PEO-PSLiTFSI(5.0-1.6)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( w_{\text{PEO}} )</th>
<th>( T_{\text{m,PEO}} ) (°C)</th>
<th>( \Delta H_{\text{m,PEO}} ) (J/g)</th>
<th>( X_{\text{c}, \text{PEO}} )</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-PSLiTFSI(5.0-1.6)</td>
<td>0.76</td>
<td>53.6</td>
<td>0.4752</td>
<td>0.003</td>
<td>-21</td>
</tr>
</tbody>
</table>

**Figure A.2.** DSC thermogram of PEO-PSLiTFSI(5.0-1.6)

Samples were constructed with Silicone spacers 300 μm thick and stainless steel shims. The results to the ionic conductivity are shown in Figure A.3. The results are from three independent samples. The error bars are shown are smaller than the markers.
Lithium symmetric cell samples were preconditioned with 0.02 mA·cm² for three cycles, where each cycle consisted of a charge, rest, and discharge. Each charge and discharge length period was 4 hours. During the preconditioning cycling (Figure A.4), the interfacial resistance increased (Figure A.5).

**Figure A.3.** Conductivity profile plotted against temperature of the second heating run.

**Figure A.4.** Representative cycling profiles of PEO-PSLiTFSI(5.0-1.6) cycling at 0.02 mA·cm⁻².
The steady state-current method was then employed to determine the transference number at 60 °C. The method used was described in Chapter 5.2.2. The chronoamperometry profiles (Figures A.6b and A.7b) from a positive bias (Figure A.6a) and a negative bias (Figure A.7a) are constant with time. The currents reported were based on the normalization from the following equations, where $I_{\Omega}$ is the current determined through Ohm’s law. The values for $\Delta V$ are from the applied potential, and $R_{\text{total}, t=0}$ is the total resistance determined from impedance spectroscopy before the start of the transference number experiment. The normalized current is thus the ratio of the measured current as a function of time divided by $I_{\Omega}$. The reported transference numbers are unity (Figures A.6c and A.7c).

$$I_{\Omega} = \frac{\Delta V}{R_{\text{total}, t=0}}$$  \hspace{1cm} (A.1)

$$\text{Normalized Current} = \frac{I_t}{I_{\Omega}}$$  \hspace{1cm} (A.2)

The interfacial impedances in each of the experiments from Figures A.6 and A.7 were found to remain constant throughout the experiment. (See Figures A.8 and A.9.) It is evident that the interfacial resistances come to an equilibrium after the preconditioning cycles discussed above.
Figure A.6. (a) A potential of 40. mV plotted against time, (b) chronoamperometry profiles plotted against time, and (c) the transference number plotted against time.
Figure A.7. (a) A potential of -40 mV plotted against time, (b) chronoamperometry profiles plotted against time, and (c) the transference number plotted against time.
**Figure A.8.** Nyquist plot of PEO-PSLiTFSI(5.0-1.6) in a lithium symmetric cell during an applied potential of 40. mV.

**Figure A.9.** Nyquist plot of PEO-PSLiTFSI(5.0-1.6) in a lithium symmetric cell during an applied potential of -40. mV.
Appendix B: PSLiTFSI in EC/DMC

Homopolymer PSLiTFSI is too glassy by itself to make solid-state membranes for ion-transport. Therefore, PSLiTFSI was mixed in with a solvent to harness the ion-conducting properties of PSLiTFSI. PSLiTFSI was synthesized with nitroxide mediated polymerization. The Blocbuilder®, described in Chapter 2.3.2, was added to STFSIK monomer with DMF at 115 °C. The reaction was allowed to proceed for 24 hours before quenching. The PSLiTFSI structure is shown in Figure B.1.

![Figure B.1. Molecular structure of PSLiTFSI. The end-groups are shown in grey and purple.](image)

Polymerization was also verified with $^1$H-NMR. The molecular weight was estimated based on the ratio of Blocbuilder® to monomer; this value is 3 kg·mol$^{-1}$. The NMR is shown in Figure B.2.
PSLiTFSI was analyzed in an Agilent 1260 Infinity Series GPC with an RI detector. The columns were a Waters Styragel HR 3 and HR 4. The solvent in this system was N-Methyl-2-pyrrolidone (NMP) with 0.05M LiBr operating at 0.75ml/min and 70 °C. The dispersity, $D$, was determined based on a calibration of PEO homopolymers. The dispersity was determined to be 1.19. Small peaks are observed at retention volumes to the right of the primary peak. This indicates that there may be smaller species of PSLiTFSI present. However, the area under the curve of these quantities is less than 1% of the area under the primary peak. With this rough estimate, we consider these quantities to be negligible.

Figure B.2. $^1$H-NMR of PSLiTFSI in deuterated acetonitrile.
The solvents considered in this study were 1,3-dioxolane/dimethoxy ethane (DOL/DME) and ethylene carbonate/dimethyl carbonate (EC/DMC). It was found that EC/DMC (mass ratio 2:3) was the best solvent for PSLiTFSI. The homopolymer and DOL/DME settled out of solution after 24 hours. The ionic conductivity studies moving forward were in EC/DMC.

The ionic conductivity of the liquid samples was measured using custom-made cells. The images here are reproduced from the operating manual.

The ionic conductivity was determined with Equation B.1, where $S$ is the effective surface area. This value is particular to the geometry of each cell. $R_{el}$ is the resistance of the electrolyte as determined from impedance spectroscopy. The raw ionic conductivity of the
solvent alone was also determined; this was subtracted from the measurements of the PSLiTFSI/(EC/DMC) solutions.

\[
\sigma(T,r) = \frac{l}{S \cdot R_d(T,r)}
\]  
(B.1)

The ionic conductivity results are shown in Figure B.5. We were able to make solutions up to 20 wt\% given the constraints on sample availability. The ionic conductivity of the solutions were high, \(5.0 \times 10^{-4} \, \text{S} \cdot \text{cm}^{-1}\) in the 20 wt\% solution. The conductivities for the two solutions are very similar to one another, and it did not change significantly with temperature. This may be due to the limited mobility of the rigid polystyrene backbone.

![Figure B.5. Ionic conductivity plotted against temperature for 10 wt\% (yellow circles) and 20 wt\% (purple triangles) solutions of PSLiTFSI/(EC/DMC).](image)

Attempts were made at determining the transference number for the lithium cation using the \(^7\text{Li}-\text{HNMR}\) pulsed-field-gradient technique using a Bruker AV-600 in the College of Chemistry at UC Berkeley; however, the signal to noise ratio for the \(^7\text{Li}\) was very low. Reproducible measurements for the lithium ion diffusion were not feasible. Improvements can be made with use of a stronger magnet and long acquisition times.
Appendix C: Teubner-Strey fits in Python

Teubner-Strey fits were applied in Chapter 6. In this appendix, the details of the fits are described. The scipy module in python was utilized to conduct the fits.

# Teubner-Strey Fits

# This script reads a .csv file containing x-ray scattering profiles and performs Teubner Strey-Fits given a temperature and sample name.
# this code will use a robust linear-squares algorithm to fit a T-S fxn of the form y=1/(e*x**2+g) + 1/(a+b*x**2+c*x**4) to data

import matplotlib.pyplot as plt
from scipy.optimize import least_squares
import numpy as np
import csv
from matplotlib import rcParams

# ------------------------------------------
def callfile(SampleName,temp):
    # I had all my files named by sample containing scattering profiles for many temperatures, in one directory
    # you can edit your directory to indicate where the file containing your data is located
    directory='C:\\Users\\Balsara\\'
    file=directory + SampleName + '_heat.csv'
    # read the file
    infile=open(file,'r')
    table=[]
    table=[row for row in csv.reader(infile)]
    infile.close()
    # now transform string objects into float values, so I started where appropriate
    for r in range(2,len(table)):
        for c in range(0,len(table[0])):
            table[r][c]=float(table[r][c])
    # now assign the table values to a particular name
    q=[]
r130C=[]
r110C=[]
r90C=[]
r80C=[]
for r in range(2, len(table)):
    q.append(table[r][0])
    r25C.append(table[r][1])
    r30C.append(table[r][2])
    r35C.append(table[r][3])
    r40C.append(table[r][4])
    r45C.append(table[r][5])
    r50C.append(table[r][6])
    r55C.append(table[r][7])
    r60C.append(table[r][8])
    r70C.append(table[r][9])
    r80C.append(table[r][10])
    r90C.append(table[r][11])

# following makes an exception for sheets containing data above 90C
if len(table[0]) > 12:
    r110C.append(table[r][12])
    r130C.append(table[r][13])

# now specify which temperatures to output to graph
Isaxs = []
if temp == '90':
    Isaxs = r90C
elif temp == '80':
    Isaxs = r80C
elif temp == '70':
    Isaxs = r70C
elif temp == '60':
    Isaxs = r60C
elif temp == '55':
    Isaxs = r55C
elif temp == '50':
    Isaxs = r50C
elif temp == '45':
Isaxs=r45C
elif temp=='40':
    Isaxs=r40C
elif temp=='35':
    Isaxs=r35C
elif temp=='30':
    Isaxs=r30C
elif temp=='25':
    Isaxs=r25C
elif temp=='110':
    Isaxs=r110C
elif temp=='130':
    Isaxs=r130C
elif temp=='':
    print('enter a valid temperature')
return q, Isaxs
# -----------------------------------------------
newtemp='30'      # newtemp is the temperature I wish to analyze
muestra='AAR3Mg'  # muestra is my sample name
#
# identify labels for graphing purposes
if muestra=='AAR1Mg':
    polymer='(9.5-3.6)'
    clr='gold'
elif muestra=='AAR2Mg':
    polymer='(9.5-5.0)'
    clr='mediumorchid'
elif muestra=='AAR3Mg':
    polymer='(9.5-7.7)'
    clr='mediumblue'
elif muestra=='AAR4Mg':
    polymer='(9.5-8.5)'
    clr='forestgreen'
# -----------------------------------------------
rcParams['font.family']='sans-serif'
rcParams['font.sans-serif']=['Arial']
size=10
# Call the files and read data------------------------
qdata, Idata=callfile(muestra,newtemp)
qdata=np.array(qdata[100:300])  # here I can specify which part of the scattering profile on which to perform the fit
Idata=np.array(Idata[100:300])  # here I can specify which part of the scattering profile on which to perform the fit

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# print(len(qdata))
# now plot the data-----------------------------
plt.figure(figsize=(3, 3), dpi=300)
plt.text(.14, newtemp + '$^\circ$C', fontsize=size)
plt.loglog(qdata, Idata, 'o', color=clr, markersize=3, label=polymer)
plt.xlabel('q (nm $^{-1}$)', fontsize=size)
plt.ylabel('Intensity (cm$^{-1}$)', fontsize=size)
plt.tick_params(labelsize=size)
plt.axis([.09, 1.5, .01, 10**2])
plt.tick_params(which='major', right='on', direction='in', length=6)
plt.tick_params(which='minor', right='on', direction='in', length=3)
plt.tight_layout()

# define the function computing residuals for least-squares minimization
# in the T-S fit
def func(x, q, I):
    # x is an array of coefficient fits where,
    Ibgd = 1/(x[3]*q**2+x[4])
    Imod = 1/(x[0]+x[1]*q**2+x[2]*q**4)+Ibgd
    return Imod-I

# now define a function to contain the T-S model
def tsmod(q, a, b, c, e, g):
    Ibgd = 1/(e*q**2+g)
    Imod = 1/(a+b*q**2+c*q**4)
    Itot = Ibgd + Imod
    return Itot

# define a function for just the background
def bgd(q, e, g):
    Ibgd = 1/(e*q**2+g)
    return Ibgd

# define a function to calculate xi (correlation length), d (domain spacing), and f
# (amphiphilicity) using the T-S results
def calc(a, b, c):
    xi = .5*(a/c)**.5+b/(4*c)**(-.5)
    d = 2*np.pi*(.5*(a/c)**.5-b/(4*c))**(-.5)
    f = 0/2*(a*c)**(0.5)
    return xi, d, f
#x0=np.ones(5) # use all ones as the initial estimate
x0=[2.6,-88,829,14,1.2] # I can adjust what the starting guesses are
# run robust least squares with loss='soft_l1', or loss='arctan', set f_scale to 0.1 which means
# that inlier residuals are approximately lower than 0.1
res_robust=least_squares(func,x0,loss='soft_l1', f_scale=0.1, args=(qdata,Idata))
# print('The results from the fit to the T-S model')
print('a=', res_robust.x[0],', b=',res_robust.x[1], 'c=',res_robust.x[2])
print('e=',res_robust.x[3], 'g=',res_robust.x[4])
# the xi, d, and f values
xi, d, f=calc(res_robust.x[0], res_robust.x[1],res_robust.x[2])
print('xi=', xi, 'd=', d, 'f=', f)
plt.plot(qdata,tsmod(qdata,*res_robust.x),color='k',label='T-S Model')
plt.plot(qdata,bgd(qdata,res_robust.x[3],res_robust.x[4]),'c--',label='Ibgd')
plt.legend(fontsize=size)
plt.savefig(muestra+'_'+newtemp+'C.png')